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**POTASH SALTS FROM TEXAS-NEW MEXICO
POLYHALITE DEPOSITS
COMMERCIAL POSSIBILITIES, PROPOSED TECHNOLOGY,
AND PERTINENT SALT-SOLUTION EQUILIBRIA**

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POTASH SALTS FROM TEXAS-NEW MEXICO POLYHALITE DEPOSITS

Commercial Possibilities, Proposed Technology, and Pertinent Salt-Solution Equilibria¹

By JOHN E. CONLEY ² AND EVERETT P. PARTRIDGE ³

INTRODUCTION

GENERAL INFORMATION ON THE POTASH INDUSTRY

Of the three chemical elements most vitally essential for plant growth the United States, before World War I, had developed ample domestic supplies of but one—phosphorus. During and shortly after the war period, the fixation of nitrogen was greatly expanded in this country, as in many others, insuring a supply adequate for agriculture as well as for munitions.

However, in spite of a search for sources of the third element, potassium, which began years before the war, attained almost frantic intensity between 1914 and 1919, and continued for 10 years thereafter, it was not until 1921 that the American Trona Corporation put its Searles Lake operations into continuous production. This company in 1926 became The American Potash & Chemical Co. but has never supplied much more than 15 percent of the potash consumed in the American market. Likewise, though discovered in 1921 in drill cuttings from oil wells, it was not until 1926 that domestic deposits of potassium salts adequate to render the United States independent of foreign sources of supply were proved to occur in the Permian Basin of Texas and New Mexico.

Detailed descriptions of the history of potassium salts in the United States have appeared elsewhere (*12, 13, 16, 22, 35, 39, 44*)⁴, so that here it is necessary to indicate only briefly the relative significance of the various domestic sources with relation to the major market in the fertilizer industry and to the imports from Europe, which still supplied an appreciable proportion of that market until the outbreak of World War II in 1939.

Figure 1 shows the location of sources that have been either exploited or seriously considered at one time or another, superimposed upon a map indicating by small letters the order of consumption of K₂O in the 15 leading States; the amount used in

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⁴ The italicized figures in parentheses refer to citations in the bibliography at the end of this report. Page references represent those in the citation and not in this paper.

these States, together with the percentage of the total consumption of potash used as fertilizer in the United States in 1939, is given in table 1.

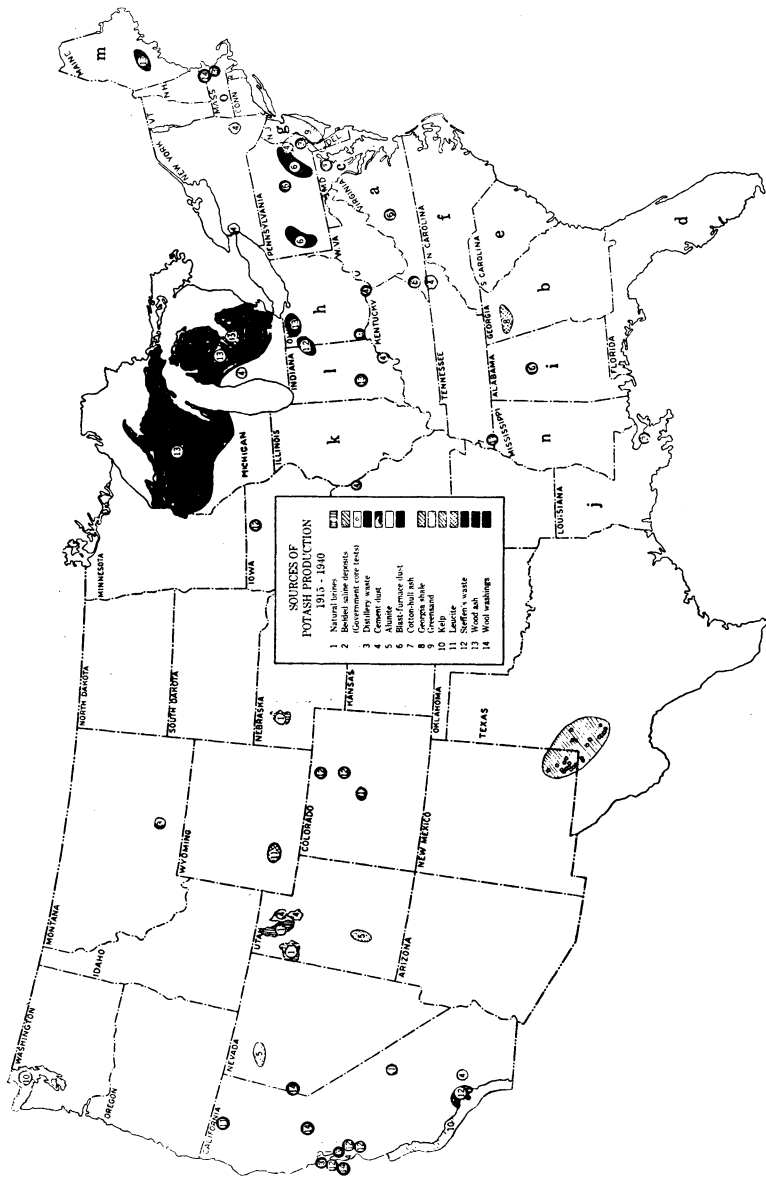


Figure 1.—Geographical sources of potash in the United States.

Figure 2 shows the domestic production and total consumption of potassium salts, in terms of tons of K_2O , with the value per unit at the plants, for each year since 1913. Considered together, these two figures tell a significant story.

TABLE 1.—Consumption of potash in fertilizers during 1939 in leading States¹

State:	Short tons K ₂ O	Percent of domestic consumption
1. Virginia	41,003	12.60
2. Georgia	35,092	10.78
3. Maryland	26,917	8.27
4. Florida	26,883	8.26
5. South Carolina	26,189	8.04
6. North Carolina	24,577	7.55
7. New Jersey	21,222	6.52
8. Ohio	21,119	6.49
9. Alabama	15,231	4.68
10. Louisiana	9,981	3.07
11. Illinois	9,749	2.99
12. Indiana	9,560	2.94
13. Maine	9,089	2.79
14. Mississippi	8,036	2.47
15. Massachusetts	7,170	2.21
Total	291,818	89.66

¹ Statistics from American Potash Institute.

In the first place, the great market for mixed fertilizer, and hence for potassium salts, has been for many years the region south of the Mason-Dixon line and east of the Mississippi River. Up until 1915 the potassium salts consumed in this region, as well as in the rest of the United States, came exclusively from Germany. Then, as this source was shut off, rapidly rising prices

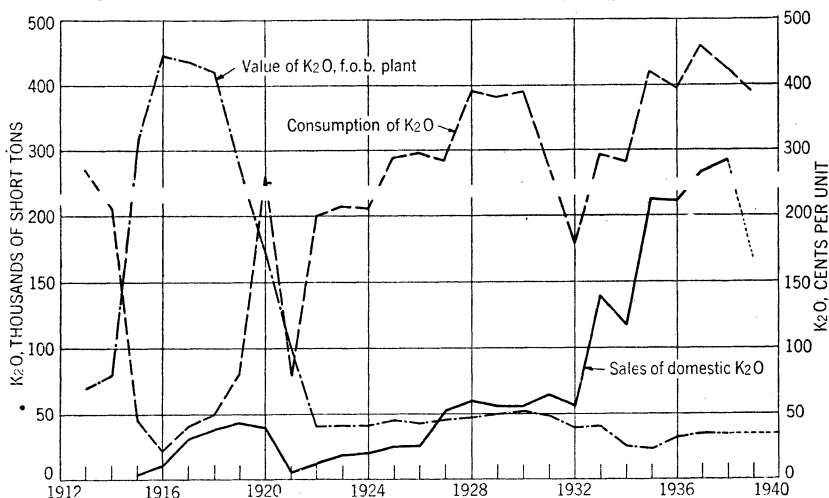


FIGURE 2.—Annual consumption and production of potash in the United States.

stimulated domestic production from every available raw material. This output reached a peak of 44,000 tons of K₂O in 1919.

When the emergency was over, only two industries survived to supply appreciable quantities of potassium salts over the post-war period in competition with the renewed imports from Europe. These were the American Potash & Chemical Corporation, which produced a refined potassium chloride from the brine of Searles Lake, Calif., and the U. S. Industrial Alcohol Co., which marketed the ash from incineration of distillery wastes at Baltimore, Md.

The Permian Basin, however, running northward from Texas across New Mexico, had long been regarded by geologists as a region in which deposits of potassium salts might be found. In 1912 the first definite indication of the existence of such deposits was observed by J. A. Udden in cuttings from an oil well (41). When samples from another well in 1921 showed significant amounts of potassium salts, interest was so aroused that a systematic exploration by the Government was authorized, in addition to private ventures.

Aimed at different objectives, both the Government core-drilling program, carried out jointly by the Geological Survey and the Bureau of Mines, and the search by private interests were successful. While the latter were locating and proving a rich deposit of potassium chloride, the Government work was demonstrating the widespread occurrence of potassium salts in the Permian Basin.

The consistent appearance of the mineral polyhalite in quantity in the first cores from the Government test holes led to the investigation described in the present bulletin. When this work was begun, no significant amounts of the easily refined chloride had been reported, and it was believed that utilization of the newly found deposits would depend on the development of processes for the recovery of potassium sulfate from polyhalite. The subsequent location of chloride deposits, both by private interests and by the Government, then raised the question whether further work on polyhalite would be justified. Study showed that potassium sulfate, in spite of an appreciably higher price per unit of K_2O than the chloride salts, constituted an important proportion of the domestic consumption, as indicated in figure 3. That this potassium sulfate might be produced economically from polyhalite had already been indicated by Wroth (44) on the basis of the early investigations. In addition, the complete utilization of the constituents of polyhalite seemed possible from both the technical

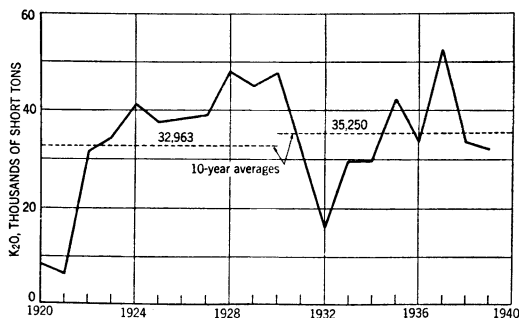


FIGURE 3.—Annual consumption of K_2O as sulfate of potash.

and economic viewpoints. The decision was made, therefore, to continue the investigation until the most promising processes for the production of fertilizer salts and the industrial chemicals from polyhalite could be evaluated.

In all of the work on polyhalite, it has been necessary to build up a background of fundamental scientific information against

which the individual chemical operations of the various processes might be viewed. Although some pertinent data were initially available, largely in the German literature, the complex chemical constitution of polyhalite and its occurrence only as an incidental salt in the great European deposits had caused it to be generally neglected. Not only was there a lack of data, but also lack of accuracy or adequate interpretation in much that had been published. A rather considerable portion of the investigation described in this bulletin was, therefore, devoted to clearing away scientific underbrush and building authentic foundations.

USES OF POTASH SALTS

The principal uses of potassium salts are in fertilizers and for various chemical applications. Approximately 95 percent of the potash sold in the United States is consumed in the form of fertilizers, and the balance is used as special chemicals.

The chief forms in which the potash occurs for fertilizer consumption are, in the order of importance: The muriate, the sulfate, manure salts, kainite, and sulfate of potash-magnesia. The order of the last three types of salts varies according to current conditions, but the muriate and sulfate have maintained first and second rank, respectively, for many years. All potash salts intended for use as fertilizers are sold on a guaranteed minimum K_2O content. The muriate, sulfate, and manure salts are usually sold upon the basis of the K_2O , while kainite and sulfate of potash-magnesia are marketed by the ton.

The muriate of potash contains not less than 48 percent K_2O , largely as the chloride, but is available in two grades corresponding to 80-percent potassium chloride equivalent to 50.5-percent K_2O and as 95- to 99-percent potassium chloride equivalent to 60- to 62.5-percent K_2O . Sulfate of potash is defined as a potash salt containing not less than 48 percent K_2O , largely as sulfate, and not more than 2.5 percent chlorine. The 90-percent potassium sulfate equivalent to 48.7-percent K_2O is the minimum grade; but as in the case of muriate, higher grades are produced. The 90- to 95-percent sulfate corresponding to 48.7- to 51.4-percent K_2O is also on the market. The manure salts include potash salts of a high chloride content containing 20 to 30 percent K_2O , but the 30-percent grade is becoming standard in the United States.

Sulfate of potash-magnesia is a salt containing not less than 25 percent K_2O or less than 25 percent sulfate of magnesia, and not more than 2.5 percent of chlorine. Here again the grades marketed range from 48 to 53 percent K_2SO_4 , equivalent to 26.0 to 28.7 percent K_2O .

Kainite is a potash salt containing potassium and sodium chlorides and sometimes sulfate of magnesia, with not less than 12 percent K_2O . Market quotations usually are made on a product with a content of 20 percent K_2O .

The chemical industry consumes a variety of potassium salts, among which potassium nitrate, the tartrates, and chlorates represent the greatest tonnages. Appreciable amounts of other potash compounds, including caustic, carbonate, chromate, ferro-

and ferri-cyanides, cyanides, and minor quantities of iodide and bromide, also are consumed. Were potassium salts obtainable as cheaply as certain sodium salts, a greatly increased chemical use of the former probably would follow. The greater solubility of the potash salts would make their use justified in many instances were the question of the unnecessary waste of a valuable plant food an unimportant consideration.

FOREIGN OCCURRENCE OF POLYHALITE

Polyhalite ($K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$), first identified in 1820 by Stromeyer (37, 38) in rock salt at Ischl, Austria, has since been reported in most of the known deposits of potassium salts; however, occurrences in quantities of industrial importance are uncommon.

The Stassfurt salt deposits in Germany represent the most important European sources of potassium salts and occur as seams in enormous beds of rock salt. Polyhalite is found in numerous localities and in appreciable amounts in some places. In one deposit, some 62 meters of halite exist, with polyhalite disseminated throughout the mass and estimated to comprise about 6 percent of the total thickness. However, these German occurrences have not been considered of industrial importance because kieserite, which furnishes all the sulfate required, is found in close proximity to the carnallite and sylvinite, which are treated for production of the muriate. The various occurrences of polyhalite in Germany and adjacent regions have been discussed by Lift (19), Schober (29), Emslie (10), Samoilov (27), and Rice and Davis (26).

Only small occurrences of polyhalite have been reported from France (5) and Italy (8), but larger quantities of this mineral are known to occur in Poland and in Russia (3). The most recent report of Kurnakov, Bokii, and Lepeskov (18) indicates that a deposit of commercial size has been discovered in the Soviet Union.

EXPLORATION OF THE POTASH DEPOSITS OF THE PERMIAN BASIN

Wroth (44, p. 14) has given a brief discussion of the legislation authorizing the search for potash salts in the salt beds known to exist in the Permian Basin of New Mexico and western Texas, as follows:

HISTORY OF LEGISLATION

The first bill authorizing the Government to undertake potash exploration by drilling (S. 3047, 68th Cong.) was introduced in 1924 by Senator Sheppard and Congressman Hudspeth, of Texas.

This bill provided \$500,000 annually for 5 years to be expended by the Geological Survey and \$50,000 annually to be expended by the Bureau of Soils to "determine the location and extent of potash deposits or occurrences in the United States and improved methods of recovering potash therefrom." The main purpose of this bill, as disclosed by the hearing, was to provide for core drilling in the Texas-New Mexico field. Hearings were held before the Mines and Mining Committees of both the Senate and the House, but the bill was never reported out of the committees and failed of enactment.

A similar bill (S. 1821) was introduced in the Sixty-ninth Congress, December 18, 1925, by Senator Sheppard and was passed by the Senate on April 14, 1926. After a hearing before the House Committee on Mines and Mining the bill was amended to provide \$100,000 a year for 5 years to be expended jointly by the Secretary of the Interior and the Secretary of Commerce, and the scope of the proposed investigations was limited to determination of "the location, extent, and mode of occurrence of potash deposits in the United States," together with the necessary laboratory tests, such as analyses, etc. This bill in its amended form was approved by the President on June 25, 1926, and under its provisions the necessary preliminary field work was started in the fall of 1926, and drilling was begun early in 1927.

This act provided that before drilling operations were undertaken the owners or lessees of lands or mineral rights within a radius of 1 mile of the proposed drilling site must sign contracts agreeing to reimburse the Government for the actual cost of the well, regardless of whether potash was discovered or not. It also provided for Government valuation of these lands and mineral rights and stipulated that no drilling should be undertaken until these conditions were agreed to by the owners or lessees of the land in question.

There are no Government lands in Texas; and as the landowners of Texas refused to agree to the conditions imposed, drilling sites were selected on the Government lands of New Mexico. Here, also, owing to the scattered private lands, such as State school lands, homesteads, oil permits, etc., the 1-mile-radius feature rendered the selection of drilling sites difficult. Accordingly, on March 3, 1927, an amendment was approved that omitted this clause and provided for royalty reimbursement to the Government if potash or oil were discovered and exploited on the tract leased as a drilling site.

The provision relating to oil has hindered somewhat the securing of drilling sites in the oil-producing areas.

The actual carrying out of the provisions of this act was entrusted to the Geological Survey of the Interior Department and the Bureau of Mines, then in the Department of Commerce.

The Geological Survey, through its knowledge of the field, designates the drilling sites. The securing of the necessary leases and the entire supervision of the drilling operations is in the hands of the Bureau of Mines. The drill cores are turned over by the Bureau of Mines to the Geological Survey for examination, analysis, and petrographic study, after which the cores are returned to the Bureau of Mines for use in technologic experiments on treatment processes, etc.

RESULTS OF DRILLING TESTS

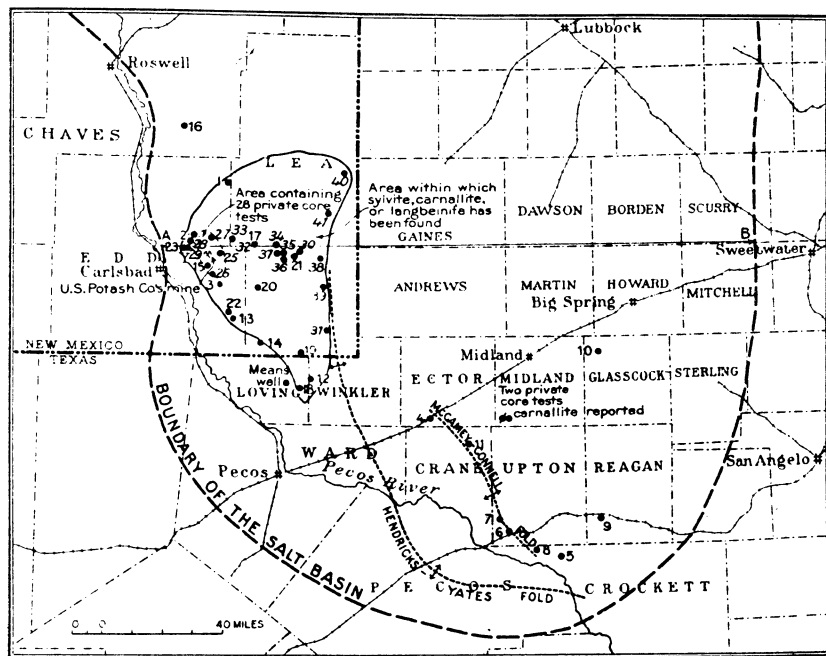
The appropriation of Government funds for core-drilling wells located by the Geological Survey and drilled by the Bureau of Mines resulted in the sinking of 23 holes in New Mexico and Texas and 1 hole in Utah. Potash salts were pierced in every well, in most instances in beds of thicknesses and with potash contents of commercial interest.

The details of the drilling operations and the results of the examination of drill cores by the Geological Survey have been reported in numerous previous Government publications and in technical journal articles. Press releases by the Geological Survey on the various phases of the potash exploration were initiated in 1921 and appeared periodically up to May 1932. Additional information has been given in papers and reports by Mansfield (20, 21), Hoots (15), Smith (35), and Wroth (44).

DATA ON POTASH SALTS FOUND IN CORES FROM GOVERNMENT DRILL HOLES

During the drilling program executed jointly by the Geological Survey and the Bureau of Mines, 24 holes were drilled, and a high percentage of core was recovered from the wells, ranging in depth

from 373 to approximately 3,000 feet. Moreover, during this period all wells being drilled by private companies were watched wherever possible, and the cuttings were checked for evidence of potash salts. The locations of the various Government and privately financed holes bored in this region have been placed on the map prepared by the Geological Survey and reproduced in figures 4 and 5. It will be noted that the majority of the wells



POTASH-BEARING WELLS SHOWN ON MAP

Nos. 1-23. Government core tests	29. S. & M. Lawrence No. 1	36. Amerada-State No.
Nos. 25-41. Churn-drilled wells that have yielded sylvite, carnallite, or langbeinite	30. Empire-State I-C	37. Cranfill & Reynolds State I-D
25. S. & M. McNutt No. 1	31. Gypsy-Humphreys No. 1	38. Continental-A.E. Meyer No. 1
26. Ohio-Workman	32. Empire-Martin No. 1	39. Continental-Wm. Meyer No. 1
27. Marland-Hale No. 1	33. Texas-Humphreys No. 1	40. Barnsdall-Bronson No. 1
28. Getty-Nicholas No. 1	34. Texas-Lynch No. 1	41. National Securities-T. A. Linam No. 1
	35. Snowden McSweeney-State No. 1	

FIGURE 4.—Location of potash-bearing wells in New Mexico and Texas.

were in southeastern New Mexico because of the Government land held in that State. The closer proximity of the potash-bearing salts to the surface and the preliminary indications of higher-grade potash minerals in that area were also contributing factors.

The data obtained from the log of the drilling tests and the examination of the drill cores have been summarized in table 2. A study of this tabulated information will disclose that many zones of potash salts were reached, and commercial deposits were

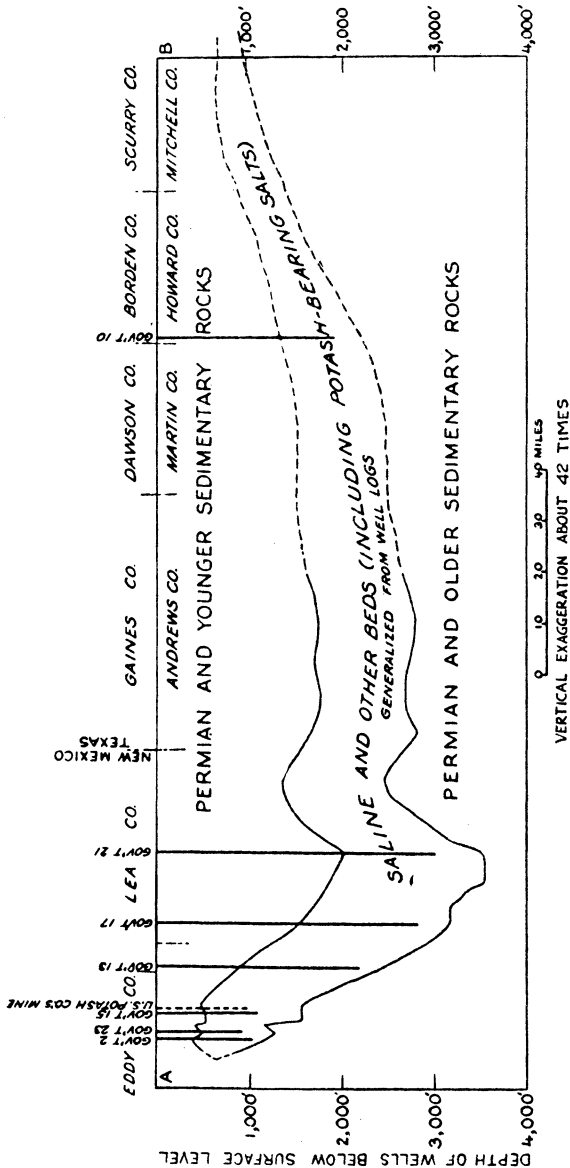


FIGURE 5.—Projected section of Permian potash field in New Mexico and Texas (according to Geological Survey, 1932).

proved in a majority of the holes. The data made available by Government drilling activities have been supplemented since 1932 by numerous exploratory holes drilled by private interests now successfully exploiting sylvinite beds discovered in this region. In general, the conclusions reached from a study of the Federal core-drilling operations have been substantiated, and a valuable domestic potash industry has been established.

10 POTASH SALTS FROM TEXAS-NEW MEXICO POLYHALITE DEPOSITS

TABLE 2.—Summary of Government core tests in the Permian Basin¹

No. of test	Location ²	Total depth	Depth to top of salts	Depth of better potash beds	Thickness of better potash beds	K ₂ O in sample		Remarks
		<i>Ft.</i>	<i>Ft.</i>	<i>Ft.</i>	<i>Ft. In.</i>	<i>Percent</i>		
1	Eddy County, N. Mex., NW. ¼ sec. 13, T. 17 S., R. 31 E.	1,847	760	1,647	4 10	7.58		Polyhalite and anhydrite. Well discloses more than 30 potash horizons, including numerous thin layers of carnallite.
2	Eddy County, N. Mex., NW. ¼ SW. ¼ sec. 14, T. 20 S., R. 29 E.	1,101	335	809 485	2 5 2 8	13.94 10.50		Polyhalite with anhydrite, halite, etc. Well penetrates more than 20 potash horizons, including some sylvite.
3	Eddy County, N. Mex., SW. ¼ SW. ¼ sec. 34, T. 22 S., R. 30 E.	1,501	365	3,467 1,459 1,475 868 1,012 1,333	8 10 15 6 3 2 3 7 3 3	11.08 8.84 13.50 12.86 12.06		Polyhalite, halite, and anhydrite. Polyhalite, halite, and anhydrite and leaner material. Polyhalite and halite. White polyhalite, anhydrite. Polyhalite and halite. Well penetrates more than 20 potash horizons.
4	Southwest Ector County, Tex., near Metz, on T. & P. Ry., Connell ranch.	2,098	930	1,935	6 7	12.86		Polyhalite and halite in 2 beds separated by about 3 feet of halite.
5	Crockett County, Tex., Harris Bros. ranch, NW. ¼ sec. 16, G. C. & S. F. Ry. survey.	1,799	1,161	1,280 1,370	3 7 5 8	9.53 5.84		Polyhalite and anhydrite. Polyhalite, halite, and anhydrite. Excludes a 10-inch layer of halite and anhydrite at 1,375 feet.
6	Upton County, Tex., sec. 100, Barleson-Sun lease, about 3 miles north of McCamey.	1,501	437	1,682 1,210 1,168	1 0 1 8 1 8	13.52 7.67 10.00		Richest bed—polyhalite. Polyhalite and halite. Polyhalite and anhydrite—richest bed.
7	Upton County, Tex., sec. 4, William Teer survey, Hughes Roxana lease, 10 miles north of McCamey.	1,230	445	632 902 1,213 690	2 3 1 11 1 11 3 7	8.24 9.22 8.87 9.50		Polyhalite and halite. Polyhalite, halite, anhydrite. Do. Excludes 8 inches of halite and anhydrite.
8	Crockett County, Tex., sec. 5, block 14, Univ. land.	1,001	468	521	5 2	6.35		Polyhalite, etc. Tests 6 and 7 both penetrated about 10 potash horizons.
9	Reagan County, Tex., NW. ¼ sec. 1, block 2, Univ. land, Big Lake district.	1,700	1,104	529 1,526 1,310	2 5 2 11 2 3	11.22 8.27 7.62		Polyhalite, anhydrite, and halite. About 10 potash horizons penetrated.
10	Glasscock County, Tex., NE. ¼ sec. 14, block 35, T. 2 S., T. & P. survey, Houston ranch.	1,842	1,283	1,370 1,575	3 2 11	7.90 15.12		Richest bed—polyhalite. More than 10 potash horizons penetrated.
11	Crane County, Tex., SE. ¼ sec. 3, block B-25.	2,070	1,081	1,313 1,658 1,779 2,010	3 6 4 3 2 5 5 9	6.80 9.82 11.71 8.36		Polyhalite and halite (22 in.). Polyhalite. Do. Polyhalite. Excludes 3 feet 4 inches of halite between two 3-foot beds.
12	Winkler County, sec. 33, block 75.	2,752	1,077	2,097 2,257	2 9 6 0	8.36 10.63		Polyhalite, anhydrite, halite. Includes richest bed. With 4 feet immediately above gives a 10-foot interval averaging 8.4 percent K ₂ O.
13	Eddy County, sec. 5, T. 24 S., R. 31 E.	2,139	850	2,267 2,737 829 1,099 1,189 1,382 1,406	9 8 3 0 2 1 2 2 2 10 2 1 8 0	7.23 10.65 13.25 10.02 11.78 11.40 12.02		Polyhalite. Polyhalite, halite, anhydrite. Polyhalite and halite. Polyhalite, halite, anhydrite, and magnesite. Polyhalite and halite. Polyhalite, halite, magnesite, and clay. Polyhalite, halite, magnesite, clay, and anhydrite: 3 ft. 3 in. ave. K ₂ O = 15.10 percent.

¹ Mansfield, G. R., and Lang, W. B., Government Potash Exploration in Texas and New Mexico: Am. Inst. Min. and Met. Eng., Tech. Pub. 212, 1929, p. 16. The Texas-New Mexico Potash Deposits: Univ. of Texas Bull. 3401 (Separate), 1935, pp. 641-832.

² All locations in New Mexico unless otherwise indicated.

TABLE 2.—*Summary of Government core tests in the Permian Basin*¹
(Continued)

No. of test	Location ²	Total depth	Depth to top of salts	Depth of better potash beds	Thickness of better potash beds	K ₂ O in sample	Remarks
		<i>Ft.</i>	<i>Ft.</i>	<i>Ft.</i>	<i>Ft. In.</i>	<i>Percent</i>	
14	Lea County, SW. ¼ SE. ¼ sec. 1, T. 26 S., R. 32 E.	2,097	1,180	1,476	2 5	12.80	Polyhalite, halite, magnesite.
				1,600	2 4	10.61	Polyhalite, halite, anhydrite, and magnesite.
				2,202	3 3	12.05	Polyhalite and anhydrite.
				1,533	2 2	12.01	Polyhalite and halite.
				1,658	6 5	12.04	Polyhalite, halite, anhydrite, magnesite, and clay; 2 ft. 3 in. ave. K ₂ O = 14.03 percent.
				1,741	3 10	13.43	Polyhalite and halite.
15	Eddy County, NE. ¼ sec. 24, T. 21 S., R. 29 E.	1,080	517	1,786	3 2	11.19	Polyhalite, halite, anhydrite, and magnesite.
				1,865	2 6	10.21	Polyhalite and anhydrite.
				2,027	3 3	12.89	Polyhalite, halite, and clay.
				941	2 7	10.70	Polyhalite, anhydrite; 2 ft. 9 in. bed at 712 ft. K ₂ O = 9.45 percent.
16	Chaves County, SE. ¼ sec. 12, T. 14 S., R. 28 E.	514	364	373	2 8	12.10	Polyhalite, halite, clay, and kieserite.
17	Lea County, SW. ¼ NE. ¼ sec. 28, T. 20 S., R. 33 E.	2,858	1,565	2,356	4 0	11.35	Sylvite, halite, polyhalite, carnallite, and clay.
				2,385	2 7	10.32	Polyhalite, halite, anhydrite, and sylvite.
				2,523	3 0	11.40	Langbeinite, halite, polyhalite, and clay.
				2,610	2 10	13.85	Polyhalite.
18	Loving County, Tex., Leeman ranch, SW. ¼ sec., 5 Blk. 28, public school land.	1,876	1,205	1,441	2 0	10.00	Polyhalite, sylvite, carnallite, halite, and anhydrite.
19	Lea County, sec. 31, T. 26 S., R. 35 E.	2,012	1,185	1,788	4 0	6.98	Halite, polyhalite, carnallite.
20	Lea County, sec. 3, T. 23 S., R. 32 E.	2,302	1,195	1,986	3 0	7.76	Polyhalite (white).
				1,832	2 0	12.93	Polyhalite, anhydrite, halite, and clay.
				2,284	3 0	13.08	Polyhalite and halite.
				2,298	4 3	9.55	Polyhalite, clay, anhydrite.
21	Lea County, SE. ¼ sec. 11, T. 21 S., R. 34 E.	3,003	2,079	2,553	5 0	8.89	Numerous horizons of polyhalite 2 ft. 4 inches to 8 ft. 3 inches, ranging from 9.80 to 5.95 percent K ₂ O.
				2,760	2 8	13.42	Polyhalite and halite.
				2,763	2 7	12.20	Polyhalite and anhydrite.
				2,760	6 0	11.54	Polyhalite and halite.
				2,814	2 5	12.20	Includes 2 beds above. Polyhalite.
22	Eddy County, SE. ¼ sec. 36, T. 23 S., R. 30 E.	1,724	609	638	2 0	10.65	Polyhalite and halite.
				682	2 7	12.63	Polyhalite, halite, and clay.
				1,152	2 1	13.62	Polyhalite and halite.
				1,175	4 2	10.91	Polyhalite, anhydrite, halite, and clay.
				1,308	2 11	10.70	Polyhalite, anhydrite, magnesite, halite, and clay.
				1,363	3 0	11.60	Polyhalite, anhydrite, halite.
23	Eddy County, NW. ¼ sec. 35, T. 20 S., R. 29 E.	904	512	1,501	2 0	12.43	Polyhalite and halite.
				1,565	2 1	11.48	Polyhalite, halite, and clay.
				623	6 0	11.52	Polyhalite, anhydrite, and halite.
24	Grand County, Utah, SE. ¼ sec. 13, T. 23 S., R. 20 E.	1,731					Well drilled 1,731 feet; a little polyhalite at various points but not in appreciable thickness.

¹ Mansfield, G. R., and Lang, W. B., Government Potash Exploration in Texas and New Mexico: Am. Inst. Min. and Met. Eng., Tech. Pub. 212, 1929, p. 16. The Texas-New Mexico Potash Deposits: Univ. of Texas Bull. 3401 (Separate), 1935, pp. 641-832.² All locations in New Mexico unless otherwise indicated.

In connection with the results presented in table 2, it should be noted that without exception polyhalite was found in every hole drilled, though not always in thicknesses of possible commercial interest. In many cases, however, the presence of large quantities of polyhalite in beds of thicknesses suitable for

economical mining was indicated. The shafts of the U. S. Potash Co. and the Potash Co. of America, now operating near Carlsbad, N. Mex., have been sunk through some of these polyhalite horizons; they have confirmed the drill-core findings and proved the existence of important beds of polyhalite in that region.

The extent of the deposits carrying salts of potash in the Permian Basin has been briefly summarized by Smith (35) as follows:

Polyhalite has been found in minute quantities as far north as Trego and Stafford Counties, Kans. Polyhalite has also been found in small quantities west of Amarillo, Tex., and further south it is commonly identified in oil-well cuttings. The area in which polyhalite has been found constitutes approximately 40,000 square miles (34) where approximately one core test has been drilled for each 400 square miles. Most of the core tests, however, are within a small area in New Mexico near the mines of the two operating companies, the United States Potash Co. and the Potash Co. of America. The area in which the most soluble potash minerals (sylvite, carnallite, and langbeinite) are found constitutes about 3,000 square miles, nearly all in New Mexico, in which 80 core tests have been drilled. The part in which as much as 14 percent potash has been found in beds 4 feet or more in thickness covers about 35 square miles, and one hole has been drilled for approximately each square mile in that area. The four known potash areas extend 17 miles north and south, and the boundaries have been reasonably well defined along the western erosion line where the potash horizons are in proximity to the top of the salt beds. The north, south, and east boundaries, however, have not been accurately determined. The potash content of the four areas mentioned is higher than the average potash content of salts in the mines of either Germany, France, Poland, Spain, or Russia. The reserves, based on a minimum of 14 percent potash in beds 4 feet or more in thickness, were estimated by the writer (Smith) in 1933 to be in excess of 100 million tons of potash salt. This reserve will be materially increased as the mines are extended and more prospect holes are drilled.

PURITY OF POLYHALITE DEPOSITS

Schaller and Henderson (28), of the Geological Survey, have studied the mineralogy of the drill cores obtained from the Government wells, as well as cuttings and specimens from private sources, and have identified a large number of alkali and alkaline earth salts, chiefly chlorides, sulfates, and carbonates of potassium, sodium, calcium, and magnesium similar to those found in the European salt deposits near Stassfurt in Germany.

The mineral salts, found in New Mexico and Texas, of special importance in connection with the recovery of the potash are: Halite, anhydrite, sylvite, polyhalite, kieserite, carnallite, langbeinite, magnesite, kainite, leonite, and more or less clay and hematite. The potash minerals of particular interest are sylvite, polyhalite, and langbeinite. These minerals usually are mixed with appreciable halite as the principal impurity which must be eliminated by mechanical or chemical means to produce high-grade potash salts.

The minerals commonly associated with polyhalite are halite and anhydrite (which predominate) and magnesite, clay, and small amounts of hematite as minor constituents. Microscopic examination of innumerable specimens of polyhalite has shown that the differences in color, which ranges from various shades of pink to reddish brown and brown, are due to the presence of hematite (Fe_2O_3). This iron mineral occurs as microscopic plates

disseminated through many of the saline minerals, especially the potash minerals, and much more commonly in the polyhalite or sylvite.

The average analysis of a carload of polyhalite obtained for experimental purposes from the U. S. Potash Co. during its shaft-

TABLE 3.—*Chemical analysis of a carload of polyhalite from the U. S. Potash Co. mine near Carlsbad, N. Mex.*

Analysis		Calculated composition	
Item	Percent	Compound	Percent
K.....	9.94	K ₂ SO ₄	21.93
Mg.....	3.34	MgSO ₄	15.15
Ca.....	12.81	CaSO ₄	34.29
Na.....	5.13	CaSO ₄ (anhydrite).....	8.17
Cl.....	7.90	NaCl.....	12.91
SO ₄	54.64	H ₂ O.....	4.53
CO ₂53	Fe ₂ O ₃ (clay and silicates).....	2.29
Insol.....	1.44	MgCO ₃73
Fe-Al oxides.....	.64	Total.....	100.00
H ₂ O.....	4.60		
Total.....	100.97	Polyhalite.....	75.9
		Halite.....	12.9
		Anhydrite.....	8.2
		Other.....	3.0
		Total.....	100.0

sinking operations in 1931 is given in table 3. This is a typical analysis of the material used in most of the experiments made in the development of the treatment processes discussed in this bulletin, although certain preliminary tests used samples of a white polyhalite obtained from Poland for experimental purposes.

CHARACTERISTIC PROPERTIES OF POLYHALITE

Polyhalite, found in white, light and dark gray, salmon, orange, brown, and various shades of red, corresponds to the formula K₂SO₄.MgSO₄.2CaSO₄.2H₂O and contains, when pure, K₂O, 15.6; MgO, 6.6; CaO, 18.6; SO₃, 53.2; and H₂O, 6.0 percent. The texture is usually fine-grained, but occasional coarser-grained specimens composed of larger distinct crystals do occur; however, the massive, compact form predominates.

It has a hardness of 2.5 to 3 and a specific gravity of 2.8. The refractive indexes are: α , 1.547; β , 1.560; γ , 1.567. The massive variety breaks with a conchoidal fracture and, aside from color, closely resembles a dense dolomitic limestone. Finely ground polyhalite dissolves only to a limited extent in either hot or cold water and after a prolonged treatment yields a solution containing low percentages of potassium and magnesium salts, even in the presence of considerable sodium chloride, which is known to increase the solubility.

The decomposition occurring when polyhalite is heated to 300° C. is very interesting and important. At this temperature polyhalite loses its water of constitution and the residual salts form a heterogeneous mixture comprising at least two phases. The physical and chemical properties of the calcined material vary greatly with the heat treatment but it consistently displays more

chemical activity. When properly calcined, polyhalite is readily decomposed by water, yielding solutions of potassium and magnesium sulfates. This phenomenon is the basis of most of the proposed processes for the extraction of the potash.

BUREAU OF MINES TECHNOLOGIC INVESTIGATIONS

The Sheppard Bill, as finally passed and signed by the President on June 25, 1926, provided funds for Government exploration of potash deposits in New Mexico and Texas and also authorized funds to be expended by the Departments of Interior and Commerce for the technologic study of methods for extracting the potash from the polyhalite deposits. That portion of the allotment assigned to the Department of Commerce, to be utilized by the Bureau of Mines (then in that Department) for laboratory investigations and development of possible extraction methods, largely was expended at the Nonmetallic Minerals Experiment Station, then on the campus of Rutgers University at New Brunswick, N. J.

The laboratory work on this phase of the program for potash development from domestic sources was carried on from August 1928 to June 1935. A considerable proportion of the effort was expended in the early stages of the investigation in reviewing the literature on potash and in preliminary reports, and an appreciable part of the final stages of the research was consumed in writing reports for publication.

Numerous technical articles were prepared and published as the work progressed, and more detailed reports covering the actual tests made were released periodically as Bureau of Mines reports of investigations. A list including the titles of all of these publications appears in the Appendix (pp. 248 to 250).

PURPOSE OF INVESTIGATIONS

The primary objective of this research was to develop methods for the commercial production of salable potash salts from the polyhalite deposits. More specifically, major attention was given to the production of salts already in use by the potash industry—the sulfate of potash, the sulfate of potash-magnesia, and muriate of potash. Other products that might find trade acceptance have also been considered—potassium sulfide, syngenite ($\text{CaSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), and potassium nitrate.

A secondary object was the investigation of possible byproducts (or coproducts) that might favor the over-all economy in potash production. Byproducts so considered were:

1. Potash chemicals: K_2SO_4 , K_2CO_3 , and K_2S .
2. Magnesium products: Epsom salts, the chloride, the basic carbonate, and calcined magnesia.
3. Technical sodium sulfate.
4. Calcium sulfate plasters.

These objectives included the collection and correlation of pertinent scientific and engineering data. In this connection, a comprehensive study of solubilities has been made.

IMPORTANCE OF POTASSIUM SULFATE

Fertilizers comprise most of the potassium sulfate consumed in the United States. Approximately 95 percent of the total consumption eventually goes into fertilizer mixtures. Furthermore, virtually all of the sulfate used in the past has been procured from Germany, except during trade interruptions.

For certain fertilizer applications the sulfate form of potash definitely is preferred. This special market arises from the demand of the growers of citrus fruits, tobacco, and potatoes. More abundant crops result from the proper use of a balanced mixed fertilizer containing potash salts. This applies also to tobacco, but the quality of this important product is impaired if the soil contains too high a quantity of chloride. Satisfactory growth occurs, but the assimilation of chloride by the plants tends to make the leaves brittle when dried and yield a fusible ash when smoked. This latter difficulty is often so pronounced as to extinguish the tobacco during smoking.

The addition of magnesia to soils deficient in this compound is important also. Insufficient magnesium salts will prevent full maturing of tobacco and other crops, so that potash fertilizers containing magnesium sulfate are desired in many instances. Formerly, this preference has assured a definite though admittedly restricted market for fertilizers containing sulfate of potash-magnesia and has maintained a constant demand in spite of the "premium price" or greater unit cost of K_2O in this particular form. Future demands will depend largely on this factor, but the lower cost of potash as muriate will favor that product wherever its use is satisfactory. Were the sulfate available at an equivalent unit cost, it is certain that those consumers who prefer the sulfate would take full advantage of the opportunity. Actually, of course, potassium nitrate (containing two fertilizer ingredients) is the compound best-suited for fertilizer mixtures were it economically possible to be so used.

SCOPE OF INVESTIGATIONS

The potash investigation has included the study of the most important ranges of the salt systems involved to acquire fundamental data not previously available; laboratory study of some 11 proposed processes for treatment to obtain pertinent data on rates of reaction, feasible concentrations of solutions, and possible recoveries as well as semi-pilot-scale tests to obtain insight into probable operating difficulties; and finally, a critical discussion of the unit steps of the various proposed processes and rough calculations to determine the probable costs of operation.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the invaluable cooperation of the equipment manufacturers whose estimates and recommendations have been employed in specifying the type and cost of machinery for the proposed extraction and recovery processes. The Hardinge Co. of York, Pa., the Door Co. of New York, the Allis Chalmers Manufacturing Co. of Milwaukee, Wis., the Bird

Machine Co. of South Walpole, Mass., Carrier Corporation, Syracuse, N. Y., Chemical Construction Co. of New York, A. O. Smith Corporation, Milwaukee, Wis., Swenson Evaporator Co., Harvey, Ill., The Turbo-Mixer Corporation, New York City, the Vulcan Iron Works, Wilkes-Barre, Pa., and the Public Service Co. of New Jersey furnished data, cost estimates, and other information that have been particularly useful.

The accumulation and interpretation of the fundamental and technologic data reported in this bulletin and used freely in the calculations have been made possible only by the efforts of predecessors and coworkers on the potash-research staff. Dr. H. H. Storch, former supervising engineer of the Nonmetallic Minerals Station, under whose direction the investigation work was initiated, deserves especial credit for the results obtained. The technical assistance rendered by Jesse M. Davidson, Loyal Clarke, Dr. Alton Gabriel, Nathan Fragen, Foster Fraas, A. A. Berk, B. A. Starrs, and W. W. Wiles, as well as the services of Cecil Davis and Ralph Whitney, machinists, and Fred Spille, under mechanic, have contributed indispensable help to the success of the investigations. Special acknowledgment is made to Loyal Clarke for critical review of the manuscript.

The cooperation of certain research institutions was solicited and encouraged during the course of these investigations, and considerable assistance was obtained in this manner. Independent studies pertaining to the fundamental phase relations of some of the salt systems were made and published during the course of the work by Hill (14), Ramsdell (25), and Koffolt and Withrow (17) in research conducted by New York University, University of Michigan, and Ohio State University, respectively.

SPECIAL CONSIDERATIONS

DEFINITIONS OF TERMS USED

The term "potash" has been used throughout this bulletin in accordance with the general custom of consumers of potassium salts in the fertilizer trade in referring to the compound K_2O ; and a potash salt would be any chemical compound containing the element potassium, irrespective of its chemical combination. The discussion of uses and economic relations has employed the commercially accepted nomenclature of the various salts, such as "muriate" and not potassium chloride, "sulfate of potash", "double-salt", "sulfate of potash-magnesia", or "kali-magnesia," instead of the equivalent chemical names. However, largely in the discussion of the fundamental data and treatment processes the scientific terms potassium sulfate, potassium chloride, sodium chloride, and so on, were used almost exclusively. Likewise, the chemical names and formulas were used interchangeably, as convenience warranted.

METHODS OF EXPRESSING CONCENTRATIONS OF SOLUTIONS

Most of the solutions dealt with in the report of this investigation were concentrated and frequently saturated with salts. The practice of expressing such concentrations as units of salt per unit of water rather than as percent was generally employed. In

written discussions this was stated in parts of salts present in 100 parts of water, but in the interest of convenience, graphs representing concentration data have been indicated in grams per hundred grams of water. A few exceptions, however, in which molal concentrations upon a percentage basis have been used for special reasons, will also be noted.

MINERALOGICAL NAMES AND CHEMICAL COMPOSITION OF SALINE MINERALS

The names and composition of the various salts mentioned in this bulletin, most of which are hydrated, are given in the following list:

<i>Mineral:</i>	<i>Single salts</i>	<i>Chemical formulas</i>
Anhydrite.....	CaSO ₄	
Epsomite.....	MgSO ₄ ·7H ₂ O	
Glauber's salt.....	Na ₂ SO ₄ ·10H ₂ O	
Gypsum.....	CaSO ₄ ·2H ₂ O	
Halite.....	NaCl	
Calcium sulfate hemihydrate.....	CaSO ₄ ·1/2H ₂ O	
Kieserite.....	MgSO ₄ ·H ₂ O	
Magnesite.....	MgCO ₃	
Mirabilite.....	Na ₂ SO ₄ ·10H ₂ O	
<i>Double salts</i>		
Astrakanite (bloedite).....	Na ₂ SO ₄ ·MgSO ₄ ·4H ₂ O	
Carnallite.....	MgCl ₂ ·KCl·6H ₂ O	
Glauberite.....	CaSO ₄ ·Na ₂ SO ₄	
Glaserite.....	Na ₂ SO ₄ ·3K ₂ SO ₄	
Kainite.....	KCl·MgSO ₄ ·3H ₂ O	
Langbeinite.....	K ₂ SO ₄ ·2MgSO ₄	
Leonite.....	K ₂ SO ₄ ·MgSO ₄ ·4H ₂ O	
Löweite.....	Na ₂ SO ₄ ·MgSO ₄ ·5/2H ₂ O	
Pentasalt.....	K ₂ SO ₄ ·5CaSO ₄ ·H ₂ O	
Polyhalite.....	K ₂ SO ₄ ·MgSO ₄ ·2CaSO ₄ ·2H ₂ O	
Schönite.....	K ₂ SO ₄ ·MgSO ₄ ·6H ₂ O	
Syngenite.....	K ₂ SO ₄ ·CaSO ₄ ·H ₂ O	
Vanthoffite.....	3Na ₂ SO ₄ ·MgSO ₄	

The term "sylvinit" has been omitted intentionally from the above lists, although it is in common use, especially in the German literature. It is not a mineral, but rather a mixture of halite and sylvite in varying proportions. This practice of designating mixtures of salt minerals by a general name has been used extensively by the Germans and "Thanite", or "Thanit," comprising a mixture of halite and kainite, is another example.

INDUSTRIAL SIGNIFICANCE OF POLYHALITE

Polyhalite presents a number of possibilities as a chemical raw material for a variety of potassium and magnesium compounds other than for use in fertilizers. Figure 6 has been prepared to indicate some of the most obvious products for which polyhalite could serve as a starting material.

Potassium sulfate would be the most important chemical product; but important tonnages of some of the listed chemicals are consumed annually in the United States, and in some instances, the major proportion is supplied by imports from foreign countries.

The mixture of potassium and magnesium sulfates, commonly known as sulfate of potash-magnesia or "kali-magnesia" represents the next largest quantity of potassium salts consumed.

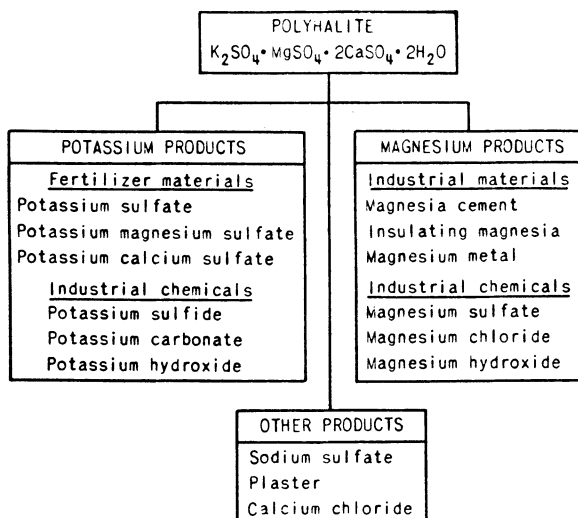


FIGURE 6.—Potential products from polyhalite and associated minerals.

Statistical data on these compounds and on the carbonate and hydroxide of potassium are given in table 4.

TABLE 4.—Imports and consumption of various potassium chemicals by United States¹

Item	Potassium sulfate		Potassium-magnesium sulfate		Potassium carbonate		Potassium hydroxide	
	Tons	Value	Tons	Value	Tons	Value	Tons	Value
1930-34 (average)								
Imports.....	58,194	\$2,404,362	218,201	\$393,536	7,035	\$681,118	3,045	\$340,881
Domestic production.....							49,348	868,000
1935								
Imports.....	70,819	2,014,626	25,876	515,281	2,063	231,551	1,713	226,165
Domestic production.....			(5)				9,518	1,260,031
1936								
Imports.....	59,581	1,812,793	13,605	276,788	1,397	150,806	1,546	209,505
Domestic production.....								
1937								
Imports.....	93,694	2,851,880	22,375	453,026	788	81,234	1,137	167,857
Domestic production.....			(5)		6,081	727,730	10,839	1,437,509
1938								
Imports.....	59,855	1,910,819	13,158	281,691	292	30,981	486	79,128
Domestic production.....			(5)					

¹ Statistics from Bureau of Mines Minerals Yearbook and various issues of Census of Manufactures.

² Represents potassium-magnesium sulfates for 1933-34 only.

³ Average for 1931-34.

⁴ Data for 1933 only.

⁵ No domestic production.

In addition to the salts of potassium now consumed for fertilizer and chemical uses, the compounds potassium-calcium sulfate and potassium sulfide warrant some attention. Syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$), which is the mineralogical name for this double sulfate of potassium and calcium, would be a new product to the fertilizer trade; but its potash content, 30.4 percent K_2O

(dehydrated basis), would justify serious consideration. Preliminary tests made with the cooperation of a larger fertilizer company have indicated that satisfactory results could be expected with the material. Aside from possible higher transportation cost, this chemical could be produced for this purpose and doubtless would compete with the other low-grade fertilizer compounds.

Potassium compounds.—Potassium sulfide probably would prove of little interest to the fertilizer trade but if available at an attractively low price perhaps would find other applications.

Surprisingly enough, no toxic effects of potassium sulfide were noted in pot tests made with barley by A. W. Blair of the New Jersey Agricultural Station. The high equivalent potash content of this compound (85.5 percent) is noteworthy, as it provides a means of possible saving in transportation costs; and utilization of this substance, probably in the form of the fused salt, would offer a raw-material source for a large number of other important potassium salts.

Magnesium compounds.—The magnesium associated with the potassium sulfate in the polyhalite molecule would present an abundant source of this element were appreciable amounts of polyhalite being treated for the potash content. Important quantities of various magnesium salts are consumed annually in the United States, and the figures on total imports are impressive. Table 5 contains data on some of the most important of these salts.

TABLE 5.—*Imports and consumption of various magnesium compounds by the United States*¹

Item	Magnesium chloride (hydrated and anhydrous)		Magnesium sulfate (Epsom salts)		Magnesium sulfate (kieserite), calcined		Calcined magnesia		Magnesium carbonate (precipitated)	
	Pounds	Value	Pounds	Value	Pounds	Value	Pounds	Value	Pounds	Value
1930-34										
Imports.....	861,138	\$8,267	8,357,367	\$51,761	389,467	\$69,426	581,958	\$26,662
Domestic production..	(²)	74,728,000	1,234,342	(²)	(²)
1935										
Imports.....	50,049	1,095	3,060,883	18,495	3,668,091	\$30,291	196,264	36,297	601,459	27,935
Domestic production..	(²)	376,978,000	116,533	(²)	(²)	14,602,000	877,741
1936										
Imports.....	31,876	584	4,334,792	25,008	5,439,651	44,664	238,039	39,098	754,084	34,396
Domestic production..	(²)	(²)	(²)	(²)
1937										
Imports.....	64,300	1,120	3,905,303	26,771	8,233,726	71,889	217,413	35,643	1,042,900	51,684
Domestic production..	(²)	82,738,000	1,216,748	(²)	(²)	13,010,000	788,215
1938										
Imports.....	81,734	1,572	1,598,316	12,328	6,386,795	66,470	91,545	15,947	940,069	53,151

¹ Data from statistics given in Bureau of Mines Minerals Yearbook and Census of Manufactures.

² No data on domestic production available.

³ Data for 1933.

Magnesia produced from magnesite and dolomite and used in refractories and in magnesia pipe covering represents the principal tonnages for these special applications, but light and dense magnesias are potential products from basic magnesium carbonate that could easily be recovered from the magnesium sulfate waste liquors remaining after the potassium sulfate is recovered. Magnesium chloride and magnesium oxides, essential ingredients of magnesium oxychloride cements, are other possible byproducts.

The presence of sodium chloride in all of the polyhalite deposits and the inevitable contamination of plant process liquors with the chloride ion suggest the possibility of recovering the magnesium chloride. A step farther in this direction is an investigation of the possibility of adding common salt to the large quantities of waste solutions high in magnesium sulfate that would await disposal or byproduct treatment in a plant extracting polyhalite. Sodium chloride and magnesium sulfate, on proper manipulation, would yield either Glauber's salt or anhydrous sodium sulfate, depending on conditions, and finally a concentrated solution of magnesium chloride that might easily lend itself to processing for the production of magnesium metal.

During the years 1934-38 approximately 4,000,000 pounds of magnesium metal were produced in the United States by one well-established company at a selling price of about 30 cents a pound. This production, under the especially favorable stimulation of increased demands for airplane manufacture, rose to 97,925,684 pounds in 1942, permitting a price drop to 22½ cents a pound.

Sodium compounds.—The most obvious of the sodium compounds that conceivably presents possibilities of byproduct development is sodium sulfate. Foreign imports of high-grade chemical sodium sulfate normally entering as salt cake have supplied the principal demands for this chemical in a market largely denied domestic producers. Natural deposits exploited without the inherent advantages of a large chemical-manufacturing establishment have not been able to compete with the salt cake produced from foreign sources.

Calcium compounds.—Two products made from calcium compounds—gypsum products and calcium chloride—deserve special mention as potential byproducts in a hypothetical plant processing polyhalite. Calcium chloride, usually in dilute concentration, is discarded as waste solutions in numerous chemical processes; however, considerable tonnages also are recovered and consumed annually. The export trade in this chemical is important also, as should be noted in table 6.

TABLE 6.—*Calcium (calcium and magnesium) chloride from natural brines sold by producers in the United States, 1934-39*

Year	Short tons	Value	Year	Short tons	Value
1934	76,719	\$1,153,159	1937	97,142	\$1,295,403
1935	83,546	1,039,103	1938	96,470	1,218,938
1936	125,911	1,909,908	1939	108,441	1,485,784

Calcium chloride imported for consumption in and exported from the United States, 1934-39

Year	Imports		Exports	
	Short tons	Value	Short tons	Value
1934	1,975	\$26,271	30,715	\$566,189
1935	2,004	26,987	30,736	525,179
1936	2,128	25,678	27,831	503,966
1937	2,205	24,908	21,732	415,309
1938	1,642	21,174	24,118	396,981
1939	996	12,314	19,382	318,199

The high calcium sulfate content of polyhalite would make utilization of that constituent desirable. For certain uses, the color of the calcium sulfate residues might be objectionable, as most of them are pink from iron compounds, present largely as hematite. Schoch (33) has investigated the potentialities of producing gypsum plaster and gypsum board from these residues and contemplated a development in which these materials would be manufactured as the major product with potassium sulfate and magnesia compounds being considered only as byproducts.

The manufacture of gypsum products is unquestionably an important industry, as indicated by the \$39,000,000 business conducted in 1937 and slightly more than \$36,000,000 worth of materials sold in 1938.

GENERAL OUTLINE OF REPORT

This report describes the treatment of polyhalite for the recovery of potassium salts and comprises two main parts and two appendixes.

Part I covers the mining, crushing or grinding, and extraction and recovery of potassium salts from polyhalite. In addition, flow sheets are given illustrating the steps involved in each process developed, as well as the quantity of materials handled and recovered. Types of equipment have been suggested, estimated costs of such equipment when installed and operated have been made, and complete production costs by each of the processes have been calculated. Finally, a market value based upon current prices of the materials produced has been assigned and transportation costs have been deducted to derive figures that approximate the potential daily margin for operating a complete chemical plant.

Part II presents the experimental data, with a limited discussion and conclusions based upon fundamental laboratory investigations.

The first appendix comprises the detailed analysis of the equipment requirements and the direct operating costs of the individual treatment steps for each of the proposed processes.

The second appendix is devoted to the solution equilibria and phase diagrams resulting from the systems comprised of the essential constituent compounds of polyhalite and sodium chloride; these compounds include K_2SO_4 , $MgSO_4$, $CaSO_4$, $NaCl$, and H_2O .

PART I. MINING, CRUSHING, CALCINATION, AND EXTRACTION OF POLYHALITE FOR RECOVERY OF POTASSIUM SALTS

MINING OF POLYHALITE

Polyhalite will be mined by the methods discussed by Wroth (44) in the original report on the commercial possibilities of the Texas-New Mexico potash deposits. Since that report was released, actual mining of the potash beds for the recovery of the mixture of sylvite and halite has been practiced (23), and mining costs are now known, though they are not available for general publication. However, the mining of polyhalite will differ slightly from the mining of sylvinite, owing to the differences in physical properties of the minerals.

Wroth's analysis of the mining has considered most of the important details and need not be repeated at this point, as those interested in all the details should consult his bulletin (44, pp. 52-72).

MINING METHOD PROPOSED BY WROTH

The method suggested by Wroth is essentially the same as that employed in coal mining where horizontal seams occur, and most of the accepted practice in that industry would apply. Briefly, the scheme used is to sink vertical two- or three-compartment shafts to intersect the deposit and to provide the means for hoisting the mined product. A second auxiliary and possibly smaller shaft, sunk at a distance from the main shaft, is required to facilitate mine ventilation and to provide the added safety of a separate means of escape for the miners in cases of emergency or accident to the hoisting shaft.

Underground mining methods employing the room-and-pillar system, operating off main entries or haulageways with the latest approved mining machinery, would be practiced with full mechanized loading and haulage by electric locomotives. Air-driven drills and special undercutting machines are indicated as essential to efficient blasting and high yields of polyhalite, as the cost of explosives is an important item in the mining costs.

Hoisting by electric machinery, with automatic self-filling and self-dumping skips, has been suggested as desirable. The proposed preliminary core-drilling program to prove the presence of economic deposits of polyhalite before the location of and the sinking of the hoisting shaft is also endorsed. In short, virtually all of the recommendations made by Wroth would apply to the operations proposed in this report.

MINING COSTS

In estimating the probable costs of mining polyhalite, the general plan indicated by Wroth has been followed closely, the main difference being that the proposed daily output would be

1,600 tons to be mined and raised to the surface in two 8-hour shifts instead of the 2,000-ton production considered in the previous work.

Some modification of the estimated costs will be necessary to determine the probable costs for mining this smaller tonnage. Mining trends during the past 10 years have been toward greater mechanization with correspondingly lower basic costs; but equipment costs and labor have increased appreciably, and taxes, social security payments, and workman's compensation have added to production costs, so that it is assumed that the net operating costs would be approximately the same as those calculated by Wroth.

To make a conservative estimate of the mining costs on this somewhat reduced scale, it has been assumed that the same preliminary development and equipment costs would be charged as were used in Wroth's calculations. The direct labor has been estimated on a pro rata basis—that is, approximately eight-tenths of that estimated for the 2,000 tons. The power cost has been increased to \$0.003 instead of \$0.002 per kilowatt-hour. Supplies have been calculated as 10 percent less than on the larger tonnage, but supervision, both direct and general, and administration have been assumed to be the same. In addition, interest on the investment has been included at the rate of 6 percent and an extra 1½ percent to offset taxes and insurance costs.

CAPITAL REQUIREMENTS

The capital costs for the development of the mining operations for the equipment of the completed mine and for the housing of employees have been itemized by Wroth (44, pp. 68-71). Details of these estimates will not be repeated at this point; but, for convenience, the summarized figures are given in table 7.

TABLE 7.—*Capital required for preliminary development and mine operations*

Item:	Value
Preliminary development	\$ 571,529.00
Operating equipment	468,776.00
Housing, etc.	175,000.00
Total capital required.....	\$1,215,305.00
Mine development chargeable to operations but required in advance.....	172,478.00
Total cash capital required.....	\$1,387,783.00

The capital costs have been based upon a production of 2,000 tons a day and therefore should be conservatively ample for a proposed 1,600-ton operation in two shifts. The preliminary development costs are to be amortized in 20 years, and the depletion cost charged in table 8 represents the pro rata daily charge upon this basis.

PRODUCTION COSTS

The other itemized costs have been presented in table 8 in order to summarize the estimated mining costs. In addition, the figures offered by Wroth have been incorporated for comparative purposes upon the larger tonnage basis.

It should be noted that the total costs for 2,000 and 1,600 tons daily production are \$2,167.67 and \$2,423.46, equal, respectively,

TABLE 8.—Summary of estimated mining costs for 1,600 tons of polyhalite per day, compared with *Wroth's*¹ estimate for 2,000 tons

Item	1,600 tons					2,000 tons ¹				
	Average number of men	Labor	Power	Supplies	Total	Average number of men	Labor	Power	Supplies	Total
Rooms:										
Drilling and blasting.....	60	\$355.00	\$9.46	\$229.68	\$594.14	74	\$438.12	\$7.88	\$255.20	\$701.20
Scraper loading.....	42	201.00	3.34	12.46	216.80	52	248.78	2.78	13.84	2,065.40
Gathering.....	10	50.80	4.44	2.16	57.40	13	66.00	3.70	2.40	72.10
Cost of 1,480 tons ²	112	606.80	17.24	244.30	865.34	139	752.90	14.36	271.44	1,038.70
Headings:										
Drilling and blasting.....	18	94.10	2.54	80.19	176.83	22	115.08	2.12	89.10	206.30
Loading.....	8	41.55	1.08	2.32	44.95	9	48.86	.90	2.58	49.34
Gathering.....	7	38.50	.62	1.44	40.56	8	44.00	.52	1.60	46.12
Extension of track, etc.....	9	43.40	70.20	113.60	11	53.00	78.00	131.00
Cost of 120 tons ²	42	217.55	4.24	154.15	375.94	50	257.94	3.54	171.28	432.76
Cost of 1,600 tons ² on main siding.....	154	824.35	21.48	398.45	1,244.28	189	1,010.84	17.90	442.72	1,471.46
Main-line haulage.....	5	26.70	9.60	1.08	37.38	6	32.00	8.00	1.20	41.20
Maintenance of tracks.....	4	20.00	9.00	29.00	4	20.00	12.50	30.00
Maintenance of cars.....	2	8.33	11.25	19.58	3	12.50	10.00	25.00
Dumping at shaft.....	3	15.00	3.60	18.60	4	20.00	4.00	24.00
Hoisting.....	17	112.50	12.00	15.93	140.43	19	125.70	10.00	17.70	153.40
Haulage and hoisting costs, 1,600 tons at surface.....	31	182.53	21.60	40.86	244.99	36	210.20	18.00	45.40	273.60
Operating costs.....	185	1,006.88	43.08	439.31	1,485.27	225	1,221.04	35.90	488.12	1,745.06
Direct supervision.....	8	78.00	52.00	130.00	8	78.00	52.00	130.00
Depreciation.....	153.20	153.20
Total direct costs.....	193	1,084.88	43.08	491.31	1,772.47	233	1,299.04	35.90	540.12	2,028.26
Administration and general expense.....	26	180.00	130.00	300.00	26	180.00	120.00	300.00
Depletion of preliminary mine development.....	95.20	95.20
Total mining cost.....	219	1,264.88	43.08	611.31	2,167.67	259	1,479.04	35.90	660.12	2,423.46
Interest on investment.....	220.41	220.41
Taxes and insurance.....	110.21	110.21
Modified total mining costs.....	2,498.29	2,498.29
Average cost per ton mined.....	1.56	1.21

² These figures become 1,850, 150, and 2,000, respectively, for 2,000 tons daily capacity.¹ See reference 44 (p. 72).

to \$1.21 and \$1.35 per ton. However, this latter figure becomes \$1.56 when interest and miscellaneous taxes are added; and total mining costs have been estimated to correspond to this amount.

CRUSHING AND GRINDING

GENERAL CONSIDERATIONS

The polyhalite as it issues from the mine requires crushing and grinding followed by a calcination treatment before the potash is recovered. Two general procedures are involved in the extraction, depending on whether hot extraction (212° F.), to produce a solution of potassium and magnesium sulfate with subsequent recovery of the potassium sulfate of 88- to 95-percent grade, or cold extraction (77°–86° F.) is employed for the production of the double potassium-calcium sulfate, syngenite, which would contain 48 to 50 percent of K_2SO_4 .

It has been shown that grinding need not be carried on beyond minus 10-mesh for the hot extraction, but better results are obtainable on finer material in the formation of syngenite. Presumably, a saving in grinding costs is possible by limiting the dry grinding to all through 10-mesh and where fine material is preferable to divert the fine fraction of the 10-mesh product to the syngenite-production step. Grinding has therefore been calculated and equipment selected to reduce the mine-run polyhalite to only 10-mesh, and where syngenite is being produced, further wet-grinding in ball mills operating in closed circuit with classifiers has been suggested.

This arrangement differs from that considered by Wroth, in that the data available at the time the first bulletin was published indicated the necessity of ball milling. Obviously, some economy should be possible in the light of this more recent information. The principal difference in selecting suitable crushing and grinding equipment is the permissible use of rolls instead of ball mills and the adoption of stage crushing.

It is proposed to effect the crushing by means of a primary crusher to reduce all oversize on a 4-inch grizzly to this size, with the undersize going to two secondary crushers delivering a minus 1-inch product. The oversize on a $\frac{1}{4}$ -inch screen will go to a set of coarse rolls, with the $\frac{1}{4}$ -inch undersize from the secondary crushers and the coarse rolls going to two sets of finishing rolls to produce 10-mesh material. Vibrating screens are to be used to remove the undersize and permit the return of oversize for additional crushing.

It is believed that this arrangement will produce a minimum of fines and thus avoid difficulty from sintering or dusting during the subsequent calcination treatment. The flow sheet illustrating the crushing, according to this plan, is given in figure 7. The capacity of the equipment should be large enough to handle the polyhalite at an average of 100 tons per hour, or at the same rate as it is mined, requiring but two 8-hour shifts to grind the necessary tonnage.

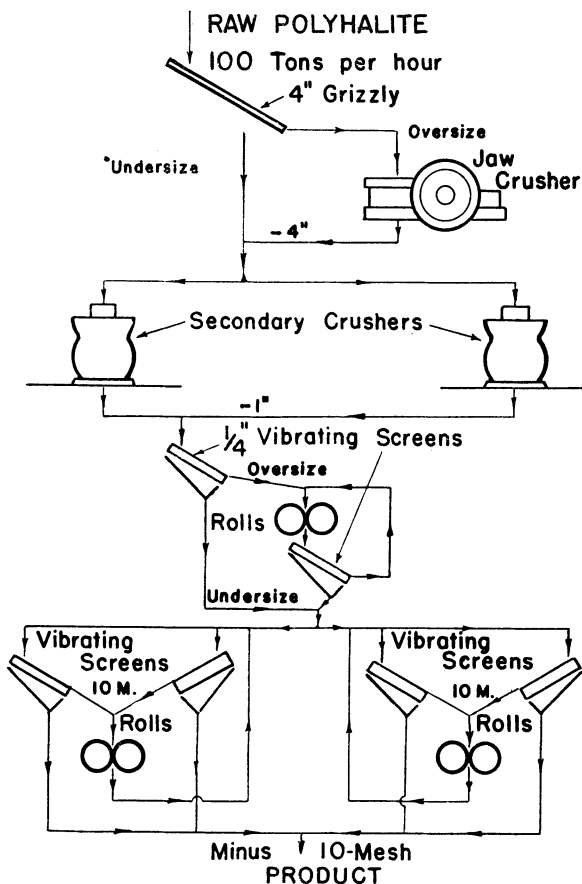


FIGURE 7.—Proposed flow sheet for crushing polyhalite.

EQUIPMENT COSTS

The estimated cost of the grinding plant, including the building and the necessary dust collectors, is \$158,000.

Primary crusher and grizzly.—The grizzly serving to divert the 4-inch oversize in the mine-run polyhalite feed will cost about \$600 installed; and the primary crusher, which may be either of the jaw or gyratory type, will cost \$22,900 completely installed and require approximately 125 hp. (connected).

Secondary crushers.—The secondary crushing will be done by two jaw crushers costing together about \$17,200 and requiring 25 hp. each, a total of 50 hp.

Vibrating screens.—The screens to be used will be of the vibratory type, actuated mechanically or electrically, and entirely enclosed to facilitate dust collection. One $\frac{1}{4}$ -inch screen to divert the oversize from the secondary crushers to the coarse crushing rolls and a second $\frac{1}{4}$ -inch screen operating with oversize return to the rolls will be required, at a total cost of about \$4,250; and each will be operated by a $7\frac{1}{2}$ -hp. motor.

Four additional 10-mesh vibrating screens will be required to handle the minus $\frac{1}{4}$ -inch product from the secondary crusher and coarse rolls. These will cost about \$9,000 installed and require about 30 hp. connected load.

Crushing rolls.—The set of coarse rolls that reduce the oversize from the secondary crushers to $\frac{1}{4}$ -inch will cost about \$18,750 installed and the two sets of finishing rolls an additional \$10,000 each or a total of \$38,750 and an estimated connected load of 75 hp.

Conveyors and elevators.—Miscellaneous conveyors and elevators, as well as automatic feed-control devices, will be necessary in the grinding operation. These have been estimated to cost possibly \$10,000 in the mill and an additional \$10,645 for conveying the finished material to the storage bins and from the storage bins to the salt-leaching operation.

Building.—The grinding plant will be housed in its own separate building and provided with concrete silos with a storage capacity of 3,200 tons, equivalent to 2 days' extraction treatment. The costs will be \$15,000 for a building and \$12,000 for the four silos, each measuring 24 feet in diameter by 40 feet in height. Miscellaneous items, such as surge bins, special control equipment, and dust collectors, would require about \$17,655, equivalent to 15 percent of the total cost of the crushing equipment.

Summarized equipment costs

Grizzly, 4-inch	\$ 600.00
Primary crusher (1)	22,900.00
Secondary crushers (2)	17,200.00
Vibrating screens, $\frac{1}{4}$ -inch (2)	4,250.00
Vibrating screens, 10-mesh (4)	9,000.00
Coarse crushing rolls	18,750.00
Finishing rolls, 2 sets	20,000.00
Conveyors and elevators in mill	10,000.00
Conveyors and elevators in storage plant	10,645.00
Building	15,000.00
Concrete storage bins (4)	12,000.00
	<hr/>
	\$140,345.00
Miscellaneous allowance (15 percent of equipment)	17,655.00
	<hr/>
Total grinding-plant cost	\$158,000.00

OPERATING COSTS

Power.—The estimated power required in the crushing operation corresponds to the following table.

	<i>Horsepower rating</i>
Primary crusher	125.0
Secondary crushers	50.0
Crushing rolls	75.0
Vibrating screens	45.0
Conveyors, elevators, feeders	40.0
	<hr/>
Total connected load	335.0

If the consumption is 85 percent of the connected horsepower and the plant is operated for a total of 16 hours, the power charge would correspond to 3,417 kw.-hr., which at \$0.003 would be \$10.25 per day.

Labor.—Three men per shift or a total of six per day at \$5.00 would require an outlay of \$30.00; other items of cost are summarized in the following table.

Summary of direct crushing costs

	<i>Cost per day</i>
Labor	\$ 30.00
Power, 3,417 kw.-hr. at \$0.003.....	10.25
Maintenance and supplies at 5 percent.....	26.33
Direct operating costs.....	66.58
Depreciation (15 years).....	35.11
Combined operating and depreciation costs.....	\$101.69

Depreciation has been included with the operating costs in order to agree with the general plan of making a specific rate for each type of equipment.

SUPERVISION

Only the cost of direct supervision, which would mean one foreman per shift at \$6.00 each, or a total of \$360.00 per month, would be charged against crushing operation; this, together with general supervision, assumed to be 40 percent of the total, would mean a daily charge of \$12 plus \$8, or a total of \$20.00 per day.

ADMINISTRATION

The arrangement for division of administration costs and general expenses equally between the mine and treatment plant will be adopted as satisfactory, especially in view of the small number of men who will work in the crushing plant and the already well-developed status of grinding operations.

SUMMARY OF CRUSHING COSTS

The summarized costs for crushing 1,600 tons of mine-run polyhalite to minus 10-mesh will be as follows:

Item	Cost of equipment	Number of men	Cost per day, 24 hours			
			Labor	Power	Maintenance and supplies	Total
Crushing.....	\$158,000	6	\$30.00	\$10.25	\$26.33	\$66.58
Direct supervision.....		2	12.00		8.00	20.00
Total direct costs.....		8	\$42.00	\$10.25	\$34.33	\$86.58
Depreciation.....						35.11
Total crushing costs.....						\$121.69
Cost per ton.....						.076

COLD-WATER LEACHING FOR REMOVAL OF SODIUM CHLORIDE FROM POLYHALITE

GENERAL CONSIDERATIONS

As pointed out in the section on the leaching of crushed raw polyhalite (see p. 152) and in the discussion of the effects of NaCl on the various equilibria involved in the hot extraction of calcined polyhalite (see p. 116) it is desirable to remove virtually all of the sodium chloride before the calcined polyhalite is leached.

In general, the most advantageous time to remove the sodium chloride from the raw polyhalite is immediately after crushing and before calcination. From a consideration of the various characteristics of the minerals involved and from a critical review of the important major factors, the best means for eliminating

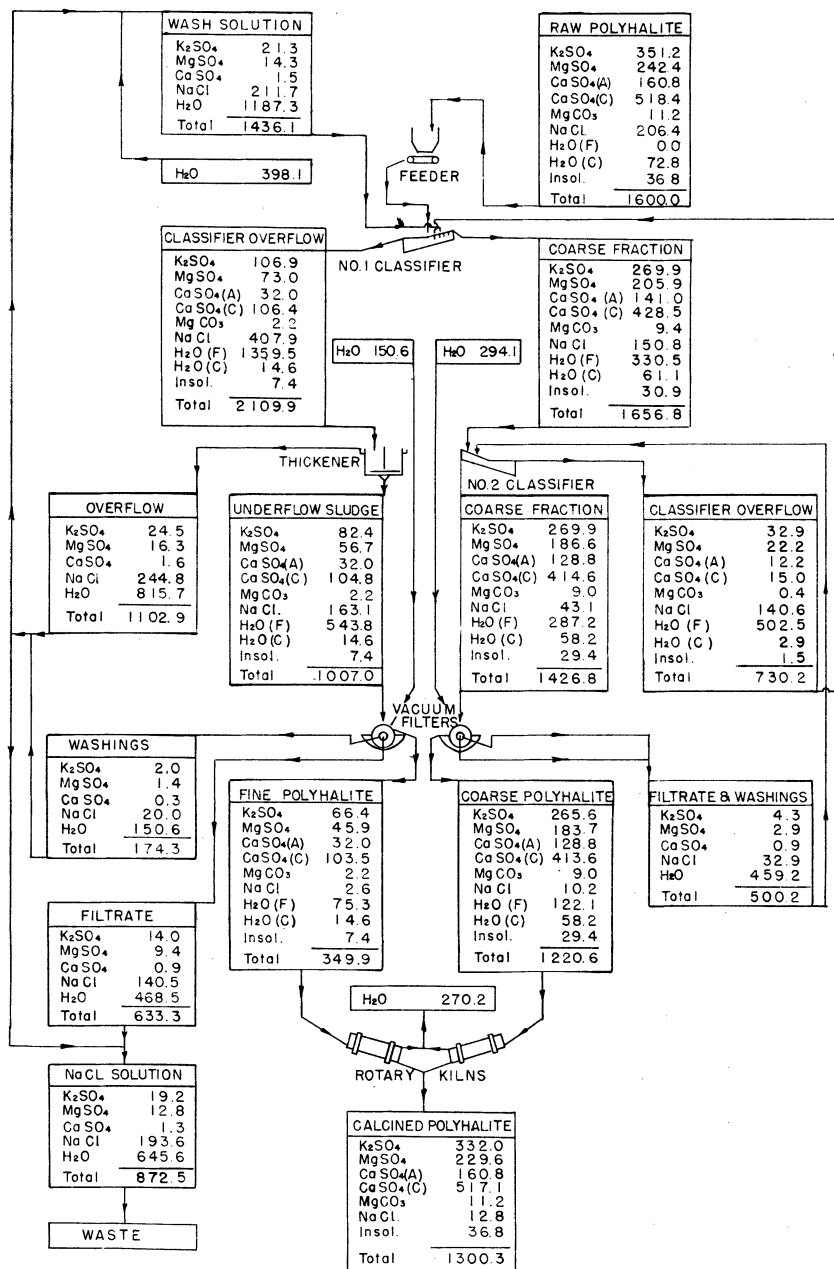


FIGURE 8.—Suggested flow sheet for washing NaCl from polyhalite.

the salt would be to crush the polyhalite to 10-mesh, then extract the salt by countercurrent leaching methods. Coarser material could be employed very satisfactorily, but for efficient subsequent extraction of the potash from the calcined polyhalite, material of smaller particle size would be required. Less difficulty would result by initial grinding to the desired size. It, therefore, appears that extraction of the salt from the 10-mesh material and the use of the wet product as feed for the rotary kiln would be the best procedure.

As several of the processes produce both concentrated extract solutions for which coarse polyhalite (10-mesh) is suitable and syngenite for which at least a minus 65-mesh calcined product is preferable, having a supply of both a coarse and a fine material is an advantage.

This condition results when the 10-mesh raw polyhalite is leached by a countercurrent extraction procedure incorporating a wet classification of the suspended solids. Within certain limits it would be possible to control the amount of coarse and fine material produced and to divert each fraction to meet the demands of the various extraction steps.

On the other hand, in those processes employing either all coarse or all fine polyhalite, the classified solids would have to be remixed after the salt had been extracted. In spite of this disadvantage, it is believed that the simplicity and expected efficiency justify the recommendation of the flow sheet as illustrated in figure 8.

COMPOSITION OF RAW POLYHALITE

Some variation in the composition of the mined polyhalite probably will occur, especially in the quantity of associated halite. To keep potash losses at a minimum, it will be necessary to limit the water used to the amount required to remove the salt without exceeding the saturation concentration for sodium chloride.

The proportions of the major constituent minerals, closely approximating the composition of one carload of polyhalite obtained from the sylvinite mining operations near Carlsbad, are given in table 9.

TABLE 9.—*Mineralogical composition of raw polyhalite to be treated for removal of NaCl*

<i>Mineral:</i>	<i>Percent</i>
Polyhalite	76.6
Halite	12.8
Anhydrite	8.2
Other—clay, magnesite, Fe_2O_3 , etc.....	2.4
Total	100.0

The majority of the processes discussed in this report are based upon the treatment of a calcined polyhalite containing approximately 1.0 percent of NaCl, although certain of the processes, notably 5 and 7A, can tolerate larger percentages.

SALT-WASHING TREATMENT

The essential feature of the salt-washing treatment is first to disperse the crushed raw polyhalite in a mixer or agitator provided with a continuous discharge into a wet classifier; vigorous

agitation is unnecessary and should be avoided. Dissolution of the salt is rapid, and the fine material is quickly removed; after a preliminary thickening, it is pumped to a vacuum filter or possibly a continuous horizontal centrifugal separator, and an amount of wash water used necessary to displace completely the retained liquor.

A portion of the filtrate corresponding to the salt entering the system is discarded, while the balance is returned to the first agitator to maintain the proper dilution pulp. Obviously, the washings are added to the agitator or mixer together with the remainder of the fresh water entering the process. Additional water also is introduced in the form of washings from the filters operating on the coarser fraction; but this portion, together with the filtrate from this operation, is returned to No. 2 classifier either after combining or possibly using separately to permit the more dilute washings to be sprayed onto the sands being discharged from the second classifier.

The scheme outlined offers a flexible arrangement where the water employed in the leaching process may be divided into three portions and used in the most effective manner to effect a thorough washing without any serious loss of potassium sulfate in the waste liquors.

As indicated in the flow sheet, the sands, with adhering liquor from the first agitator, are discharged to a second classifier to allow time enough for dissolution of the coarser particles of halite. The overflow discharges to the No. 1 classifier and the sands to a top-feed vacuum filter or to a continuous horizontal or vertical centrifuge so arranged as to permit a washing treatment.

Finally, the washed sands or "fines" may be stored for separate calcinations or combined in any desired proportions.

In the salt-washing operations as indicated in the flow sheet, figure 8, the waste solution resulting from the treatment of 1,600 tons of crude polyhalite will amount to 872.5 tons per day, equivalent to approximately 174,500 gallons of waste plant liquor. It will be noted that 193.6 tons of NaCl, or about 94 percent of the salt, are removed. The losses of potassium and magnesium sulfates in this solution are 19.2 and 12.8 tons, corresponding to 5.5 and 5.3 percent, respectively, of these constituents of the crude polyhalite.

EQUIPMENT AND OPERATING COSTS

The preliminary mixing or agitating of the raw polyhalite is desirable to insure efficient dispersion; once this is accomplished, the subsequent retention in the classifiers is designed to effect the necessary dissolution of the salt.

Feeding.—The feeding arrangement, including the transportation of the crushed polyhalite from the storage silos, might be arranged in various ways. Presumably, a small surge bin placed between the conveyors and the feed to the salt leaching will be necessary to insure smooth operation. This bin, together with the elevators, motors, feed device, and controls, will cost \$1,925. Power will be about 90 kw.-hr. per day and the services of one

man for one-third of his time, or a total of 8 hours, at \$0.60, equivalent to \$4.80 per day.

Operating costs of feeding crushed polyhalite to salt leaching operation

Item:	Cost per day, 24 hours
Power—90 kw.-hr. at \$0.003.....	\$ 0.27
Labor—8 hours at \$0.60.....	4.80
Maintenance and supplies.....	1.00
Total direct operating cost.....	6.07
Depreciation (15 years).....	.40
Combined operating and depreciation costs.....	6.47

Mixing.—A 6-foot by 6-foot steel tank provided with an efficient motor-driven agitator, such as the “Turbo-Mixer” type, and having a dished bottom to facilitate discharging will be required. The cost of this agitator installed will be \$1,255 and it will require an 8-hp. motor consuming 144 kw.-hr. every 24 hours.

The operating charges, including the depreciation and the cost of the fresh water added directly to the agitators at this point, would be as follows:

Operating costs of mixing

Item:	Cost per day, 24 hours
Labor— $\frac{1}{3}$ man per shift at \$5.00.....	\$ 5.00
Power—144 kw.-hr. at \$0.003.....	.43
Maintenance and supplies.....	.11
Water—95.5 M gal. at \$0.05.....	4.78
Direct operating cost.....	10.32
Depreciation, 10 percent.....	.42
Total operating and depreciation costs.....	10.74

Classifying.—The classifying treatment might be effected in any one of several types of standard machines; either the helical screw, the rotary flight-lifting, or the reciprocating-rake type could be adapted to the purpose. Costs would vary slightly, but the variation in range would be small.

Two suitable classifiers would cost about \$6,300 each completely installed, and doubtless a somewhat larger machine would be required to handle the full feed of the No. 1 classifier than merely the sands from this classifier. However, the same capacity has been assumed; and a classifier of the rake type, 5 feet wide by 27 feet long, operated with 6 hp., would be required.

Power and labor costs would be relatively low, as it is believed that only about one-third of the time of one attendant would be necessary to keep the classifiers operating satisfactorily. The other costs are given in the following summary.

Operating costs of classifiers

Item:	Cost per day, 24 hours
Power—12 hp. or 216 kw.-hr. per day at \$0.003.....	\$ 0.64
Labor—1 man-day	5.00
Maintenance and supplies.....	1.00
Total direct cost.....	6.64
Depreciation, 10 percent.....	4.20
Combined operating and depreciation costs.....	10.84

Thickening.—To lighten the burden on the filter handling the overflow solids, a thickener will be used to receive the overflow from No. 1 classifier. A 45-foot thickener provided with a large triplex pump costs about \$1,100, which completely installed with a reinforced-concrete tank and thickener driving mechanism will be \$5,755 and require a total of 7 hp. to operate. Labor and maintenance costs will be relatively small and are summarized as follows:

<i>Operating costs of thickening of No. 1 classifier overflow</i>	
<i>Item:</i>	<i>Cost per day, 24 hours</i>
Power—126 kw.-hr. at \$0.003.....	\$ 0.37
Labor—2 hr. per day at \$0.60.....	1.20
Maintenance and supplies.....	.28
	<hr/>
Direct operating cost.....	1.85
Depreciation (15 years).....	1.30
	<hr/>
Combined operating and depreciation costs.....	3.15

Filtering.—Vacuum filters or centrifuges may be used. The filtering operation is the major item of expense both in equipment and operating costs. The extent to which the NaCl may be extracted depends largely on the efficiency of the filtrate separation and the effectiveness of the subsequent washing. Virtually all of the halite present in the raw feed goes into solution readily, and the principal difficulty is to assure thorough displacement of the retained liquor. This is slightly more difficult on the fine material, but fortunately only 274.9 tons (dry weight) of these “fines” will require treatment in comparison with 1,099.5 tons of the coarse product each 24 hours.

It is believed that the horizontal continuous centrifugal filter could be applied on this separation; if so, the maker's recommendation would entail the use of two machines on the coarse fraction and one machine on the fine portion, costing about \$20,000 each, installed. However, pilot-plant tests would be necessary to determine their feasibility and to measure power consumption. To assure a liberal allowance for the liquid-solid separation, estimates will be based upon the use of rotary vacuum filters designed for top feeding on the coarse fraction.

It is estimated that 2,200 square feet of filtering area will be necessary to handle the sands and about 1,100 square feet for the fine polyhalite, thereby indicating the probable use of two filters on the coarse fraction and one on the fine material. The estimated costs of these three filters, with all necessary accessories completely installed, will be \$91,000.

The power consumption would be about 6,000 kw.-hr. per day, and possibly 1 man per shift at \$5.50 for each filter would be necessary. If a set of filter cloths would last 6 months, the operating costs would be as follows:

Operating costs of filtering

<i>Item:</i>	<i>Cost per day, 24 hours</i>
Power—6,000 kw.-hr. at \$0.003.....	\$ 18.00
Labor—3 men per shift or total of 9 at \$5.50.....	49.50
Maintenance and supplies.....	9.90
Water—106,718 gal. at \$0.05M.....	5.34
	<hr/>
Direct operating cost.....	82.74
Depreciation (10 percent).....	30.33
	<hr/>
Combined operating and depreciation costs.....	113.07

The water used in washing the filter cakes has been charged against the filtering operation, but actually the major portion of this item should be placed against the leaching step.

SUMMARIZED SALT-LEACHING COSTS

The estimated costs of equipment and direct operating and depreciation charges will be as follows:

*Summarized equipment and operating costs of extracting 1,600 tons
of minus 10-mesh polyhalite*

<i>Item:</i>	<i>Equipment</i>	<i>Operation cost per 24 hours¹</i>
Feeding	\$ 1,925	\$ 6.47
Mixing	1,255	10.74
Classifying	12,600	10.84
Thickening	5,755	3.15
Filtering	91,000	113.07
	<hr/>	
Total	\$112,535	\$144.27
Cost per ton of feed.....		.090

¹ Includes depreciation.

PROCESSES FOR UTILIZATION OF POLYHALITE

In attempting to separate the constituents of polyhalite, three main lines of attack have been followed: (1) The use of water and heat in solution processes employing no added chemicals; (2) the chemical decomposition of polyhalite by such reagents as lime or ammonia and carbon dioxide; and (3) the reduction of the complex sulfate to a mixture of sulfides and oxides as a preliminary to solution processes.

PRINCIPAL METHODS OF ATTACK

In order to separate polyhalite into its constituent salts, the first method of attack might conceivably be direct leaching of the complex salt with water. The rate of decomposition with both cold and boiling water is, however, too slow for an industrial process, although rapid enough to make crude polyhalite a satisfactory fertilizer material. To break down the relatively inert triple sulfate, three essentially different lines of attack have been employed. These depend respectively on extraction with water (both hot and cold, but with no added chemicals), partial precipitation by added chemicals, and reduction.

Obviously, all three general methods might be applied to the properly ground crude polyhalite, or a preliminary treatment such as calcination might be employed to facilitate subsequent treat-

ment. In general, dehydration of the polyhalite produces a mixture that responds much more readily to treatment. In the processes utilizing hot- and cold-water extractions, this calcination is virtually indispensable; in those treatments involving partial precipitation with added chemicals more complete dissolution, more rapid rates of decomposition, and higher recoveries on much coarser ground material are obtained. In the reduction process calcination is unnecessary, as the preheating treatment of the polyhalite accomplishes this dehydration before or coincident with the process of reduction. Calcination does assure better results, so that this preliminary treatment has been adopted as a desirable precautionary step in the majority of the processes developed.

A number of variations of each general method will be discussed in greater detail in subsequent sections. At this point a broad delineation will suffice.

METHODS DEPENDING ON CALCINATION

Calcination for only a few minutes at a temperature not exceeding 500° C. greatly accelerates the attack of water upon polyhalite. Two general processes dependent on this initial "unlocking" step are indicated in the skeleton flow diagrams of figure 20 (p. 109). In the first of these, the calcined polyhalite is treated with water at the atmospheric boiling point to dissolve potassium and magnesium sulfates, and the solid residue of calcium sulfate is rapidly separated from the extract liquor. Crystalline potassium sulfate and the double salt schönite are then recovered from this liquor by suitable evaporation and fractional crystallization.

In the second general process dependent upon calcination, cold water is employed to dissolve all of the magnesium sulfate from the calcine, leaving the major portion of the potassium sulfate combined as syngenite in the solid residue. It is then possible to recover this potassium sulfate by treating the syngenite with water at an elevated temperature, separating the ultimate residue of calcium sulfate, and evaporating the liquor.

METHODS DEPENDING ON PARTIAL PRECIPITATION

Direct chemical decomposition of polyhalite by substances that will form insoluble compounds of calcium and magnesium is the second alternative general method of attack. The use of ammonia and carbon dioxide or of lime theoretically should achieve this end. In the first, precipitation of calcium carbonate and magnesium hydroxide would be anticipated, leaving ammonium sulfate in solution with the potassium sulfate derived from the polyhalite. In the second, calcium sulfate would be left in the solid residue with the precipitated magnesium hydroxide, and the liquor would contain potassium sulfate.

Actually, when processes of this type are attempted at ordinary temperatures, the separation of potassium sulfate from calcium and magnesium compounds is poor unless the concentration of potassium sulfate in the extract liquor is limited to an impractically low value. The most effective procedure of this type is the treatment of polyhalite with lime and water at a high temperature in an autoclave.

Although decomposition by means of ammonia and carbon dioxide does not effect a complete separation of the constituents of polyhalite, this process may be applied to advantage in recovering potassium sulfate from syngenite produced by the treatment of calcined polyhalite with water at ordinary temperatures.

METHOD DEPENDING ON REDUCTION

Reduction offers a third general method of breaking down polyhalite. The complex sulfate is almost completely converted into a mixture of sulfides and oxides by reaction with hydrogen or with mixtures of carbon monoxide and hydrogen in the temperature range from 830° to 900° C. By treatment of the reduction product with water, potassium sulfide may be easily separated from the insoluble calcium and magnesium compounds. The potassium sulfide liquor may then be treated with carbon dioxide to produce potassium carbonate.

CALCINATION OF WASHED POLYHALITE

The logical arrangement for handling crushed and washed polyhalite after the salt-leaching treatment is to charge the wet product directly to rotary calciners and thereby effect both the drying and dehydration in a simple operation. Additional economy could be accomplished by utilizing some of the heated air issuing from coolers receiving the calcined polyhalite.

COMPOSITION OF POLYHALITE

The composition of a typical polyhalite before and after washing and after calcination is presented in table 10.

TABLE 10.—*Mineralogical composition of polyhalite before and after calcination, percent*

Mineral constituent	Amount present		
	Before washing	After washing	After calcination
Polyhalite.....	76.6	76.00	86.18
Halite.....	12.8	.87	1.05
Anhydrite.....	8.2	8.13	9.82
Water (free).....	0	12.55	0
Other.....	2.4	2.45	2.95
Total.....	100.0	100.00	100.00

After calcination, which expels all of the free water retained in the washed polyhalite, as well as the combined water in the polyhalite molecule, the composition and size distribution of the calcine made from 10-mesh raw polyhalite will be as indicated in table 11.

It should be noted that the above calcined polyhalite differs slightly from the assumed composition of the washed polyhalite principally in the anhydrite content. This latter composition gives a typical analysis, including particle-size distribution, and represents the average calcined material employed in the subsequent discussion of extraction processes.

TABLE 11.—*Composition and size distribution of calcined polyhalite*

<i>Composition: Compound:</i>		<i>Percent</i>
K ₂ SO ₄		25.50
MgSO ₄		17.64
CaSO ₄ (anhydrite)		12.35
CaSO ₄ (polyhalite)		39.81
NaCl98
MgCO ₃86
Fe ₂ O ₃ + insol.		2.83
<i>Size distribution:</i>		<i>Weight, percent</i>
<i>Size</i>		<i>(cumulative)</i>
On 10-mesh		0
On 20-mesh		49.2
On 28-mesh		63.2
On 35-mesh		72.7
On 65-mesh		88.4
On 100-mesh		93.6
On 150-mesh		94.9
Through 150-mesh		5.1

CALCINATION TREATMENT THERMAL REQUIREMENTS

The calcination of minus 10-mesh polyhalite entails the evaporation of the free moisture and the absorption of heat in the dissociation of the polyhalite molecule and the expulsion of the water of constitution in the form of water vapor. Storch and Clarke (36) have determined the heat of dissociation of polyhalite as $66,000 \pm 5,000$ calories per mole, which corresponds to approximately 209 B.t.u. per pound if a value of 70,000 calories is selected. Thus, a material containing 86.9 percent polyhalite would consume 182 B.t.u. to effect this dissociation.

The polyhalite will be calcined in a rotary kiln, based upon the following assumptions:

1. Calcining temperature at 500° C. (932° F.).
2. Flue-gas temperature at 400° F.
3. Discharge temperature of calcines from coolers at 400° F. with 50 percent heat recovery.
4. Loss of 12 percent of thermal input to kiln as radiation and conduction.
5. Use of crude oil as fuel.

Composition of typical Texas crude oil

<i>Constituent:</i>	<i>Weight, percent</i>
Sulfur	1.75
Carbon	85.05
Hydrogen	12.30
Nitrogen70
Oxygen	Nil
Specific gravity, 35.0° (A.P.I.) = 0.8500 60° F. per 60° F.	
Heating value, 19,600 B.t.u. per pound or 138,000 B.t.u. per gallon.	

Combustion data for crude oil, using 10 percent excess air [Basis, 1 ton of oil]

Item	Constituent	Weight, percent	Pounds per ton	Pound-moles per ton	O ₂ required, pound-moles	Combustion products, pound-moles
1	C	85.05	1,701.0	141.9	141.9	141.9 CO ₂
2	H ₂	12.30	246.0	123.0	61.5	184.5 H ₂ O
3	S	1.75	35.0	1.1	1.1	1.1 SO ₂
4	N ₂	.70	14.0	.5	8.5	186.0 N ₂
5	O ₂	Nil	Nil	Nil	235.5	21.45 O ₂
6	H ₂ O	Nil	Nil	Nil	Nil	14.55 H ₂ O

¹ From combustion air.

Oxygen for theoretical combustion = 214.5 pound-moles (items 1, 2 and 3).

Oxygen for 10 percent excess = 21.45 pound-moles.

Total oxygen = 235.55 pound-moles.

Air to supply oxygen = $\frac{235.55}{0.21} = 1,120$ pound-moles.

Nitrogen in combustion air = $1,120 - 235.5 = 885.5$ pound-moles.

Water in combustion air, saturated at 70° F. = $0.013 \times 1120 = 14.55$ pound-moles.

Heat content of combustion products at 400° F.

[70° F. datum plane]

Component	Pound-moles per ton of oil burned	Sensible heat, B.t.u. per pound-mole	Total heat content, B.t.u. $\times 10^3$
CO ₂	141.9	3,174.7	450.0
H ₂ O.....	184.5	2,798.9	516.0
SO ₂	1.1	3,134.0	3.4
N ₂	886.0	2,314.5	2,050.6
O ₂	21.45	2,314.5	49.6
H ₂ O.....	14.55	2,798.9	4.0
			<u>3,073.6</u>

Heating value (gross) of 1 ton oil = $2,000 \times 19,600 = 39.2 \times 10^6$ B.t.u.
 Radiation loss = 12 percent, then net heat from oil fuel = $0.88 (39.2 \times 10^6) - 3,074 \times 10^3$
 = 31.4×10^6 .

Most of the flow sheets were set up to process 1,600 tons of polyhalite, as mined, per day. After the removal of the sodium chloride this leaves 1,374.4 tons of solids (dry basis) which in turn yield 1,301.6 tons of calcined product. Additional thermal input will be required to heat the solid polyhalite to the temperature of dissociation and to evaporate the water retained after the salt-washing treatment. The various operations requiring heat are therefore as follows:

1. Sensible heat input to raise crude polyhalite from 70° F. to decomposition temperature.
 - a. Polyhalite content of 86.9 percent.
 - b. Anhydrite, halite, etc., 13.1 percent.
2. Heat input for dehydration of polyhalite.
3. Heat for evaporation of free water.
4. Radiation and conduction losses from kiln.

The distribution of the heat input exclusive of the radiation loss already deducted from the oil to be used, will be:

1. Heat in discharge of solids from coolers—temperature assumed at 400° F., but if only one-half is recuperated, effective temperature will be $400^\circ \text{ F.} + \frac{(942 - 400)}{2} = 671^\circ \text{ F.}$

$671^\circ - 70^\circ = 601^\circ$, net temperature increase in solids above condition when fed to kiln. The total heat lost to calcines corresponds to:

1. $1,301.6 \times 2,000 \times 601 \times (\text{specific heat of } 0.2) = 273.9 \times 10^6$ B.t.u.
2. For heat of dissociation:
 $1,374.4 \times 2,000 \times 209 = 574.5 \times 10^6$ B.t.u.
3. To evaporate free water and discharge at 400° F. in flue gases:
 $197.4 \times 2,000 \times \left(\frac{3798.9}{18} + 970 \right) = 444.3 \times 10^6$ B.t.u.

Therefore, total heat consumed in calcining 1,374.4 tons of polyhalite would be the sum of items 1, 2, and 3 or $1,292.7 \times 10^6$ B.t.u.

$$\frac{1,292.7 \times 10^6}{31.4 \times 10^6} = 41.17 \text{ tons or } 277 \text{ barrels of oil.}$$

The net work accomplished by the combustion of the 277 barrels of oil in the rotary kilns is to evaporate 197.4 tons of free water retained in the 1,374.4 tons of washed polyhalite and decompose the polyhalite. The thermal requirement to do this is the sum of

items 2 and 3 above, which total $1,018.8 \times 10^6$ B.t.u. Calculations show that this is approximately 63 percent of the gross heating value of the oil used. Upon this same basis, 1 barrel of oil will produce 4.7 tons of calcined product. For convenience, this relation will be employed in all subsequent calculations of fuel requirements for drying and calcining polyhalite.

CONDITIONS REQUIRED FOR CALCINATION

The pertinent factors involved in the calcination of polyhalite will be discussed on pages 109 to 124, so that only the minimum time and temperature necessary to effect satisfactory results need be stated here. The optimum temperature is about 480°C . The minimum time requirements are as follows:

Calcination temperature $\pm 2^\circ\text{C}$	460°C .	500°C .
Minimum time heating 300° to temperature..	10 minutes	6 minutes
Minimum time at temperature.....	6 minutes	2 minutes

The hot calcines may be discharged in any convenient manner, and although heat recuperation is desirable to increase the thermal efficiencies, this means of reducing fuel requirements for calcination has not been considered in the cost estimates. However, the warm polyhalite could be charged directly to the extraction treatment. Storage of the calcined product also would be provided to supply feed for the leaching plant during shut-downs or interruptions in the flow of calcines from the kilns.

EQUIPMENT AND OPERATING COSTS

Equipment.—The calcination will be done in two 8-foot by 160-foot brick-lined rotary kilns, provided with dust-settling chambers and collectors and with each kiln discharging to an 8-foot by 80-foot cooler. These kilns and coolers, provided with all necessary burners, motor drives, reduction gears, feeders, dust collectors, brick stacks, and essential controls, will cost \$160,000 installed.

Power.—The power necessary to operate these calciners is a minor item; it will amount to some 2,000 kw.-hr. per day and will cost about \$6.00.

Labor.—Possibly one kiln operator and two helpers will be needed for each shift at \$6.00 each, or a total of \$72.00 per day.

Fuel.—The cost of fuel will be \$277 per day, assuming oil at \$1 per barrel, delivered; possibly some decrease in cost could be obtained by recuperating more of the heat from the coolers. (See p. 38 for basis of fuel calculations.)

Repairs and maintenance.—The upkeep on rotary kilns operating on this type of material would be less than on cement or lime kilns, which operate at higher temperatures, but an unknown amount of corrosion would be unavoidable from the hydrochloric acid vapors evolved by the residual salt in the washed polyhalite. Assuming that the lining repairs of the kilns would correspond to one complete replacement each year, the daily costs for maintenance and repairs would be \$65.00.

Summarized costs of calcination of 1,374.4 tons of polyhalite

<i>Item:</i>	<i>Cost per day, 24 hours</i>
Power—2,000 kw.-hr. at \$0.003.....	\$ 6.00
Labor—3 burners, 6 helpers.....	72.00
Fuel—277 bbl. at \$1.00.....	277.00
Maintenance and supplies.....	65.00
Total direct operating cost.....	\$420.00
Depreciation, 10 percent.....	53.33
Total costs	\$473.33
Average cost per ton of calcine.....	.345

It should be noted that this estimate of probable cost of calcining the polyhalite is considerably higher than the figure calculated by Wroth (44). Although the size of operation is slightly smaller in the present calculations, which would tend to increase operating costs, the principal difference appears to result from the assumed thermal efficiencies. These were approximately 80 percent in the previous estimates and 63 percent in the present work.

EXTRACTION AND RECOVERY PROCESSES

GENERAL CONSIDERATIONS

Obviously, the production costs of a chemical plant treating polyhalite for the manufacture of potassium salts and other by-product chemicals would vary according to the size of operations and the percentage of rated capacity maintained.

Potassium sulfate is preferred for certain fertilizer applications, notably in citrus fruit and tobacco growing. If available at somewhat lower unit costs for the equivalent K_2O content, some increase in consumption might result in excess of the normal rate of growth. However, it is extremely unlikely that the sulfate ever would offer any serious bid for the place now occupied by the muriate as the dominant potash fertilizer.

BASIS FOR POTASH PROCESSES

The various potash-extraction processes have been considered upon the basis of the mining and crushing of 1,600 tons of crude polyhalite daily, in two 8-hour shifts, and the three-shift operation of the treatment plant for a total of 300 days per year in all processes but No. 8. In this instance, only 30 percent of the potash would be derived from polyhalite and the balance from sylvinite. Presumably, for this process, joint mining of polyhalite and sylvinite would be practiced, and mining and crushing costs and equipment would be essentially the same; the salt-leaching and calcination steps would be on a proportionate scale.

The quantity of potash produced by these different processes would range from approximately 39,500 to 52,200 tons of equivalent K_2O per year, depending on the recoveries obtained. These outputs slightly exceed the 10-year average (1930–39) of 35,200 tons of K_2O consumed in the form of sulfate and are of the order of the banner year of 1937, in which 52,888 tons of K_2O were used in fertilizers as sulfate of potash and sulfate of potash-magnesia.

The normal increase in consumption could be handled by three-shift operation of the mining and crushing units and by operation

of the treatment plant in excess of the 300 twenty-four-hour days taken as the average yearly operating time. Obviously, operation of the plant at less than the 300-day basis with the correspondingly decreased capacity has not been considered. Revision of costs would be necessary to provide for this contingency.

During the development of possible methods for the extraction and recovery of the potassium sulfate from polyhalite, some 11 processes were proposed. Two of these proposed processes were critically reviewed by Wroth, and detailed estimates were made on equipment and production costs. These two flow sheets have been included with the other methods subsequently developed in view of a slightly smaller proposed scale of operations and with some modifications based upon more technical information gained by the additional study.

Equipment and estimated production costs have been presented for processes 1 and 2 in order to place them on an equitable basis of comparison with the other processes.

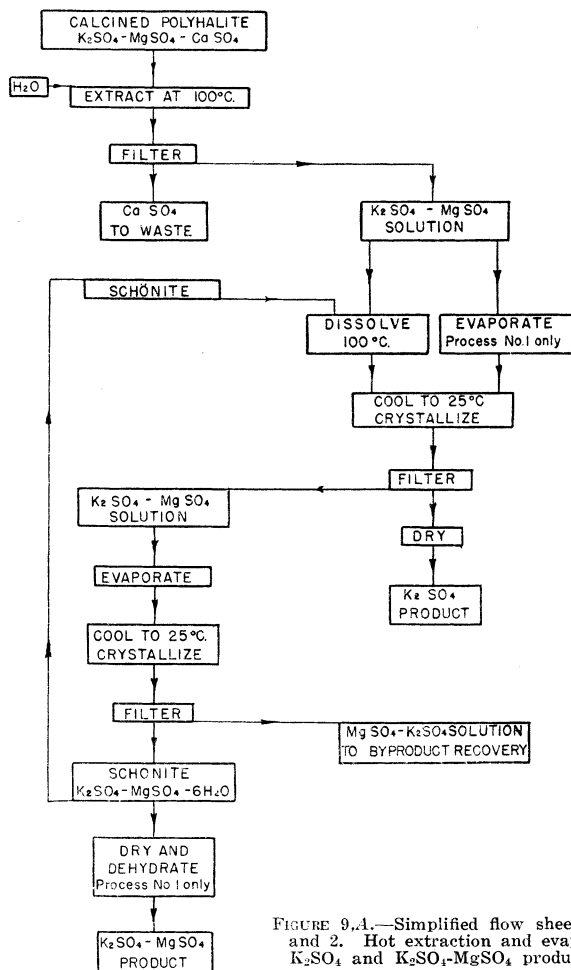


FIGURE 9.1.—Simplified flow sheet of processes 1 and 2. Hot extraction and evaporation to yield K₂SO₄ and K₂SO₄-MgSO₄ products.

CONDENSED FLOW SHEETS OF PROCESSES

Straight-line flow sheets illustrating the essential steps of all of the proposed Bureau of Mines processes are presented in figure 9. Further details have been incorporated into the flow sheets and into the discussion offered in the following sections dealing with the individual processes. It should be noted, however, that the condensed flow sheets indicate the extraction of calcined polyhalite as a single step at 100°C ., whereas actually in the expanded processes the filter cake from this extraction is given a cold, countercurrent, decantation-washing extraction to yield a dilute solution for make-up in the hot extraction. Likewise, in many of the processes involving the production of syngenite

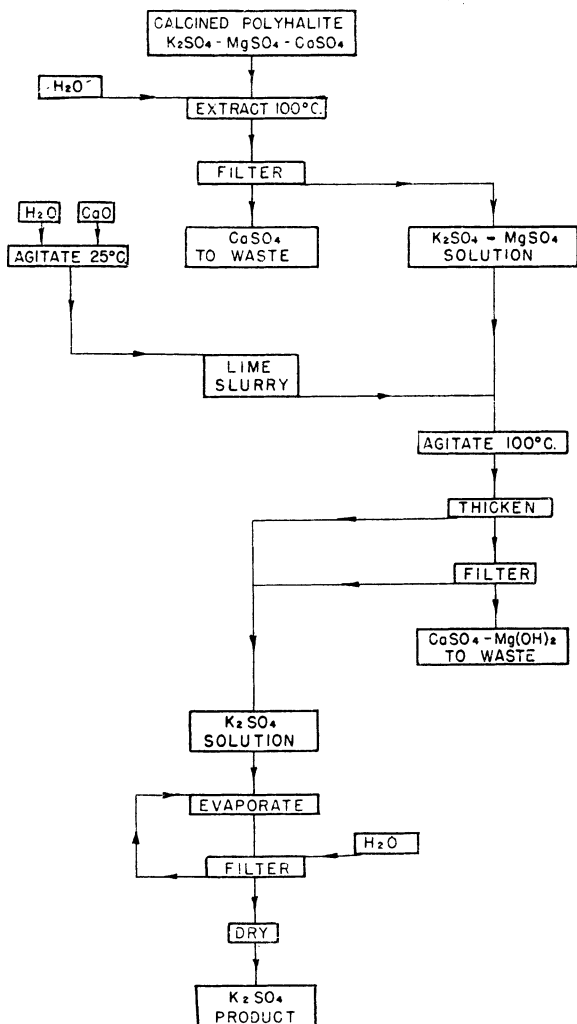


FIGURE 9,B.—Simplified flow sheet of process 3. Hot extraction, lime treatment, and evaporation to yield K₂SO₄ product.

($\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$), this compound is usually made in two steps by employing, first, an excess of calcined polyhalite to assure a high concentration of MgSO_4 solution for discard and to yield a syngenite-gypsum mixture that is subsequently converted to syngenite under conditions favorable for a high-quality product and for rapid reaction rates.

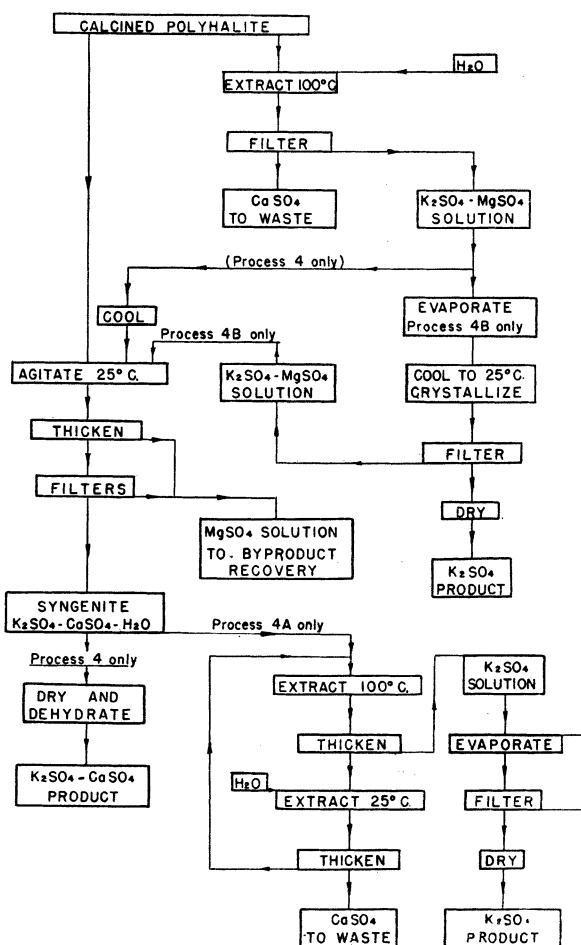


FIGURE 9.C.—Simplified flow sheet of processes 4, 4A, and 4B. Combined hot extraction and cold reaction to yield syngenite and K_2SO_4 .

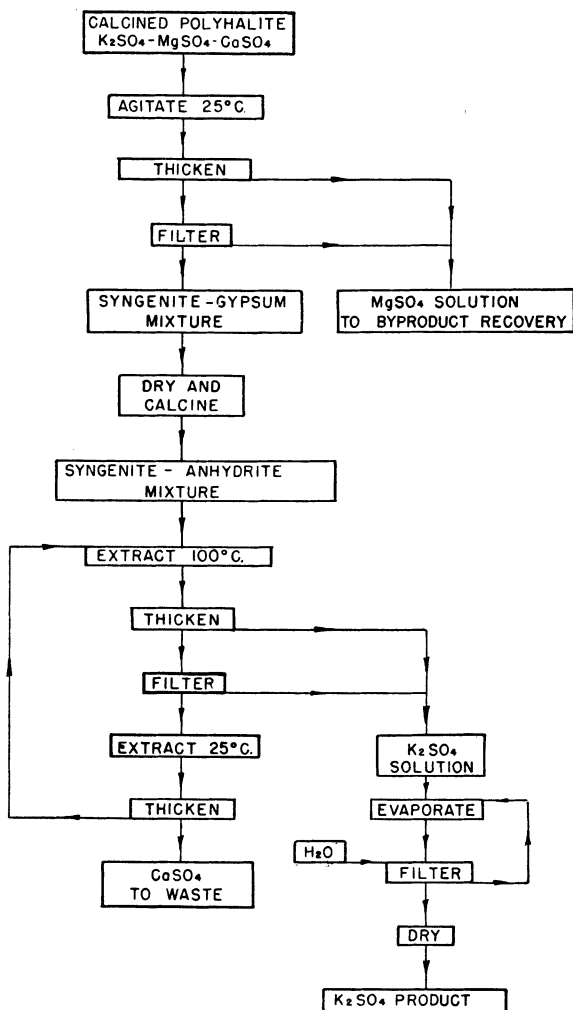


FIGURE 9,D.—Simplified flow sheet of process 5. Incomplete syngenite formation, calcination of syngenite-gypsum mixture, and extraction and evaporation to yield K₂SO₄.

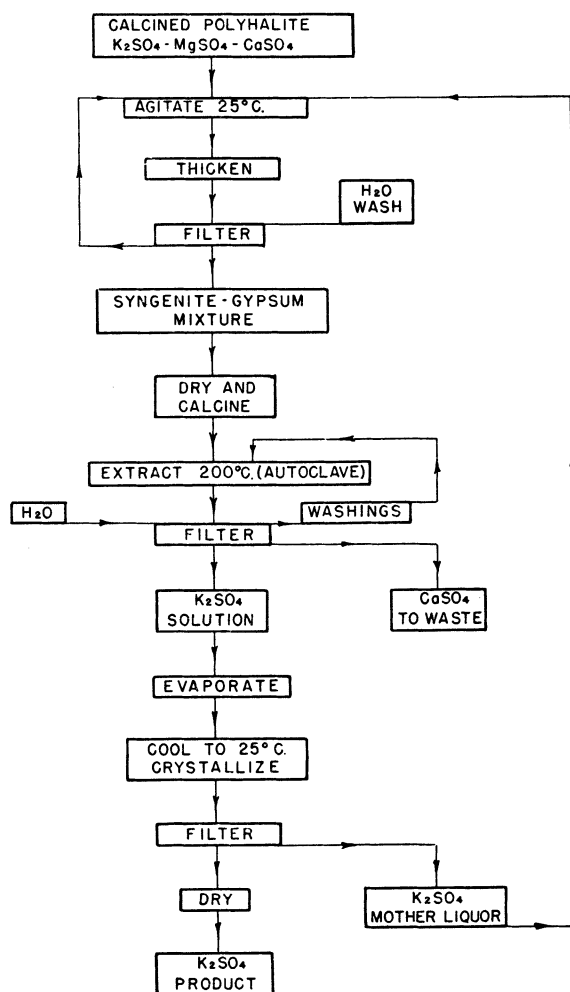


FIGURE 9,E.—Simplified flow sheet of process 5A. Autoclave extraction of syngenite-gypsum at 200° C. to yield K₂SO₄.

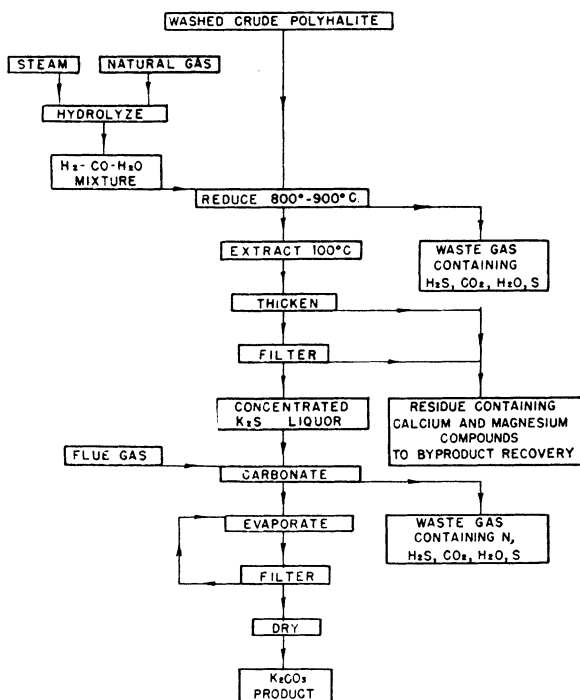


FIGURE 9,F.—Simplified flow sheet of process 6. Reduction process utilizing natural gas to yield K₂SO₄.

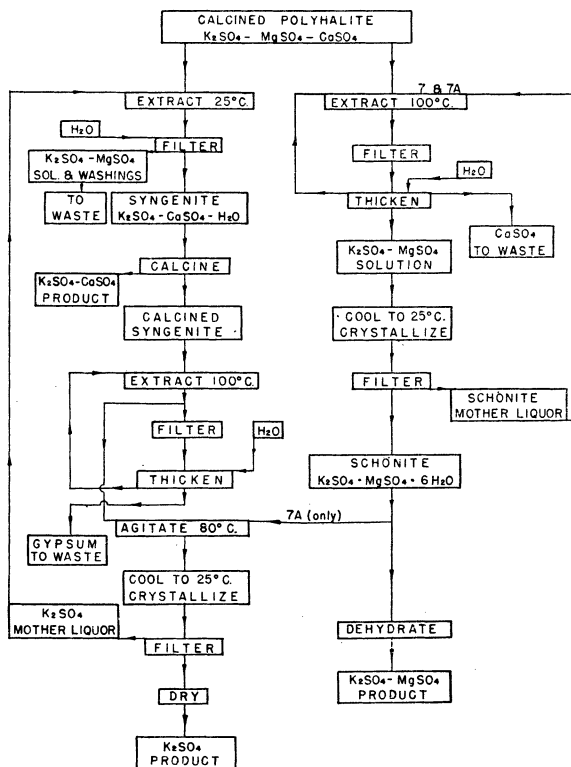


FIGURE 9.G.—Simplified flow sheet of processes 7 and 7A. Production of syngenite, schönite, and K_2SO_4 by hot and cold extractions of calcined polyhalite involving no evaporation.

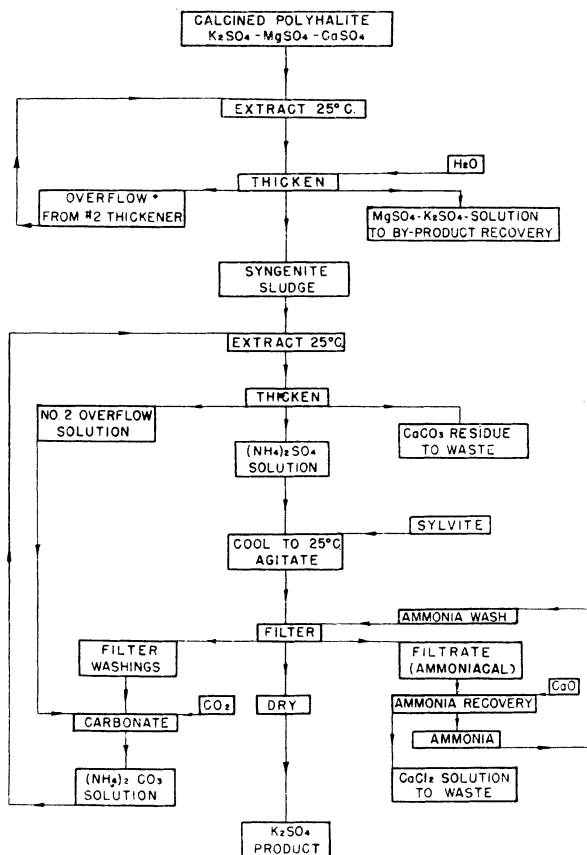


FIGURE 9,H.—Simplified flow sheet of process 8. Production of K_2SO_4 from calcined polyhalite and sylvite through syngenite and ammonia.

POTASH PRODUCTION FROM POLYHALITE BY PROCESS 1

The essential features of the production of potassium salts by this process, illustrated in figure 10, are:

1. The hot-water extraction of calcined polyhalite to produce an insoluble gypsum residue to be discarded and a concentrated extract solution of potassium and magnesium sulfates.
2. The addition of sodium chloride in the final washing of the gypsum residues up to the maximum amount that will not affect final recoveries.
3. Evaporation of the hot concentrated extract to yield a crop of pure potassium sulfate on cooling and crystallization.
4. Final evaporation of the potassium sulfate mother liquor to produce (a) a crystal crop of schönite which on dehydration yields the mixed sulfates commonly sold as sulfate of potash-magnesia; and (b) a concentrated mother liquor high in magnesium sulfate, which contains all of the dissolved sodium chloride and is discharged to waste or byproduct recovery.

DETAILS OF PROCESS

The extraction of the potassium and magnesium sulfates is accomplished by adding 1,301.6 tons of calcined polyhalite, previously washed, to approximately 1.0 percent of $NaCl$, together with 3,505.8 tons of dilute make-up solution, to steam-heated con-

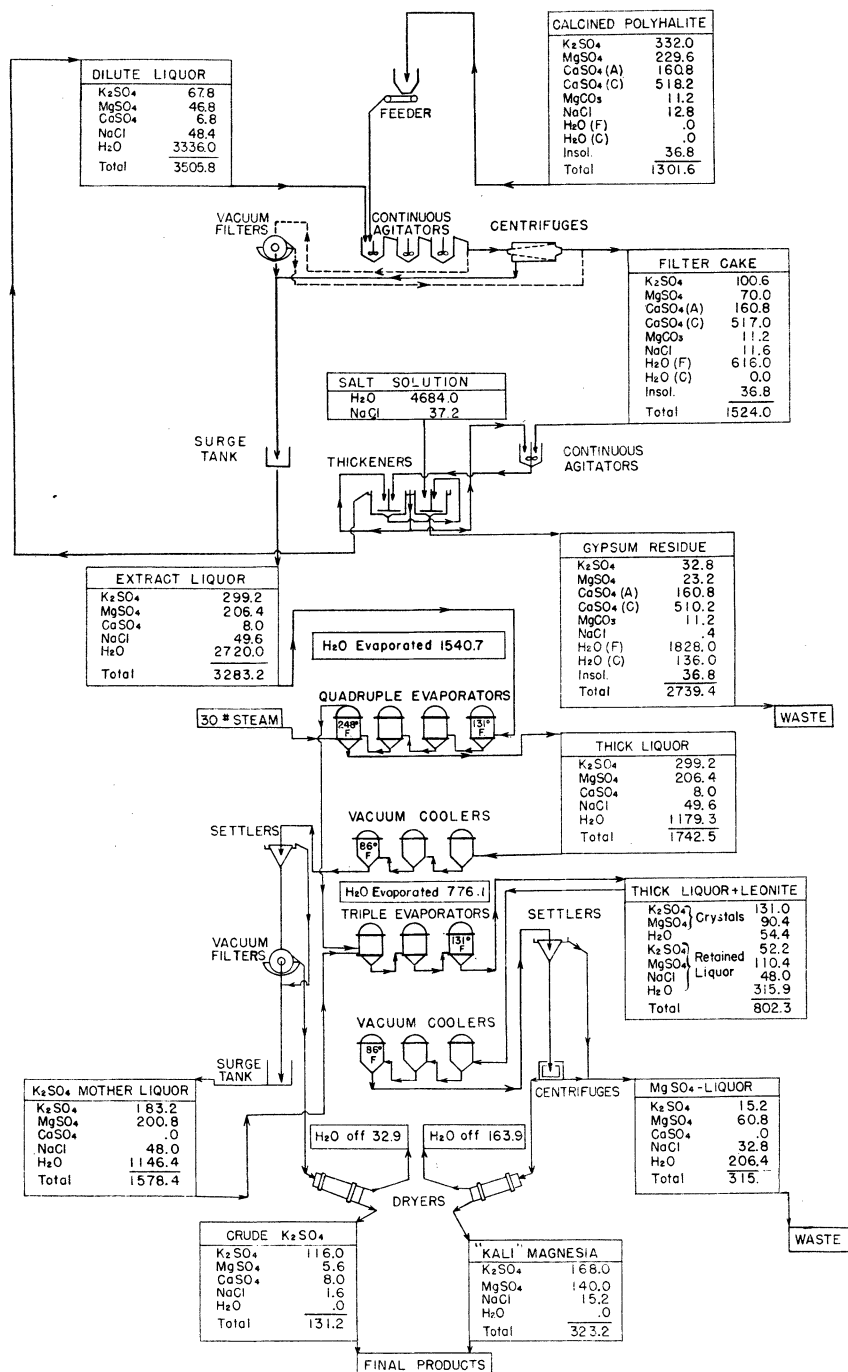


FIGURE 10.—Suggested flow sheet for treatment process 1.

tinuous agitators proportioned and operated to assure a 15-minute solid-liquid contact at a temperature closely approaching 212° F. The agitator overflow discharges either to two large, horizontal, continuous centrifuges or to four 14-foot by 18-foot rotary vacuum filters in order to separate 1,524.0 tons of filter cake from the 3,283.2 tons of extract solution carrying 563.2 tons of dissolved salts daily.

Both vacuum filters and horizontal continuous centrifuges are indicated as possible means for effecting this filtration. Obviously, large-capacity vacuum pumps provided with condensers to remove the vaporized water are necessary to handle the tonnages involved. The continuous centrifuge has been suggested by the maker, and while not actually tested on this particular proposed operation, it is believed to be feasible since it is in use in similar commercial operations. The costs for this latter type of equipment probably would be considerably less and power consumption possibly about the same as for vacuum filters. Machines of this type represent a phase of liquid clarification developed since the process tests were made.

The clear filtrate is pumped to the evaporators via a surge or storage tank, and the filter cake is repulped and fed to a series of four thickeners operating for countercurrent decantation washing. Repulping is accomplished by adding the 1,524 tons of wet filter cake to the necessary amount of overflow from No. 2 thickener and by discharging the mixture into No. 1 thickener. Water amounting to 4,684 tons and 37.2 tons of NaCl are fed to No. 4 thickener, while a clarified overflow of 3,505.8 tons containing 169.8 tons of dissolved salts for use as make-up solution for the extraction agitators flows from No. 1 thickener. The underflow solids are discharged at a pulp dilution of 2:1 and total 2,739.4 tons each 24 hours.

The sodium chloride is added in the final thickener to retard the formation of syngenite in the washing step and to assure higher extraction in the agitators. This salt probably would be supplied by diverting the proper quantity of the concentrated liquor from the salt-washing operation. Actually, 166.4 tons or about 20 percent of the waste salt solution would supply this 37 tons of NaCl, together with 3.67 tons of K_2SO_4 and 2.45 tons of $MgSO_4$, which would mean reclamation of possibly 3 tons of potassium sulfate daily.

The extract solution, containing 299.2 tons of K_2SO_4 and 206.4 tons of $MgSO_4$, is introduced to quadruple-effect evaporators at 131° F. or any higher working temperature. If the continuous centrifuges are used for the filtering step, this temperature might be as high as 180° to 190° F., which would effect a considerable economy in heat. This same result would be accomplished by the countercurrent flow of the evaporator feed, as indicated in the flow sheet. By this arrangement, steam exhausting from the turbines generating the electric power for the whole plant is introduced into the first effect of the battery of evaporators to produce a final thick liquor for crystallization of K_2SO_4 and the evaporated water as steam at atmospheric pressure to supply the

second effect of the K_2SO_4 evaporators and the first effect of the triple evaporators used in the evaporation of the K_2SO_4 mother liquors. The 1,742.5 tons of thick liquors produced daily are discharged from the fourth effect of the K_2SO_4 evaporators and pass through heat exchangers to heat up the evaporator feed. Saturation occurs at $180^\circ F.$ so that the heat equivalent to the temperature drop from 248° to possibly $190^\circ F.$ can be recovered by means of heat exchangers to heat up the evaporator feed. Additional heat is conserved by the use of heat exchangers on the cooling water from the first vacuum crystallizer. In the absence of exact operating data, it can only be assumed that average quadruple-effect evaporator economy is attained in the evaporation step; that is, 3.2 pounds of water will be expelled for each pound of steam consumed.

Assuming that force-feed circulating evaporators are employed and all crystallization is restricted to the vacuum coolers, the solubility relations of K_2SO_4 require that two-thirds of the evaporation be accomplished over $85^\circ C.$ ($185^\circ F.$) to prevent separation of K_2SO_4 .

Laboratory tests have shown that any convenient rate of cooling may be utilized with the thick liquors, except in the range from 130° to $95^\circ F.$, in which not less than 2 hours should be consumed to obviate the formation of schönite, which would otherwise contaminate the K_2SO_4 crystal crop.

Vacuum coolers have been recommended for this purpose to obtain the proper control with efficient and economical operation. The 1,742.5 tons of thick liquor, therefore, are charged to the vacuum crystallizers at 185° to $190^\circ F.$ and permitted to boil under reduced pressure, so applied as to limit the final temperature to $86^\circ F.$ in the last cooler. The crystal crop obtained will be separated in conical settlers, and the mother liquor is pumped through heat exchangers, then into triple-effect evaporators operating with parallel feed and vapor flow. Full advantage is taken of the additional evaporation obtainable in the vacuum coolers to remove the total of 1,540.7 tons of water evaporated every 24 hours in the K_2SO_4 step.

The 1,578.4 tons of potassium sulfate mother liquor containing 183.2 tons of K_2SO_4 and 200.8 tons of $MgSO_4$ fed daily to the triple-effect evaporators produce a crystal crop of 82.5 and 193.3 tons of schönite ($K_2SO_4 \cdot MgSO_4 \cdot 6 H_2O$) in the second and third effects, respectively, on the evaporation of 776.1 tons of water daily in the evaporators and coolers. Forced-circulation evaporators provided with salt traps or possibly a multiple trap are employed. The schönite separating in the coolers operating at an end temperature of $86^\circ F.$ amounts to 69.3 tons daily, making a total of 345.1 tons in all.

Vacuum filters probably are used to separate the K_2SO_4 from its mother liquor, but centrifuges would work to advantage on the possibly somewhat coarser schönite crystals. The schönite mother liquor is discharged to waste or to a magnesia-recovery plant, and the crystal crops are dried in oil-fired rotary dryers to produce 131.2 tons of crude K_2SO_4 and 323.2 tons of kali-magnesia by driving off 32.9 and 163.9 tons of water, respectively.

The production of both anhydrous K_2SO_4 and sulfate of potash-magnesia (kali-magnesia) is a desirable feature of this process in that both these chemicals find a ready market. However, the proportion of the latter product is considerably greater than the normal ratio of these materials consumed in the fertilizer industry. This raises the point as to the advisability of operating according to the proposed flow sheet, and the answer would be found only by an actual attempt to market the finished products.

DETAILED EQUIPMENT REQUIREMENTS AND DIRECT OPERATING COSTS

Details of the various operations in the essential steps, as well as the type of equipment to be used, are presented in appendix A, pages 163 to 172. Direct operating costs also are discussed in that section.

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The summary of equipment and direct operating costs, including the depreciation charge, is presented in table 12. These data show that the extraction-plant equipment will cost \$913,620 and the total direct operating cost will amount to \$2,316.54 every 24 hours, equivalent to a cost of \$1.448 per ton of polyhalite mined. With the \$267.89 depreciation charges added and with a credit of \$60.36 daily for steam saved, the net direct operating costs, plus depreciation, will equal \$2,524.07 or \$1.577 per ton of polyhalite.

TOTAL PRODUCTION AND EQUIPMENT COSTS

The final total production and equipment costs, together with the estimated building expenditures necessary to properly house the mine and treatment plants, have been summarized in table 13. These data include the equipment costs for mining, crushing, treatment plant, and housing these units, and dwellings for employees, as well as the production costs, comprising direct operation, direct supervision, administration, and general expense, and the usual fixed costs.

GENERAL

As all the processes discussed, with the exception of No. 8, are based upon the treatment of 1,600 tons of raw polyhalite per day, the costs of mining and crushing equipment (estimated at \$468,776 and \$158,000, respectively, inclusive of suitable buildings for housing the plants) are common to all. However, to be certain that the treatment equipment estimates are ample an additional 20 percent has been added to the actual estimated figures. This extra allowance provides for minor equipment, such as pumps, heat exchangers, piping, and special control-laboratory apparatus.

HOUSING

A flat estimate of \$175,000 has been made to cover costs of development of the camp site, roads, lighting, and employee residences. The treatment plants of the various processes vary considerably, and an effort has been made to consider this variation by assuming a general building cost equal to 20 percent of the treatment-equipment allotment; for process 1 this means a \$220,000 investment in buildings.

TABLE 12.—*Summarized equipment, direct operating and depreciation costs for process 1 (1,600 tons of raw polyhalite per day)*

Operation	Equipment costs	Number of employees	Operating costs per day, 24 hours						Total costs		Cost per ton raw polyhalite		
			Power	Labor	Steam	Fuel	Water	Maintenance and supplies	Total direct operating costs	Depreciation	Total combined cost	Direct	Combined (1)
Salt washing.....	\$112,535	12	\$19.71	\$65.50	\$10.12	\$12.29	\$107.62	\$36.65	\$144.27	\$0.067	\$0.090
Calcination.....	160,000	12	6.00	72.00	\$277.00	65.00	420.00	53.33	473.33	.293	.296
Hot extraction.....	5,885	4	2.43	22.80	\$433.60	32.64	3.50	494.97	1.72	496.69	.309	.310
Filtering gypsum.....	115,000	9	13.50	54.00	6.50	74.00	57.50	131.50	.046	.082
Cold extraction.....	74,000	3	3.60	18.00	23.57	4.00	49.17	16.50	65.67	.031	.041
Evaporating K ₂ SO ₄	137,000	9	24.00	54.00	335.60	46.15	11.40	521.15	30.45	551.60	.326	.345
Crystallizing K ₂ SO ₄	150,000	3	5.40	18.00	12.00	12.60	12.60	60.50	33.33	93.83	.038	.059
Filtering K ₂ SO ₄	7,500	1½	1.35	9.00	3.00	13.35	2.50	15.85	.008	.010
Drying K ₂ SO ₄	12,000	1½	1.90	9.00	18.00	2.62	31.52	2.67	34.19	.020	.021
Evaporating schönite.....	75,000	6	12.00	36.00	259.20	39.20	5.00	351.40	16.67	368.07	.220	.230
Crystallizing schönite.....	15,200	1½	1.35	9.00	2.40	2.61	1.25	16.61	3.40	20.01	.010	.013
Filtering schönite.....	19,500	3	3.45	18.00	118.00	7.50	28.95	6.50	35.45	.018	.022
Drying schönite.....	30,000	3	4.80	18.00	6.50	147.30	6.67	153.97	.092	.096
Totals.....	913,620	68½	99.49	403.30	1,092.80	413.00	166.89	141.06	2,316.54	267.89	2,584.43	1.448	1.615
Deduct steam saving.....	60.36	60.36	60.36	.038	.038
Revised totals and final net unit costs.....	1,032.44	2,256.18	2,524.07	1.410	1.577

¹ Includes depreciation.² Subject to deduction of \$53.04 for steam saved.³ Subject to deduction of \$7.32 for steam saved.

TABLE 13.—*Total production and plant costs for process 1*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Mining.....	185	\$468,776	\$1,006.88	\$ 482.39	\$1,489.27
Crushing.....	6	158,000	30.00	36.58	66.58
Treatment.....	69	2,096,344	403.30	1,852.88	2,256.18
Total direct operating costs.....	260	1,723,120	1,440.18	2,371.85	3,812.03
Direct supervision:					
Mining.....	8		78.00	52.00	130.00
Crushing.....	2		12.00	8.00	20.00
Treatment.....	10		82.00	55.00	137.00
Total direct supervision.....	20		172.00	115.00	287.00
Total direct costs.....	280		1,612.18	2,486.85	4,099.03
Administration and general expense:					
Mining.....	26		180.00	120.00	300.00
Treatment.....	22		163.00	109.00	2 2.00
Total administration and general costs.....	48		343.00	229.00	572.00
Buildings:					
Camp, streets, etc.....		175,000			
Treatment plant.....		220,000			
Total cost.....		395,000			
Fixed charges:					
Depreciation:					
Buildings.....				65.83	65.83
Mining, 3.71.....				153.20	153.20
Crushing, 6.67 percent.....				35.11	35.11
Treatment, 11.4 percent.....				321.47	321.47
Total depreciation.....				575.61	575.61
Taxes (1½ percent of valuation ² and insurance.....				105.91	105.91
Interest on investment (6 percent).....				423.64	423.64
Total fixed charges.....				1,105.16	1,105.16
Amortization, preliminary mine development.....				95.20	95.20
Total production costs.....	328	2,118,120	1,955.18	3,930.74	5,871.44

¹ See tables 7 and 12, pp. 23 and 53.² 120 percent of actual estimated costs; see table 12, p. 53.³ Includes depreciation on equipment for preliminary and current mine development.⁴ Operating-equipment plant cost.**DIRECT OPERATION AND PRODUCTION COSTS**

The direct operating costs represent the figures resulting from the analysis of the mining expenses given in table 8 (p. 24); the crushing costs summarized in the table on page 28; and the treatment estimates given in table 12.

DIRECT SUPERVISION ³

For directly supervising the treatment plant, two subforemen and a shift foreman will serve under the plant superintendent. This entails the following monthly expenses:

1 plant superintendent, at \$350 per month.....	\$ 350
3 shift foremen, at \$300 per month.....	900
6 subforemen, at \$200 per month.....	1,200

Total\$2,450

The daily cost is \$81.67, which, if assumed to be 60 percent of the supervision costs, gives a total daily expenditure of approximately \$137.

⁵ See reference 44 (p. 96).

ADMINISTRATION AND GENERAL EXPENSE

The general office salaries of \$1,400 for the manager, chief accountant, and clerk have been divided equally between the mine and treatment plant—\$700 charge per month against each. In addition, a chemical engineer at \$625 per month and a personnel of five clerks, bookkeepers, and timekeepers, with total monthly salaries of \$900, are required. This means an expenditure of \$2,225 each month for treatment-plant administration.

The general expense is summarized as follows:

<i>General expense per month</i>	
1 master mechanic, at \$350 per month.....	\$ 350
2 assistants, at \$275 per month.....	550
1 chief chemist, at \$300 per month.....	300
3 assistant chemists, at \$150 per month.....	450
2 samplers, at \$150 per month.....	300
6 laborers, at \$120 per month.....	720
	<hr/>
	\$2,670

Administration and general expenses are therefore \$4,895 per month or approximately \$163 per day which, at an assumed 60 percent of the necessary outlay, means an additional \$109 for supplies and other items to total \$272.

FIXED CHARGES

The fixed costs comprise expenditures covering depreciation, taxes, insurance, and interest on the invested capital. Depreciation has been calculated upon an average basis for the type of equipment under consideration and was taken at 5.0, 3.7, 6.67, and 11.4 percent for the buildings, mining equipment, crushing equipment, and treatment plant, respectively. Taxes and insurance were assumed to be $1\frac{1}{2}$ percent of the actual cost price or about $2\frac{1}{2}$ percent of assessed valuation (60-percent basis). A 6-percent interest charge also has been included on the entire capital investment, exclusive of the \$571,529 preliminary mine-development expenditure, which accounts for the \$95.20 daily charge to effect amortization in 20 years.

FINAL PRODUCTION COSTS

Upon this basis, table 13 discloses a total daily production cost of \$5,871.44, equivalent to \$3.67 per ton of polyhalite mined, \$20.67 per ton of K_2SO_4 , and \$0.38 per unit of K_2O in the form of crude sulfate of potash and sulfate of potash-magnesia.

CAPITAL REQUIREMENTS

The capital requirements have been included with that of the other processes in table 35 (p. 105).

EXTRACTION AND RECOVERY OF K_2SO_4 FROM CALCINED
POLYHALITE BY PROCESS 2

Process 2 represents a modification of process 1 so arranged as to produce all of the potash salts in the form of crude K_2SO_4 ; by modification it can produce K_2SO_4 and sulfate of potash-magnesia in any desired ratio.

DETAILS OF PROCESS

The hot extraction of the calcined polyhalite is accomplished exactly the same as in process 1, except that slightly less sodium chloride is necessary to assure the somewhat lower top concentration of K_2SO_4 of 9.9 grams per 100 grams of water. Obviously, more water can be employed in the hot extraction, and more cold water can be added to the washing thickeners to supply the increased daily overflow of 3,699.2 tons of solution carrying 108.0 tons of dissolved salts. The concentration of K_2SO_4 in this overflow is only 1.59 grams per 100 grams of water, a fact that will make higher extractions possible; recovery depends on the subsequent treatment and actually is smaller.

Similarly, the hot extract solutions are increased to 3,554.4 tons daily, which corresponds to 9.9 grams of K_2SO_4 per 100 grams of water. This amount of solution is required to handle the 1,120.0 tons of wet schönite crystals being recycled daily.

The essential differences of processes 2 and 1 are:

1. Elimination of the first evaporation to produce thick liquors for cooling to crystallize the potassium sulfate.

2. The combining of all of the evaporation in the operation making schönite.

3. The dissolution of the schönite by proportioned hot K_2SO_4 -extract liquors, which produce the K_2SO_4 crystal crop on cooling.

4. Recovery of a total of 245.6 tons of K_2SO_4 as a high-grade product (93.2 percent K_2SO_4), in comparison with 284.0 tons of K_2SO_4 recovered in process 1 as 116.0 tons of K_2SO_4 as an 88.5-percent product and 168.0 tons of K_2SO_4 as a 52-percent sulfate of potash-magnesia.

The flow sheet for this process (fig. 11) indicates the difference in procedure and includes the various quantities of materials handled every 24 hours. As in process 1, 1,301.6 tons of calcined polyhalite are charged by automatic feeders to continuous agitators, with 3,699.2 tons of dilute wash-water make-up.

After a 15-minute retention, the reaction mass is filtered to produce 3,554.4 tons of extract liquor, which is charged to slurry mixers with 1,120.0 tons of wet schönite, and a filter cake which is repulped and washed at atmospheric temperature by counter-current decantation thickeners whose final overflow serves as make-up for the hot extraction agitator. The underflow of extracted solids, amounting to 899.2 tons (dry weight), is discarded to waste.

The dissolution of the schönite produces a solution saturated with K_2SO_4 at 158° F., so that operation above this temperature is advisable to decrease reaction time, although operation down to 130° F. may be entirely feasible. On cooling of the reaction mixture, 30.0 tons of K_2SO_4 and virtually all of the $CaSO_4$ present are coprecipitated as 19.0 tons of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$).

The 4,674.4 tons of pregnant liquor are pumped at 130° F. to the vacuum coolers and cooled to 86° F. in not less than 2 hours, then finally to 59° F. (15° C.) with the crystallization of 205.6 additional tons of K_2SO_4 , inclusive of retained mother liquor. To cool the solutions to 59° F., which is somewhat lower than the available cooling-water temperature of 80° F., boosters or vapor compressors are required on the final stage of vacuum cooling.

The crystallized K_2SO_4 and mother liquor are pumped to settlers, from which the thickened salts are discharged to continuous centrifuges to separate the 333.0 tons of wet K_2SO_4 daily; and the filtrate, with the overflow from the conical settlers, is charged to the schönite evaporators. The wet K_2SO_4 is charged to rotary dryers to expel 69.6 tons of water and produce 263.4 tons of dry product.

The 4,341.4 tons of K_2SO_4 mother liquor are then pumped to the triple-effect evaporators, where 2,566.4 tons of water are evaporated. Final cooling to 59° F. is done in vacuum crystallizers. The feed liquors will require preheating by means of heat exchangers before feeding to the evaporators, which are operated with parallel vapor and liquor flow.

The separation of langbeinite ($K_2SO_4 \cdot 2MgSO_4$) must be avoided during the evaporation of the K_2SO_4 mother liquors, and this is accomplished by limiting the proportion of water evaporated to less than 50 percent above 212° F. or 75 percent above 153° F. No crystallization must take place above this latter temperature. One arrangement meeting these requirements would be operation of the first effect at 215° F., the second effect at 176° to 185° F., and the final effect at 131° F., with approximately one-third of the total evaporation in each effect. If the evaporation is conducted according to this scheme, no crystallization occurs in the first effect; but 116.2 and 663.0 tons of leonite ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) separate daily in the second and third effects, respectively. Then if the leonite mother liquor enters the vacuum coolers at 131° F. (55° C.), and cooling is applied down to 59° F., an additional 90.0 tons of schönite are obtained. No special precautions in the cooling are necessary, except that the low temperature indicated necessitates the installation of steam-jet boosters or vapor compressors to remove the vapor and bring about the final cooling.

The 1,775.0 tons of crystallized salts and mother liquor are circulated through salt traps and eventually pumped to a conical settling tank, where the thickened salts are discharged to a continuous centrifuge; the clarified overflow and centrifuged liquor, with the washings (amounting to 918.8 tons daily), are discarded or sent to the magnesia-recovery plant. Wash water, amounting to possibly 264.0 tons each day, is used in the spray washing of the schönite, with the dissolution of 48.8 tons per day. This loss is justified for the purpose of displacing the $MgSO_4$ present at 32 to 33 grams per 100 grams of H_2O in the mother liquor, which must be eliminated from the circuit at this point.

EQUIPMENT AND OPERATING COSTS

The modification of process 1, to operate according to the flow sheet for process 2 (given in fig. 11), results in slightly increased equipment and operating costs. Combining elimination of the water into the single schönite-evaporation step increases the volume of water to be expelled daily by 249.6 tons and a large investment will be needed in evaporators to handle this increase. Likewise, dissolution of the schönite necessitates extra slurry mixers or agitators, and the slightly lower concentrations of the

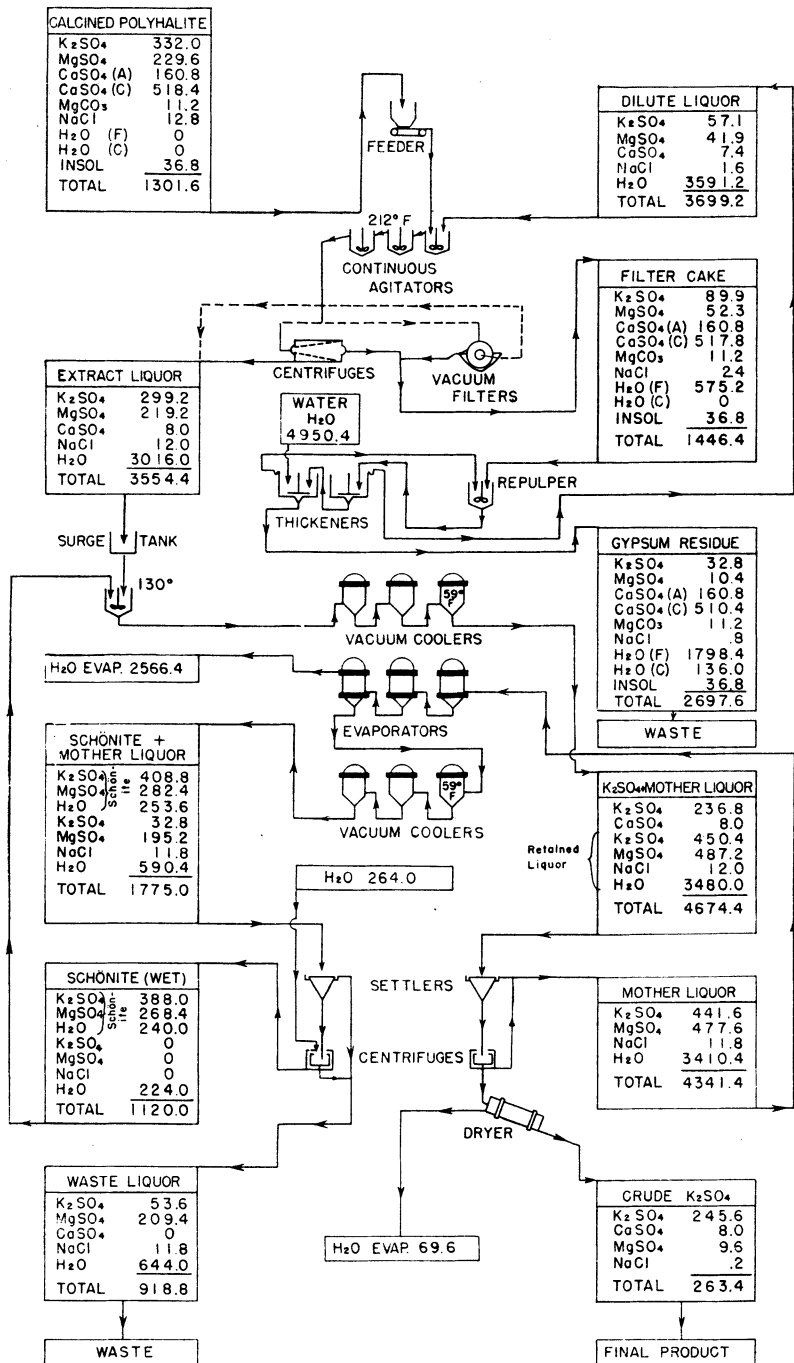


FIGURE 11.—Suggested flow sheet for treatment process 2.

polyhalite-extract liquors require extractors of greater capacity. Some economy should result from the decreased costs of drying the K_2SO_4 product instead of the dehydrated double salt, schönite ($K_2SO_4 \cdot MgSO_4 \cdot 6 H_2O$).

DETAILED EQUIPMENT REQUIREMENTS AND DIRECT OPERATING COSTS

The detailed discussion of the equipment requirements and the estimation of labor and other items comprising the direct operating costs have been placed in appendix A, pages 172 to 179.

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The summary of equipment and direct operating costs is presented in table 14. From these tabulated data it should be noted that 65 men are needed to operate the treatment plant, which requires an expenditure of \$1,003,360 for equipment exclusive of the building. The direct operating costs are estimated at \$2,521.83 per day and correspond to \$1.576 per ton of raw polyhalite. Including depreciation, estimated at different rates according to the type of equipment, the combined costs are estimated at \$1.759 per ton of polyhalite.

TOTAL PRODUCTION AND EQUIPMENT COSTS

Table 15 summarizes the complete equipment and production expenditures per 24-hour day and includes the costs of the mining, crushing, treating, direct and general supervision, general office expense, housing costs for all mine, crushing, and treatment plants, and employee residences. Fixed charges, comprising depreciation of all buildings and equipment as well as insurance and taxes, have been included. Also, a daily charge of \$95.20 for amortizing the preliminary mine development has been added.

The basis for charges other than the direct operating costs has been discussed in connection with process 1, on page 52. However, it should be noted that the larger equipment costs, which have been increased by 20 percent for minor accessory equipment allowance, necessitate a \$250,000 allotment for plant buildings.

Reference to the table shows that the total plant investment, exclusive of the power plant, is \$2,245,808 and the daily production cost \$6,211.25. This corresponds to a treatment cost of \$3.88 per ton of raw polyhalite mined or to \$25.29 per ton of K_2SO_4 (100-percent basis), produced; also to \$0.467 per unit of K_2O .

CAPITAL REQUIREMENTS

The amount of capital required for the proposed plant is included with similar data for the other processes on page 105.

EXTRACTION OF CALCINED POLYHALITE BY PROCESS 3

GENERAL CONSIDERATIONS

This process represents a different method for recovering the potassium sulfate from the concentrated extracts obtained by the hot extraction of calcined polyhalite. The principal differences are the removal of the magnesium sulfate from the extract liquors by precipitation with a lime slurry and the complete evaporation of the resulting relatively pure potassium sulfate solution to

TABLE 14.—*Summarized equipment, direct operating, and depreciation costs for process 2 (1,600 tons of raw polyhalite per day)*

Operation	Equipment costs	Number of employees	Operating costs per day, 24 hours						Total costs		Cost per ton raw polyhalite	
			Power	Labor	Steam	Fuel	Water	Maintenance and supplies	Total direct operating costs	Depreciation	Operating costs	
											Only	Plus depreciation
Salt washing.....	\$112,535	12 1/4	\$19.71	\$65.50	\$10.12	\$12.29	\$107.62	\$36.05	\$0.067	\$0.090
Calcination.....	160,000	12	6.00	72.00	65.00	420.00	53.33	.262	.296
Hot extraction.....	6,425	4	2.43	27.80	\$548.00	\$277.00	36.19	3.90	612.82	1.90	.383	.384
Filtering gypsum.....	115,000	9	13.50	54.00	6.50	74.00	57.50	.046	.082
Cold extraction.....	74,000	3	3.60	18.00	23.11	3.30	48.81	16.50	.031	.041
Dissolving soda.....	10,000	3	3.24	18.00	2.30	24.54	3.30	.015	.017
Crystallizing K ₂ SO ₄	185,000	3	6.75	18.00	15.00	31.20	13.42	1,863.37	41.10	.054	.080
Evaporating soda.....	228,000	9	36.00	54.00	855.60	123.20	15.00	2,083.80	50.97	.677	.709
Crystallizing soda.....	36,700	3	2.40	18.00	4.80	3.77	3.15	38.01	8.15	.024	.029
Filtering soda.....	40,000	3	6.90	18.00	13.00	53.07	13.33	.027	.035
Filtering K ₂ SO ₄	15,000	2	2.70	12.00	6.00	20.70	50.70	73.00	.013	.016
Drying K ₂ SO ₄	20,700	1 1/2	3.48	9.00	37.00	6.67	56.15	4.60	.035	.038
Totals.....	1,003,360	64 3/4	106.71	379.30	1,423.40	314.00	242.55	170.53	2,615.99	292.03	1.635	1.818
Credit for steam saved.....	94.16	94.16059	.059
Net costs, totals.....	1,329.24	2,521.83	1.576	1.769

¹ Subject to a deduction of \$80.00 for saving in steam.² Subject to a deduction of \$14.16 for saving in steam.

TABLE 15.—*Total production and plant costs for process 2*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Treatment.....	65	² \$1,204,032	\$ 379.30	\$2,142.53	\$2,521.83
Other ³	191	626,776	1,036.88	518.97	1,555.85
Total direct operating costs.....	256	1,830.808	1,416.18	2,661.50	4,077.68
Direct supervision.....	20		172.00	115.00	287.00
Total direct costs.....	276	1,830.808	1,588.18	2,776.50	4,364.68
Administration and general expense ³	48		343.00	229.00	572.00
Buildings:					
Camp site, etc.....	175,000
Treatment plant.....	240,000
Total cost.....	415,000
Fixed charges:					
Depreciation:					
Buildings.....	69.17	69.17
Treatment.....	360.44	² 360.44
Other ³	188.31	188.31
Total depreciation.....	617.92	617.92
Taxes and insurance, 1½ percent.....	112.29	112.29
Interest on investment, 6 percent.....	449.16	449.16
Total fixed costs.....	1,179.37	1,179.37
Amortization preliminary mine develop- ment.....	95.20	95.20
Total production costs.....	324	2,245,808	1,931.18	4,280.07	6,211.25

¹ See tables 7 and 12, pp. 23 and 53, for break-down.² 120 percent of the values for actual estimates; see table 14, p. 60.³ See table 13, p. 54, for break-down.

recover the potash. No double salts of potash and magnesia are produced. However, the magnesia is eliminated as hydroxide, together with the equivalent sulfate in the form of calcium sulfate, and this mixture obviously could be treated with carbon dioxide and ammonia to recover the magnesia as a valuable by-product.⁶

The sodium chloride originally present in the calcined polyhalite remains in the K₂SO₄ solutions and eventually is recovered in toto with the final products. Therefore, polyhalite low in salt would be desirable to insure a high-grade K₂SO₄. One percent of NaCl is increased to 2.3 percent chloride in the finished potash; and this is but slightly less than the 2.5-percent tolerance of sulfate fertilizers.

The successful operation of the process depends on the use of more-dilute solutions than are employed in processes 1 and 2, and correspondingly larger equipment capacities are required. This applies especially to the hot-extraction and final evaporation steps, but this disadvantage is offset to a large extent by the much-increased over-all recovery of the potassium sulfate. An extra filtering step involving a hot mixture of Mg(OH)₂ and gypsum also is required, and this can be accomplished on continuous vacuum filters. The continuous centrifugal filter may be applicable to this operation also and has the added advantage of delivering somewhat hotter solutions for the evaporator feed.

⁶ See reference 27 in list of Bureau of Mines publications (p. 249).

DETAILS OF PROCESS

The soluble salts are extracted by feeding 1,301.6 tons of calcined polyhalite to a series of continuous agitators of a capacity that allows an extraction time of 20 minutes with 6,126.6 tons of dilute liquor (comprising 5,196.3 tons of overflow from the countercurrent washing of the gypsum residue from the hot extraction and 930.3 tons of overflow solution from the countercurrent thickener being used to wash the $\text{Mg}(\text{OH})_2$ -gypsum mixture free from retained K_2SO_4 solution).

The limiting factor of this extraction step is the proportioning of the polyhalite: water ratio to prevent a K_2SO_4 concentration in excess of 6.4 grams per 100 grams of water. This is essential to prevent any appreciable formation of pentasalt ($\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$) and loss of potash during the lime treatment for removal of the magnesia in the subsequent step. During this precipitation the concentration of K_2SO_4 is permitted to drop to 5.8 grams per 100 grams of H_2O .

The hot extract and extracted-polyhalite residue, largely CaSO_4 , are pumped from the agitators to continuous filters where 6,096.0 tons of clarified filtrate containing 350.4 tons of K_2SO_4 and 229.6 tons of MgSO_4 and 1,332.2 tons of wet filter cake are handled daily. The hot filtrate is charged directly to slurry mixers or agitators, where it is treated with 335.2 tons of a lime slurry containing 112.0 tons of quicklime corresponding to approximately a 5-percent excess of the precipitation requirements, while the filter cake is repulped and washed by countercurrent decantation in thickeners to which 6,441.7 tons of water are added daily. The distribution of the water for the dilute solution make-up for the hot extraction agitators may be adjusted between the thickener washings, the gypsum residue, and the thickeners employed in washing the magnesium hydroxide precipitate from the lime treatment. This arrangement offers a flexible means of control that should assure optimum results. The low K_2SO_4 content of the overflow from the polyhalite-residue thickeners should result in virtually a 100-percent dissolution of all the potash salts in that material, and even the small amount of pentasalt formed during the lime treatment of the hot extract solution should be dissolved completely in the thickeners handling the washing of the magnesium hydroxide precipitate.

After a 5-minute agitation with the lime slurry, the mixture is filtered as rapidly as possible to produce 5,605.6 tons of filtrate containing 316.0 tons of K_2SO_4 , with all of the NaCl originally present in the calcined polyhalite, and a filter cake which is repulped and washed by countercurrent decantation, as previously described. The clear filtrate is fed continuously to multiple-effect evaporators, where all of the water is driven off; and the $\text{Mg}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ filter cake, after thorough washing, is discharged daily as 1,361.6 tons of thickened sludge.

The flow sheet illustrated in figure 12 shows evaporation of 5,186.1 tons of water for recovery of the K_2SO_4 from solution. Only forced-circulation, quadruple-effect evaporators should be

used, thus dispensing with the vacuum coolers, which entail an extra investment and greater operating expense.

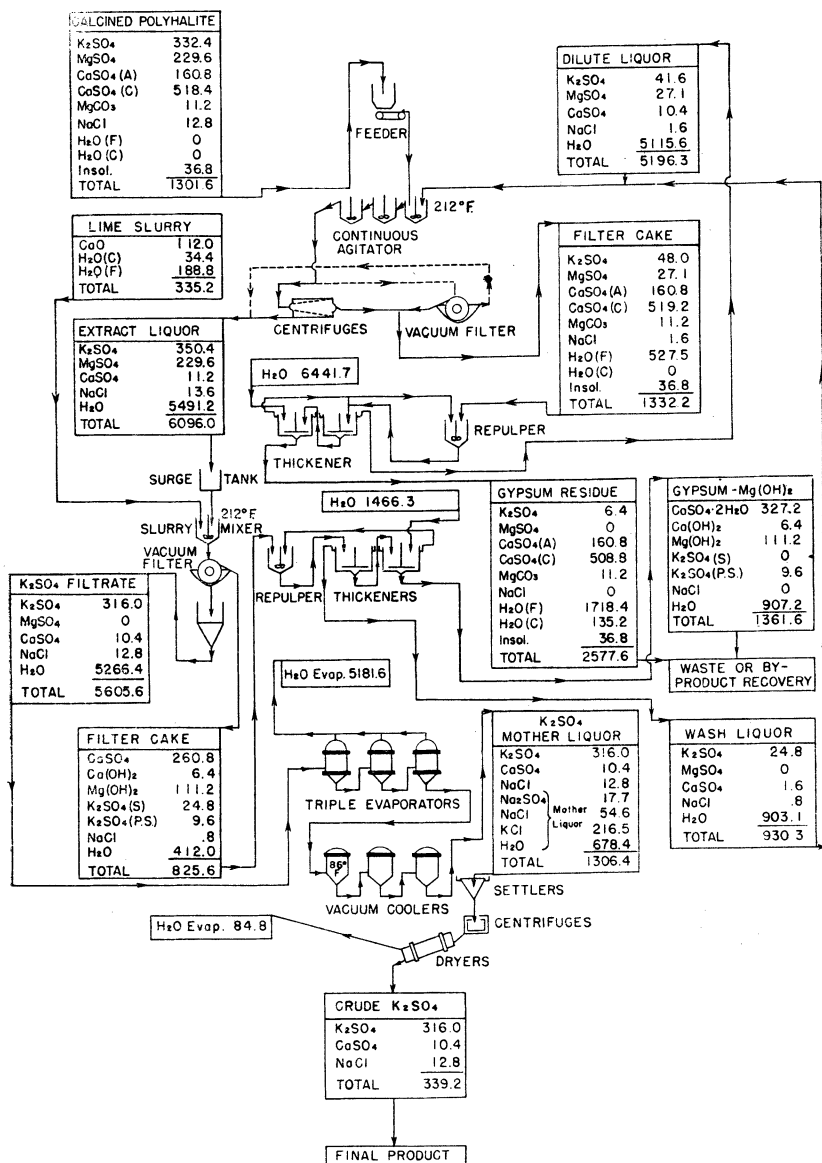


FIGURE 12.—Suggested flow sheet for treatment process 3.

During evaporation the solution first becomes saturated with K₂SO₄, but eventually the NaCl increases in concentration until secondary salts resulting from double decomposition are formed and crystallize from solution in amounts depending on the tem-

perature in the particular effect. Calculations show that the solution becomes saturated with K_2SO_4 at $100^\circ C.$ when 75.8 percent of the water is evaporated and at $55^\circ C.$ when 66.9 percent is expelled. Then, at $55^\circ C.$ ($131^\circ F.$) saturation with NaCl occurs when 97 to 98 percent of the water has been driven off. Actually, the solid phases formed on saturation with NaCl are glaserite ($K_3Na(SO_4)_2$) and finally KCl, which appears as a solid phase at the end point.

Therefore, in a quadruple-effect evaporator, with parallel liquor and vapor flow, no crystallization should occur in the first or second effects, and only 9 to 10 percent of the total crystal crop should separate in the third effect, while the balance of the K_2SO_4 , contaminated with a mixture of glaserite and KCl, separates in the fourth effect. Obviously, salt traps are required on the two last effects only. Circulating pumps are provided for transporting the crystal crops suspended in mother liquor, which are subsequently returned to the evaporators. This results in the evaporation of about 5,181.6 tons of water in the evaporators proper, the balance of 84.8 tons being expelled in the dryers. If handled in this manner, purer K_2SO_4 can be separated from the third effect if desired, but unless the NaCl is maintained at 1 percent or less in the washed polyhalite all of the crystal crop must be remixed or blended in order to meet the chloride specifications.

The crystallized salts with retained mother liquor are then dried in oil-fired rotary dryers to expel the 84.8 tons of moisture and produce 339.2 tons of crude K_2SO_4 containing 316 tons equivalent to 98 percent of the potash originally present in the calcined polyhalite; thus, the product should contain over 93 percent K_2SO_4 .

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The equipment and direct operating costs for the treatment plant are summarized in table 16. From these data it will be noted that 67 men are required to operate the plant and that an expenditure of \$1,205,660 is necessary, not including the buildings. The direct operating costs are \$4,106.06 per day, corresponding to \$2.57 per ton of raw polyhalite treated. Including a depreciation charge of 11.4 percent of the investment distributed upon the basis of a 300-day operating year, the combined costs are \$4,526.21 per day and equivalent to \$2.83 per ton.

TOTAL PRODUCTION AND EQUIPMENT COSTS

Table 17 summarizes the complete equipment and production expenditures per 24-hour day and includes the costs of the mining, crushing, treating, direct and general supervision, general-office expense, housing for all mine, crushing, and treatment plants, and employee living quarters. Fixed charges, comprising depreciation of all buildings and equipment, as well as insurance and taxes on the whole investment, have been included. Also, the daily charge of \$95.20 to amortize the preliminary mine development has been added.

TABLE 16.—*Summarized equipment, direct operating, and depreciation costs for process 3 (1,600 tons of raw polyhalite per day)*

Operation	Equip- ment costs	No. of em- ployees	Power	Labor	Steam	Fuel	Water	Re- pairs	Total	Cost per ton ¹
Salt washing.....	\$112,535	12	\$19.71	\$65.50			\$10.12	\$12.29	\$107.62	\$0.067
Calcining.....	160,000	12	6.00	72.00		\$277.00		65.00	420.00	.262
Feeding extraction agitators.....	1,925	1	.27	4.80				1.00	6.07	.004
Extracting polyhalite (hot).....	6,750	3	3.24	18.00	\$756.00		65.89	3.75	846.88	.529
Filtering gypsum residue.....	145,000	9	20.25	54.00				9.75	84.00	.053
Washing gypsum-residue.....	74,000	3	3.60	18.00			22.25	4.00	47.85	.030
Precipitating Mg(OH) ₂	2,250	2	1.08	9.00	76.40	660.00	5.32	2.00	753.80	.471
Filtering Mg(OH) ₂	57,500	6	6.75		36.00	(²)		4.75	47.50	.030
Washing Mg(OH) ₂	55,500	2	2.70	12.00			4.06	3.00	21.76	.014
Evaporating K ₂ SO ₄ liquors.....	450,000	12	85.50	72.00	1,296.00		186.50	37.50	1,677.50	1.048
Filtering K ₂ SO ₄	19,500	3	3.45	18.00				7.50	28.95	.018
Drying K ₂ SO ₄	20,700	2	3.48	9.00		45.00		6.65	64.13	.040
Totals.....	1,105,660	67	156.03	352.30	2,164.40	982.00	294.14	157.19	4,106.06	2.566
Depreciation at 11.4 percent.....									420.15	.263
Combined operating and depreciation.....									4,526.21	2.829
Lime plant.....	³ 100,000									
Total plant investment.....	1,205,660									

¹ Per ton of raw polyhalite.² Cost of 120 tons of lime.³ Operating and depreciation included in item (1).TABLE 17.—*Total production and plant costs for process 3*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Treatment.....	67	² \$1,326,673	\$ 352.30	\$3,753.76	\$4,106.06
Other.....	191	626,776	1,036.88	518.97	1,555.85
Total direct operating costs.....	258	1,953,449	1,389.18	4,272.73	5,661.91
Direct supervision.....	20		172.00	115.00	287.00
Total direct costs.....	278	1,953,449	1,561.18	4,387.73	5,948.91
Administration and general expense ³	48		343.00	229.00	572.00
Buildings:					
Camp site, etc.....		175,000			
Treatment plant.....		265,000			
Total cost.....		440,000			
Fixed charges:					
Depreciation:					
Buildings.....				73.33	73.33
Treatment.....				504.18	504.18
Other ³				188.31	188.31
Total depreciation.....				765.82	765.82
Taxes and insurance, 1½ percent.....				119.67	119.67
Interest on investment, 6 percent.....				478.68	478.68
Total fixed costs.....				1,364.17	1,364.17
Amortization, preliminary mine develop- ment.....				95.20	95.20
Total production costs.....	326	2,393,449	1,904.18	6,076.10	7,980.28

¹ See table 13, p. 54, for break-down.² 120 percent of the values for actual estimates, (see table 16, p. 65).³ See table 12, p. 53, for break-down.

The basis for charges other than the direct operating costs has been discussed in connection with process 1 (p. 52). However, it should be noted that the treatment-plant investment, which represents a 20-percent extra allowance for minor accessory equipment, requires a \$265,000 allotment for buildings.

Reference to the table will show the total plant investment, exclusive of the power plant, to be \$2,393,449 and the daily production cost \$7,980.28. This corresponds to a treatment cost of \$4.99 per ton of polyhalite mined, or to \$25.25 per ton of K_2SO_4 (100-percent basis) produced; also to 46.7 cents per unit of K_2O .

CAPITAL REQUIREMENTS

The amount of capital required to construct and operate this process is \$3,967,450, and the distribution of the capital has been indicated together with all the other processes in table 35 (p. 105).

PRODUCTION OF SYNGENITE FROM POLYHALITE BY PROCESS 4

DETAILS OF PROCESS

In this process, calcined polyhalite containing approximately 1 percent of $NaCl$ is treated to extract the magnesium sulfate completely and leave as much of the K_2SO_4 as possible in the form of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$), which subsequently is dehydrated by calcination. Only the calcium sulfate originally combined in the polyhalite is involved in the formation of syngenite, while that present as anhydrite goes through the treatment virtually unaffected. Complete conversion of the active calcium sulfate to syngenite assures the highest attainable grade of syngenite, provided all of the magnesium is extracted. All of the magnesium sulfate is dissolved from the calcined polyhalite initially, but minor amounts of re-formed polyhalite and the unavoidable retention of a small amount of the magnesium sulfate liquor results in the recovery of a small percentage (1 to 2 percent) of $MgSO_4$ in the final dry product.

The basis of this process is the extraction of calcined polyhalite in two portions by a hot- and a cold-extraction treatment, respectively, with discarding of the residue from the former and employment of the potash obtained in the extract liquor to convert the excess calcium sulfate of the second portion into syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) at atmospheric temperature.

Obviously, the polyhalite formula, $K_2SO_4 \cdot MgSO_4 \cdot 2CaSO_4 \cdot 2H_2O$, has a mole ratio of $1K_2SO_4 : 2CaSO_4$, so that, with no losses of potash, equal portions of calcined polyhalite are extracted in each step, and half of the $CaSO_4$ (combined) is discarded. However, losses of K_2SO_4 do occur, amounting to about 10 percent of the total amount in the fraction extracted hot plus an additional 20 percent of the combined K_2SO_4 in the polyhalite treated in both steps; this latter loss is limited by the final K_2SO_4 equilibrium concentration in the magnesium sulfate waste liquor. This condition affects the relative amounts to be charged to each part of the process and requires that approximately 62.4 percent of the total calcined polyhalite be treated by hot extraction and the remainder (37.6 percent) at $86^\circ F$.

Care is essential to control the sodium chloride concentrations to prevent excessive loss of potassium sulfate. A limited amount of $NaCl$ is beneficial during the hot-extraction step to insure high concentrations and a minimum volume of water for leaching purposes, but the equilibrium concentrations of the K_2SO_4 during the syngenite-formation step rise with the increase in amount of salt.

Therefore, the raw polyhalite is washed to remove as much NaCl as feasible; then a portion of this salt is added to the wash waters destined for eventual use as make-up solution for the hot-extraction step.

The essential steps of the process are presented in the flow sheet given as figure 13, in which 812.1 tons of calcined polyhalite are extracted daily at a temperature approaching 212° F., and 489.3

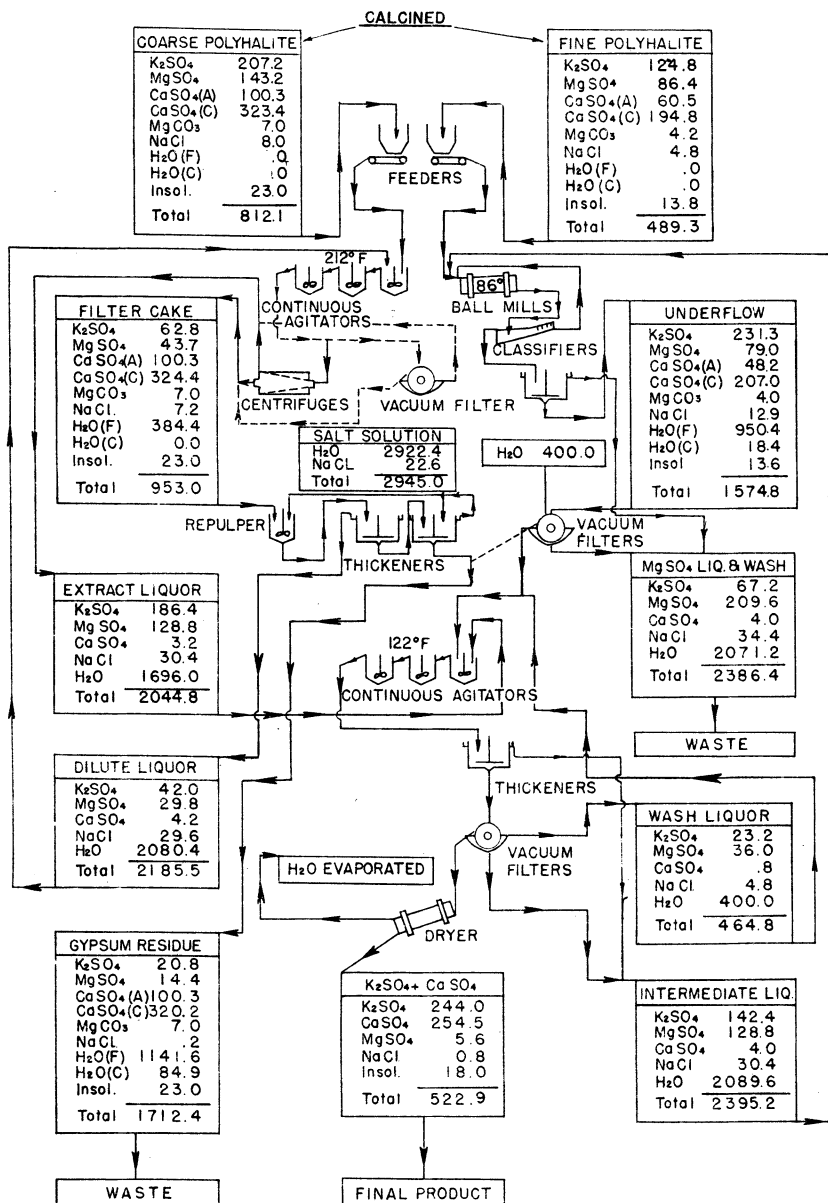


FIGURE 13.—Suggested flow sheet for treatment process 4.

tons are treated with various process liquors to bring about rapid, efficient conversion to syngenite and eliminate the magnesium sulfate.

The method used in the hot extraction is exactly the same as in process 1, in which an effort is made to attain the maximum concentration consistent with high recoveries. The extraction is made in continuous agitators discharging to continuous rotary vacuum or centrifugal filters to produce a clarified extract solution (to be used in the syngenite formation step), and a residue essentially calcium sulfate, which after washing in countercurrent thickeners is discharged to waste. As in the other hot-extraction procedures, the 2,185.5 tons of cold overflow obtained in the washing operation are used for make-up solution, and heat is conserved by passing this solution through heat exchangers to cool the hot extract liquor. Cooling of the extract liquor is carried to the point where the mixture resulting from the addition of the syngenite-gypsum and the syngenite wash liquor will maintain a temperature of 122° F. in the agitators.

Formation of the syngenite is accomplished by adding the 489.3 tons of the finer fraction of the calcined polyhalite directly to ball mills operating in closed circuit with a classifier to effect a more rapid interaction between the calcined polyhalite and the intermediate liquor from the second or final syngenite conversion step, whereby a large proportion of the magnesium sulfate passes into solution and the preponderance of calcium sulfate assures a rapid lowering of the K_2SO_4 to permit discarding the solution without serious loss of potash. Maintenance of temperatures as low as possible at this stage likewise is desirable to favor better recoveries.

Ball mills in this stage grind the fine fraction of the calcined polyhalite to minus 65-mesh to accelerate the conversion to syngenite-gypsum from the mixture of 489.3 tons of dry calcined polyhalite, the 2,395.2 tons of intermediate liquor, and the 1,108.3 tons of wet-classifier oversize returned daily to the ball-mill feed. Syngenite forms in the classifier as well as in the ball mill, and an average retention of 90 minutes in the ball mill, classifier, and thickener should result in a drop from 6.8 grams of K_2SO_4 to about 3.0 grams per 100 grams of water, corresponding to the conversion of 56.6 percent of the $CaSO_4$ to syngenite. The classifier overflow at about a 4 : 1 liquid : solid ratio discharges to a thickener, where a portion of the overflow is returned to the classifier and the remainder is discharged to waste, and the 1,581.9 tons of sludge carrying 624.4 of solids are pumped to vacuum filters and the filter cake washed with 400.0 tons of water daily. The washings and filtrate—with the necessary amount of thickener overflow to total 2,386.4 tons containing 209.6 tons of $MgSO_4$, which is being eliminated from the system—are discarded or diverted to the magnesia-recovery plant every 24 hours.

The 880.0 tons of washed syngenite-gypsum are added wet to the first of a series of three continuous agitators, with the 2,044.8 tons of K_2SO_4 extract liquors at 11.0 grams of K_2SO_4 per 100 grams of water and the 464.8 tons of wash liquor from the

syngenite filters. Retention of the mixture for a total of 90 minutes at 122° F. should result in the complete conversion of the active calcium sulfate to syngenite, with simultaneous decrease of the K_2SO_4 concentration to about 6.8 grams per 100 grams of water. Both the elevated temperature and the large excess of K_2SO_4 available shorten the reaction time. The extra time that the syngenite-gypsum from the first stage and the syngenite from the second stage are retained in the thickeners assures completion of the desired reactions.

The overflow from the agitators is thickened and filtered, and the clarified intermediate liquor (amounting to 2,395.2 tons per day) is returned to the ball mills in the first stage. The filter cake, consisting of syngenite but also containing all of the anhydrite and other insoluble constituents present originally in the fine fraction of the calcined polyhalite, is washed with 400.0 tons of water daily to remove most of the retained $MgSO_4$ and $NaCl$ and keep the K_2SO_4 content as high as possible.

The 947.7 tons of washed filter cake are conveyed to the oil-fired rotary dryers, where 424.8 tons of free and combined water are driven off and a total of 522.9 tons of dehydrated syngenite ($K_2SO_4 + CaSO_4$) is produced containing 244.0 tons—about 46.6 percent—of K_2SO_4 .

This product is slightly lower in potash than the commercial brand of sulfate of potash-magnesia, which is sold in the market upon the basis of 40 percent K_2SO_4 but usually contains 48 to 52 percent of potassium sulfate. It also does not carry the same amount of $MgSO_4$, which is one of the desirable constituents of the product now sold on the market, but a limited amount of $MgSO_4$ could purposely be allowed to remain in the syngenite. The quantity that could be retained is limited by the allowable tolerance of chloride simultaneously recovered. Further improvement of grade of syngenite would result as the anhydrite in the polyhalite decreased, and this condition could be effected by selection of the raw material.

The two-stage syngenite-formation step is an important operation and has been incorporated in several of the processes to be discussed later. The feasibility of this process would depend on the response of the fertilizer trade toward this new compound and would be influenced greatly by the price at which the product could be sold. If it could be sold only upon the basis of the K_2O content at a unit cost equivalent to that for 90 percent K_2SO_4 , the increased transportation costs would introduce a serious difficulty in the marketing of the syngenite. The possibility of even a penalty for low $MgSO_4$ content must be considered also. The other processes, involving the conversion of the syngenite to K_2SO_4 and to the double sulfate of potash-magnesia, have been developed to obviate these possible disadvantages.

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The equipment and direct operating costs for the treatment plant are summarized in table 18. From these data it will be noted that 65 men are required to operate the plant and that an expenditure of \$753,415 is necessary, not including the buildings.

The direct operating costs are \$1,577.46 per day, equivalent to \$0.986 per ton of raw polyhalite treated. Including a depreciation charge of 11.4 percent of the investment distributed on the basis of a 300-day operating year, the combined costs are \$1,863.75 per day or \$1.165 per ton.

TOTAL PRODUCTION AND EQUIPMENT COSTS

Table 19 summarizes the complete equipment and production expenditures per 24-hour day and includes the costs of the mining,

TABLE 18.—*Summarized equipment, direct operating, and depreciation costs for process 4 (1,600 tons of raw polyhalite per day)*

Operation	Equipment costs	No. of employees	Power	Labor	Steam	Fuel	Water	Repairs ¹	Total	Cost per ton ²
Salt washing.....	\$112,535	12	\$19.71	\$65.50			\$10.12	\$12.29	\$107.62	\$0.067
Calcining.....	160,000	12	6.00	72.00		\$277.00		65.00	420.00	.265
Feeding.....	3,500	2	.54	9.60				1.00	11.14	.007
Extracting polyhalite (212° F.).....	3,960	3	2.16	18.00	\$286.00		20.35	2.50	329.01	.206
Filtering gypsum.....	86,500	6	10.20	36.00				5.00	51.20	.032
Washing gypsum (70° F.).....	53,000	3	2.25	18.00			14.70	2.70	37.65	.024
Ball-milling syngenite-gypsum.....	15,000	1½	3.10	9.00				5.00	22.10	.014
Classifying and thickening syngenite-gypsum.....	6,500									
Filtering syngenite-gypsum.....	18,760	1½	.90	9.00				1.06	10.96	.007
Agitating syngenite.....	65,000	6	11.55	36.00			4.80	6.75	59.10	.037
Thickening syngenite.....	9,000	3	4.32	18.00	130.40			5.00	157.72	.099
Filtering syngenite.....	18,760	¼	.60	1.20				.43	2.23	.001
Drying syngenite.....	65,000	6	11.55	36.00			4.80	6.75	59.10	.037
Total.....	140,000	9	7.50	46.80		232.00		23.33	309.63	.194
Depreciation at 11.4 percent.....	753,415	65¼	85.38	375.10	416.40	509.00	54.77	136.81	1,577.46	.986
Combined total.....									286.29	.179
									1,863.75	1.165

¹ Includes supplies.

² Per ton of raw polyhalite.

TABLE 19.—*Total production and plant costs for process 4*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Treatment.....	66	² \$904,098	\$375.10	\$1,202.36	\$1,577.46
Other ³	191	626,776	1,036.88	518.97	1,555.85
Total direct operating.....	257	1,530,874	1,411.98	1,721.33	3,133.31
Direct supervision.....	20		172.00	115.00	287.00
Total direct costs.....	277	1,530,874	1,583.98	1,836.33	3,420.31
Administration and general expense ³	48		343.00	229.00	572.00
Buildings:					
Camp site, etc.....		175,000			
Treatment plant.....		190,000			
Total costs.....		365,000			
Fixed charges:					
Depreciation:					
Buildings.....				60.83	60.83
Treatment.....				239.54	² 239.54
Other ³				188.31	188.31
Total depreciation.....				488.68	488.68
Taxes and insurance (1½ percent).....				94.79	94.79
Interest on investment.....				379.16	379.16
Total fixed costs.....				962.63	962.63
Amortization, preliminary mine development.....				95.20	95.20
Electric power, surcharge.....				105.30	105.30
Total production costs.....	325	1,895,874	1,926.98	3,228.46	5,155.44

¹ See table 13, p. 54, for break-down.

² 120 percent of values of actual estimates, see table 18.

³ See table 12, p. 53, for break-down.

crushing, treating, direct and general supervision, general office expense, housing for all mine, crushing, and treatment plants, and employees' living quarters. Fixed charges, comprising depreciation of all buildings and equipment, as well as insurance and taxes on the whole investment, have been included. Finally, the daily charge of \$95.20 to amortize the preliminary mine development has been added.

The basis for charges other than the direct operating costs has been discussed in connection with process 1, on page 52. However, it should be noted that the treatment-plant investment, which represents a 20-percent extra allowance for minor accessory equipment, requires a \$190,000 allotment for buildings.

Reference to the table will show that the total plant investment, exclusive of the power plant, is \$1,895,874, and the daily production cost is \$5,155.44. This corresponds to a treatment cost of \$3.22 per ton of polyhalite mined or to \$21.13 per ton of K_2SO_4 (100-percent basis) produced; also to 39.1 cents per unit of K_2O .

CAPITAL REQUIREMENTS

The estimated capital required to construct and operate this process is \$3,084,880, and the distribution of the capital has been indicated with that for all the other processes in table 35 (p. 105).

EXTRACTION AND RECOVERY OF K_2SO_4 FROM CALCINED POLYHALITE BY PROCESS 4B

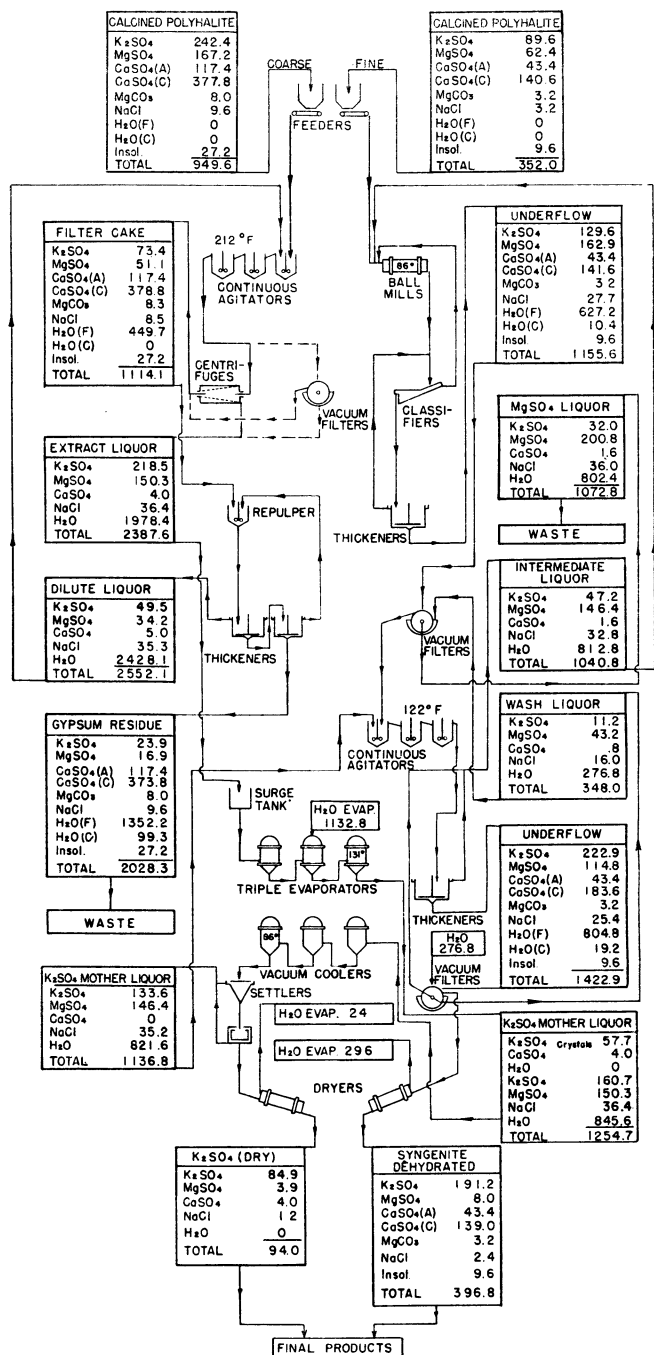
GENERAL CONSIDERATIONS

This process represents a combination of processes 1 and 4, arranged to produce crude K_2SO_4 by evaporation of the concentrated extract liquors and to make syngenite by treating a second batch of calcines with the mother liquors from the K_2SO_4 crystallization. By this procedure a portion of the K_2SO_4 is recovered from the solutions as sulfate of potash, and all of the $MgSO_4$ is discarded as filtrate from the syngenite-formation step.

DETAILS OF PROCESS

As may be seen in the flow sheet (fig. 14), 949.6 tons of calcined polyhalite are extracted at 212° F. to produce 2,387.6 tons of solution containing 11.0 grams of K_2SO_4 and 7.6 grams of $MgSO_4$ per 100 grams of water. From this solution 94.0 tons of crude sulfate of potash containing 84.9 tons of K_2SO_4 are recovered on evaporation and cooling. The 352.0 tons of the fine fraction of calcined polyhalite are diverted to the syngenite step, which is conducted in two stages, as in process 4, ultimately to produce 396.8 tons of syngenite containing 191.2 tons of K_2SO_4 . Thus, while approximately 73 percent of the polyhalite is added to the hot-extraction step, only about 31 percent of the total K_2SO_4 is recovered as a 90-percent K_2SO_4 product.

The limitation of the process is defined by the quantity of recoverable K_2SO_4 in the cold mother liquors from the evaporated solutions, and this must be balanced against the $CaSO_4$ in the fine fraction of calcined polyhalite being converted to syngenite. Thus, the 133.6 tons of K_2SO_4 in the mother liquor must be equivalent to that in the fine polyhalite plus that unavoidably discarded in



the MgSO_4 waste liquor and that retained by the final syngenite filter cake in spite of the washing treatment. Obviously, the final syngenite filter cake is washed to remove the excess of MgSO_4 and NaCl rather than the retained K_2SO_4 . The proportion of 90-percent K_2SO_4 and of syngenite recovered is not subject to change without corresponding modification of the process. Less K_2SO_4 could be produced than indicated on the flow sheet by merely permitting some of the K_2SO_4 to pass through in the mother liquors and by increasing the K_2SO_4 in the fine fraction by an equivalent amount, but a greater production of K_2SO_4 than is indicated would cause an appreciable decrease in the over-all recovery, as well as in the quantity of syngenite produced.

In general, the precautions and procedures described and outlined for processes 1 and 4 also apply to this process in the corresponding unit steps; salt is washed out of the polyhalite and returned in the proper amount to the final thickener of the series of thickeners washing the gypsum residue; slow cooling of the evaporated K_2SO_4 solution in the temperature range 131° to 95° F. is done in not less than 2 hours; temperatures in the ball milling are maintained as low as possible, and in the agitators producing the syngenite temperatures up to 122° F. are used. The principal difference between this step and that in process 4 is the use of the wash liquor from the syngenite filters as a wash for the syngenite-gypsum filter cake, thereby decreasing the volume of water in the process with a corresponding saving of K_2SO_4 discarded in the waste magnesium sulfate solution.

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The equipment and direct operating costs for the treatment plant are summarized in table 20. According to this table the cost of the equipment (exclusive of the buildings) is \$836,545, and 72 men are required to operate the plant. The direct operating costs are \$2,059.43 per day, equivalent to \$1.29 per ton of raw polyhalite treated. Including a depreciation charge of 11.4 percent of the investment, distributed upon the basis of a 300-day operating year, the combined costs are \$2,377.32 per day or \$1.49 per ton of polyhalite treated.

TOTAL PRODUCTION AND EQUIPMENT COSTS

Table 21 summarizes the complete equipment and production expenditures per 24-hour day and includes the costs of mining, crushing, treatment, direct and general supervision, general office expense, housing for all mine, crushing, and treatment plants, and employees' living quarters. Fixed charges, comprising depreciation of all buildings and equipment, as well as insurance and taxes on the whole investment, have been included. Finally, the daily charge of \$95.20 to amortize the preliminary mine development has been added.

The basis for charges other than the direct operating costs has been discussed in connection with process 1 (pp. 52 to 55). However, it should be noted that the treatment-plant investment, which represents a 20-percent extra allowance for minor accessory equipment, requires a \$200,000 allotment for buildings.

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TABLE 20.—*Summarized equipment and direct operating costs for process 4B (1,600 tons of raw polyhalite per day)*

Operation	Equip- ment costs	No. of em- ployees	Power	Labor	Steam	Fuel	Water	Re- pairs ¹	Total	Cost per ton ²
Salt washing.....	\$112,535	12	\$19.71	\$65.50	\$.....	\$.....	\$10.12	\$12.29	\$107.62	\$0.067
Calcining polyhalite.....	160,000	12	6.00	72.00	277.00	65.00	420.00265
Feeding polyhalite.....	3,500	2	.54	9.60	1.00	11.14007
Extracting polyhalite.....	3,960	3	2.16	18.00	306.00	23.75	352.41220
Filtering gypsum.....	86,500	6	10.20	36.00	5.00	51.20032
Washing gypsum.....	64,000	3	2.71	18.00	17.42	3.20	41.33	.026
Evaporating K ₂ SO ₄ extract.....	100,000	6	18.00	36.00	283.20	40.80	8.40	386.40	.242
Crystallizing K ₂ SO ₄	32,000	1½	3.60	9.00	8.60	5.32	2.70	29.22	.018
Filtering K ₂ SO ₄	5,750	1½	1.05	9.00	2.50	12.55	.008
Drying K ₂ SO ₄	10,000	1½	1.35	9.00	13.00	2.25	25.30	.016
Ball-milling syngenite-gypsum.....	11,250	1½	6.48	9.00	3.75	19.23	.012
Classifying syngenite-gypsum.....	4,850
Thickening syngenite-gypsum.....	15,000	1½	.70	9.00	1.17	10.87	.007
Filtering syngenite-gypsum.....	45,000	4	8.70	24.00	4.50	37.20	.023
Agitating syngenite.....	7,200	3	8.70	18.00	80.60	4.00	111.30	.070
Thickening syngenite.....	15,000	¾	.43	1.5075	2.68	.002
Filtering syngenite.....	45,000	4	8.70	24.00	3.53	4.50	40.73	.025
Drying syngenite.....	115,000	9	6.00	46.80	159.00	20.00	231.80	.145
Totals.....	836,545	71¾	\$105.03	414.40	678.40	449.00	100.94	143.51	\$1,891.28	1.296
Depreciation charge, 11.4 percent.....	317.89	.199
Credit for steam ⁴	10.40	\$2,209.17	1.495
Revised totals.....	668.00	2,198.77	1.489

¹ Includes supplies.

² Per ton of raw polyhalite.

³ Subject to an electric power surcharge of \$178.55.

⁴ Equivalent to water evaporated in vacuum coolers.

TABLE 21.—*Total production and plant costs for process 4B*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Treatment.....	72	² \$1,003,854	\$ 414.40	\$1,476.88	\$1,891.28
Other ³	191	626,776	1,036.88	518.97	1,555.85
Total direct operating.....	263	1,630,630	1,451.28	1,995.85	3,447.13
Direct supervision.....	20	172.00	115.00	287.00
Total direct costs.....	283	1,630,630	1,623.28	2,110.85	3,734.13
Administration and general expense ⁴	48	343.00	229.00	572.00
Buildings:					
Camp site, etc.....	175,000
Treatment plant.....	200,000
Total cost.....	375,000
Fixed charges:					
Depreciation:					
Buildings.....	62.50	62.50
Treatment.....	381.47	381.47
Other ³	188.31	188.31
Total depreciation.....	632.28	632.28
Taxes and insurance (1½ percent).....	100.28	100.28
Interest on investment (6 percent).....	401.12	401.12
Total fixed costs.....	1,133.68	1,133.68
Amortization, preliminary mine develop- ment.....	95.20	95.20
Electric power, surcharge.....	178.55	178.55
Total.....	331	2,005,630	1,966.28	3,747.28	5,713.56
Credit for steam.....	10.40	10.40
Total production costs.....	3,736.88	5,703.16

¹ See table 13, p. 54, for break-down.

² 120 percent of values of actual estimates; see table 20.

³ See table 12, p. 53, for break-down.

Reference to the table will show that the total plant investment, exclusive of the power plant, is \$2,005,630, and the daily production cost is \$5,703.16. This corresponds to a treatment cost of \$3.56 per ton of polyhalite mined, to \$20.66 per ton of K_2SO_4 (100-percent basis) produced, and to 38.2 cents per unit of K_2O .

CAPITAL REQUIREMENTS

The estimated amount of capital required to construct and operate this process is \$3,279,630, and the distribution of the capital has been indicated, with that for all the other processes, in table 35 (p. 105).

EXTRACTION OF CALCINED POLYHALITE FOR RECOVERY OF POTASSIUM SULFATE BY PROCESS 5

GENERAL CONSIDERATIONS

This process is based upon the extraction of calcined polyhalite at 77° to 86° F. to produce a concentrated solution of magnesium sulfate relatively low in potassium sulfate (which may be discarded without serious loss of the potash), and a mixture of syngenite and gypsum that is calcined and extracted at the boiling temperature to make a potassium sulfate solution (containing but minor amounts of magnesium sulfate or other salts), which subsequently is evaporated to dryness. The product resulting from this method can be maintained at 90 percent or more K_2SO_4 , depending on the effectiveness of the washing of the syngenite-gypsum mixture for removal of the magnesium sulfate.

A calcined polyhalite containing appreciable quantities of sodium chloride may be treated by this process, although the losses of K_2SO_4 increase with the salt content. Likewise, a somewhat finer material (minus 65-mesh) will give better results than the minus 10-mesh calcines used in many of the other processes.

Less precise control is necessary in the evaporation step as no fractional crystallization is involved. However, in order to facilitate the hot extraction of the K_2SO_4 , it is essential to calcine the syngenite-gypsum mixture to dehydrate the gypsum resulting from the decomposition of the calcined polyhalite and remaining as free gypsum in the solid residue produced. A rapid liquid-solid separation also is desirable as soon as the optimum concentration of K_2SO_4 has been attained in the hot extraction of the syngenite-gypsum mixture. The various steps of the process are given in the flow sheet (fig. 15).

DETAILS OF PROCESS

In process 5, 1,367.8 tons of calcined polyhalite containing 5.79 percent NaCl are charged to a series of continuous agitators and treated with 2,381.6 tons of make-up liquor, to which an additional 3,203.3 tons of concentrated magnesium sulfate solution containing 2,211.8 tons of water and 580.0 tons of dissolved salts are added to maintain the proper liquid : solid ratio in the agitators.

The agitator overflow, which has been retained for 90 minutes, is discharged to a thickener, where approximately one-third of

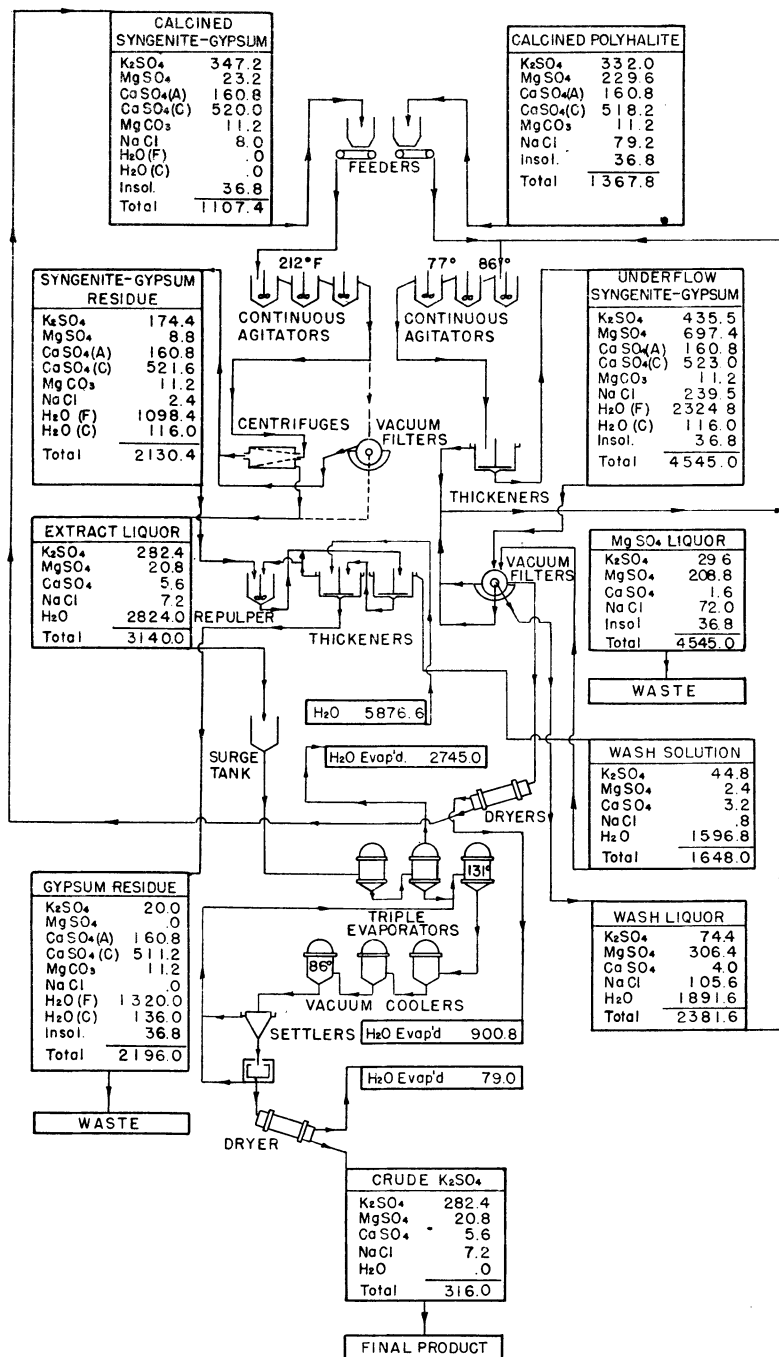


FIGURE 15.—Suggested flow sheet for treatment process 5.

the liquor is separated as clarified overflow, and the balance of 4,545.0 tons per day that settles as a thickened sludge is pumped to the rotary vacuum filters.

Only a portion of the filtrate, or a total of 1,008.0 tons of liquor carrying 208.8 tons of MgSO_4 , must be eliminated from the system daily. This quantity of MgSO_4 , plus the 20.8 tons obtained in the final K_2SO_4 product, is equal to the 229.6 tons of MgSO_4 entering the process in the calcined polyhalite. The syngenite-gypsum filter cake is washed thoroughly with the necessary quantity of dilute solution overflowing from the gypsum washing thickeners, for which purpose a maximum of 1,648.0 tons of liquor containing 1,596.0 tons of water could be used.

The wet-washed syngenite-gypsum filter cake, amounting to 2,008.2 tons, is discharged from the filters and conveyed to the rotary calciners, where 900.8 tons of free and combined water are expelled, by heating for 5 minutes at 950°F . The 1,107.4 tons of calcined product are then elevated to storage feed bins and automatically fed to the continuous agitators operating at approximately 212°F ., in which the charge is retained for $2\frac{1}{2}$ hours.

The agitator overflow is filtered hot, to yield 3,140.0 tons of K_2SO_4 solution containing 282.4 tons of K_2SO_4 and 20.8 tons of MgSO_4 and a filter cake amounting to 2,130.4 tons of wet solids every 24 hours. The hot filtrate is pumped to the multiple-effect evaporators, while the filter cake is repulped and washed by countercurrent methods in thickeners to which all of the water entering the process, and amounting to 5,876.6 tons daily, is added to the last thickener.

The 5,812.0 tons of clarified overflow from the washing thickeners are divided into one portion of 4,164.0 tons, with its 4,038.0 tons of water for use as make-up for the hot extraction, and a second portion of 1,648.0 tons, with 1,596.8 tons of water for use in washing the syngenite-gypsum filter cake free of concentrated MgSO_4 liquor. The settled gypsum residue from the last thickener is discharged as 2,196.0 tons of sludge with 1,320.0 tons of free water, a portion of which is subject to reclamation and reuse.

The hot extract liquor from the syngenite decomposition is pumped to a battery of quadruple-effect forced-circulation vacuum evaporators, where 2,745.0 tons of water are evaporated every 24 hours to recover the 316.0 tons of dissolved salts largely as K_2SO_4 . Recovery of the crystallized salts is effected by salt traps and conical settling tanks and final dewatering by centrifugal filters. The flow sheet indicates the use of vacuum coolers, but these are unnecessary unless an excessive quantity of MgSO_4 resulting from inefficient washing of the syngenite-gypsum filter cake accumulates in the system; this would necessitate periodic cooling of the thick liquors for recovery of the K_2SO_4 and discard of the MgSO_4 and NaCl .

Even with moderate amounts of MgSO_4 and NaCl retained in the syngenite-gypsum mixture and eventually appearing as soluble salts in the evaporator liquors, a gradual building up of these two salts occurs. Among the compounds resulting from the double

decomposition of these salts and K_2SO_4 are leonite ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$), glaserite [$K_3Na(SO_4)_2$], and finally KCl. This means that when the evaporators are first put into operation (for instance, a quadruple-effect arrangement with parallel liquor feeding), and assuming an evenly distributed temperature drop in all four evaporators, no crystals other than syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) should separate in the first two effects; relatively pure K_2SO_4 , with some syngenite, would separate in the third effect and K_2SO_4 , with minor amounts of possibly leonite, should crystallize in the final effect.

However, as the $MgSO_4$ and NaCl build up, glaserite and eventually sylvite (KCl) appear at the end point, and if no corrective means are applied an ever increasingly large proportion of these compounds will separate and lower the quality of the final K_2SO_4 product; also, serious difficulty would arise from gradual accumulation of $MgCl_2$. However, the salts other than K_2SO_4 cannot appear in the recovered solids in amounts exceeding input. These quantities could be tolerated in the final K_2SO_4 product.

If a chloride-free product is desired, this may be obtained by bleeding solution from the final evaporator. This requires the removal of approximately 56.3 tons of thick liquor containing 5.3 tons of $MgSO_4$, 2.6 tons of NaCl, and 4.4 tons of K_2SO_4 and 44.0 tons of water every 24 hours. This solution can be returned to the system by adding it to the continuous agitators producing the syngenite-gypsum mixture. The net effect of this modification is the lowering of the $MgSO_4$ and NaCl indicated in the final product in the flow sheet (fig. 15), by 5.3 and 2.6 tons, respectively.

The crystal crop of crude K_2SO_4 obtained from the salt traps and settling cones, after removal of excess water in centrifuges, is charged to oil-fired rotary dryers where 79.0 tons of water (free and combined) are expelled to produce 316.0 tons of crude sulfate of potash containing 282.4 tons of K_2SO_4 ; or if bleeding of the evaporators is practiced the same quality of K_2SO_4 is obtained in approximately 308 tons of product.

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The equipment and direct operating costs for the treatment plant are summarized in table 22. From these data it will be noted that 80 men are required to operate the plant and that an expenditure of \$1,233,735 is necessary, not including the buildings. The direct operating costs are \$2,954.88 per day, corresponding to \$1.816 per ton of raw polyhalite. Including a depreciation charge of 11.4 percent of the investment distributed upon the basis of a 300-day operating year, the combined costs are \$3,423.70 per day, equivalent to \$2.14 per ton of polyhalite treated.

TOTAL PRODUCTION AND EQUIPMENT COSTS

Table 23 summarizes the complete equipment and production expenditures per 24-hour day and includes the costs of the mining, crushing, treating, direct and general supervision, general office expense, housing for all mine, crushing, and treatment plants, and employees' living quarters. Fixed charges, comprising deprecia-

TABLE 22.—*Summarized equipment and direct operating costs for process 5 (1,600 tons of raw polyhalite per day)*

Operation	Equip- ment cost	No. of em- ployees	Cost per day, 24 hours							Cost per ton (²)
			Power	Labor	Steam	Fuel	Water	Re- pairs ¹	Totals	
Salt washing.....	\$112,535	12	\$19.71	\$65.50	\$.....	\$.....	\$10.12	\$12.29	\$107.62	\$0.067
Calcining polyhalite.....	160,000	12	6.00	72.00	277.00	65.00	420.00	.265
Feeding polyhalite and syngenite-gypsum.....	3,950	2	.54	9.60	2.00	12.14	.008
Extracting polyhalite.....	13,500	3	5.40	18.00	5.00	28.40	.018
Thickening syngenite-gypsum.....	21,300	¾	.97	1.20	1.05	3.22	.002
Filtering syngenite-gypsum.....	130,000	6	23.10	36.00	19.16	13.50	91.76	.057
Calcining syngenite-gypsum.....	225,000	12	9.00	61.20	494.00	37.50	701.70	.438
Extracting calcined syngenite-gypsum.....	22,500	6	6.75	36.00	493.20	33.88	5.00	574.83	.359
Filtering gypsum residue.....	175,000	6	20.25	36.00	15.00	17.25	71.25	.045
Washing gypsum residue.....	85,200	3	3.90	18.00	16.08	4.30	42.28	.026
Evaporating K ₂ SO ₄ extract.....	240,000	12	36.00	72.00	686.00	99.00	20.00	913.00	.057
Filtering K ₂ SO ₄	18,750	3	3.24	18.00	3.25	24.49	.015
Drying K ₂ SO ₄	26,000	3	3.24	18.00	42.00	5.85	69.09	.043
Totals.....	1,233,735	80¾	138.10	461.50	1,179.20	808.00	178.24	189.74	2,954.88	1.816
Depreciation, 11¼ percent.....	140,646	468.82	.293
Combined operating and depreciation costs.....	3,423.70	2.140

¹ Includes supplies.² Per ton of raw polyhalite.TABLE 23.—*Total production and plant costs for process 5*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Treatment.....	81	² \$1,480,482	\$ 461.50	\$2,493.38	\$2,954.88
Other ³	191	626,776	1,036.88	518.37	1,555.85
Total direct operating.....	272	2,107,258	1,498.38	3,012.35	4,510.73
Direct supervision.....	20	172.00	115.00	287.00
Total direct costs.....	292	2,107,258	1,670.38	3,127.35	4,797.73
Administration and general expense ³	48	343.00	229.00	572.00
Buildings:					
Camp site, etc.....	175,000
Treatment plant.....	300,000
Total costs.....	475,000
Fixed charges:					
Depreciation:					
Buildings.....	79.16	79.16
Treatment.....	562.53	562.53
Other ³	188.31	188.31
Total depreciation.....	830.05	830.05
Taxes and insurance.....	129.11	129.11
Interest on investment.....	516.44	516.44
Total fixed costs.....	1,475.60	1,475.60
Amortization, preliminary mine costs.....	95.20	95.20
Total production costs.....	340	2,582,258	2,013.38	4,927.15	6,940.53

¹ See table 13, p. 54, for break-down.² 120 percent of values for actual estimates given in table 22.³ See table 12, p. 53, for break-down.

tion of all buildings and equipment, as well as insurance and taxes on the whole investment, have been included. Finally, the daily charge of \$95.20 to amortize the preliminary mine development has been added.

The basis for charges other than the direct operating costs has been discussed in connection with process 1 (p. 52). How-

ever, it should be noted that the treatment-plant investment, which represents a 20-percent extra allowance for minor accessory equipment, requires a \$300,000 allotment for buildings.

Reference to the table will show that the total plant investment, exclusive of the power plant, is \$2,582,258, and the daily production cost is \$6,940.53. This corresponds to a treatment cost of \$4.38 per ton of polyhalite mined or to \$24.58 per ton of K_2SO_4 (100-percent basis) produced; also to 45.4 cents per unit of K_2O .

CAPITAL REQUIREMENTS

The amount of capital required to construct and operate this process is estimated at \$3,956,260, and the distribution of the capital has been indicated (together with that for all the other processes) in table 35 (p. 105).

EXTRACTION AND RECOVERY OF POTASSIUM SULFATE BY PROCESS 5A

GENERAL CONSIDERATIONS

This process has been devised in an attempt to permit economic recovery of K_2SO_4 from polyhalite without the necessity of evaporating large quantities of water but obviously has transferred the operation to the syngenite dryers, where the volume of total water to be expelled has been reduced slightly.

The basis of the scheme employed is to extract the calcined polyhalite at 77° F. (30° C.) in order to obtain the $MgSO_4$ in solution and precipitate the K_2SO_4 essentially as syngenite which is washed virtually free of $MgSO_4$. This syngenite is dried to expel the retained water and then subjected to extraction under pressure at about 392° F. to yield a concentrated solution of K_2SO_4 ; the potash is then recovered by flash evaporation and cooling of the solution to crystallize out the sulfate.

Actually the syngenite is produced in two stages, as indicated in the syngenite process previously discussed (see p. 43). The pressure extraction is effected also in two stages because the rate of decomposition of the syngenite and equilibrium conditions favoring the fixation of K_2SO_4 as pentasalt ($K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$) necessitate the final extraction at a lower concentration. High extractions are accomplished in this manner, but equipment costs of suitable autoclaves are virtually doubled.

Furthermore, the quantity of water that can be expelled by flash evaporation of the concentrated liquors is slightly less than desired so that evaporators are required to supply a safe margin. However, the evaporator investment should be very much less than in the other processes. Continuous crystallizers are essential also, and vacuum coolers instead of evaporators have been suggested for this purpose.

The success of the process depends on thorough removal of the $MgSO_4$ from the syngenite to prevent the fixation and consequent loss of a proportionate amount of K_2SO_4 as secondary polyhalite during the pressure extraction. Likewise, the flow sheet given in figure 16 is based upon a 61-percent decomposition of the syngenite, which is 76.2 percent of the theoretical maximum attainable, and a top concentration of 25.2 grams of K_2SO_4 per 100 grams of water instead of the equilibrium limit of about 32.0.

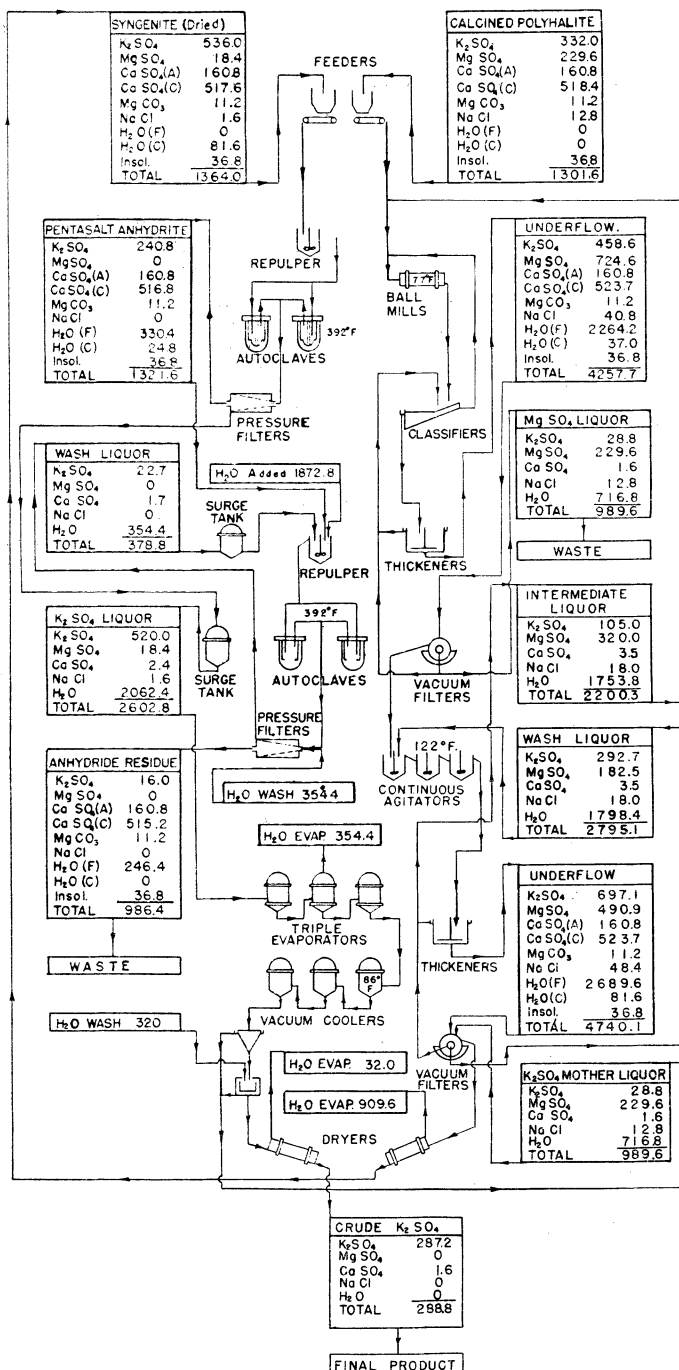


FIGURE 16.—Suggested flow sheet for treatment process 5A.

Similarly, the second stage is operated at a top concentration of 9.62 grams of K_2SO_4 , which is nearly 4.0 grams per 100 grams of water, less than the theoretical attainable concentration at 200° C. with pentasalt and anhydrite as solid phases. (See fig. 48, p. 149.) One apparent advantage of having to limit the $MgSO_4$ concentration is that the final K_2SO_4 product may be obtained virtually free from this salt. For fertilizer purposes, the presence of some $MgSO_4$ is not objectionable, however.

The operation of the pressure autoclaves and the subsequent separation of the extract liquor from the solid residue without releasing the pressure entail careful control, but with proper equipment this should be accomplished without serious difficulty.

DETAILS OF PROCESS

The 1,301.6 tons of calcined polyhalite resulting from the salt leaching and calcination of 1,600 tons of raw polyhalite are fed to ball mills operating in closed circuit with hydraulic classifiers, together with 2,200.3 tons of intermediate liquor obtained from the second or syngenite-formation step. This liquor at approximately 6.0 grams of K_2SO_4 per 100 grams of water when added to the ball mills, classifier, and thickener is lowered to about 4.0 grams per 100 grams of water and after filtration is discarded to waste with all of the $MgSO_4$ dissolved from the calcined polyhalite. Obviously, the minus 10-mesh polyhalite is ground in the ball mills and classified at 65-mesh, whereupon the leaching time is decreased to 1½ hours if the temperature is not permitted to rise much above 77° F.

The classifier overflow carries 1,132.2 tons of syngenite-gypsum mixture at about a 3:1 liquid : solid ratio and discharges to a thickener from which the clarified overflow mixed with the necessary volume of filtrate from the vacuum filters is recycled through the classifier. The underflow, consisting of syngenite-gypsum and retained solution, amounting to 4,257.7 tons daily, is collected and pumped to rotary vacuum filters to recover 2,512.2 tons of wet filter cake which is charged without washing to a series of continuous agitators with 2,795.1 tons of wash liquor originating as K_2SO_4 mother liquor that has been used to displace all of the retained solution in the syngenite filter cake. Meanwhile, 989.6 tons of the filtrate from the syngenite-gypsum, which contains 229.6 tons of $MgSO_4$, are discharged to waste or to magnesia recovery.

The wash liquor being charged to the syngenite agitators is passed through exchangers to absorb enough heat to produce a temperature of 122° F. when added to the agitator charge. After 90 minutes retention, the syngenite produced is discharged to a thickener, and if the K_2SO_4 content of the wash liquor is maintained at any amount less than 303.2 tons per day no excessive loss of K_2SO_4 will occur, as this is the amount that can be fixed by the $CaSO_4$ present in the polyhalite.

The clarified overflow and filtrate from the syngenite filters, totaling 2,200.3 tons, are pumped to the ball mills in the first stage while the underflow, with as little solution as possible, is transferred to the vacuum filters to obtain 2,353.1 tons of filter cake

after washing on the filters with 1,961.6 tons of K_2SO_4 mother liquor. Special provision to obtain a dry cake, possibly by use of compression rollers, is recommended to reduce the excessive volumes of liquids retained by the syngenite filter cake. Drying costs, which represent a major treatment expense, vary directly with the moisture content of this product.

The washed syngenite is conveyed to oil-fired rotary dryers where only the free water (amounting to 909.6 tons) need be expelled. This yields 1,364.0 tons of dried material containing 536.0 tons of K_2SO_4 , of which 287.2 tons ultimately are recovered as finished product, 16.0 tons are lost as pentasalt in the anhydrite residue, and 232.8 tons are recycled through the syngenite-formation step. The dry syngenite is repulped with 2,562.4 tons of extract liquor and washings from the second-stage pressure extraction of the syngenite, and then pumped into the first-stage agitators, which are heated for 60 minutes by steam jackets to 392° F. (200° C.) and discharged under pressure to pressure-leaf filters of the Sweetland, Vallez, or Kelly type (possibly the last), where a drop to about 356° F. (130-pound gage pressure) is feasible without reaching saturation with the K_2SO_4 . The 1,321.6 tons of filter cake (now largely anhydrite), with some residual syngenite and a minor amount of pentasalt, are repulped with 378.8 tons of wash water from the second pressure treatment and 1,872.8 tons of fresh water and then recharged to the second-stage autoclaves; the concentrated liquor (25.2 grams K_2SO_4 per 100 grams H_2O), amounting to 2,604.8 tons, is pumped to double-effect evaporators under pressure. The autoclaves are heated to 392° F. for 60 minutes by steam jackets and by passing make-up solutions through heat exchangers before adding to the repulpers.

The discharge from the second-stage autoclaves is forced into pressure-leaf filters by the pressure in the autoclaves, and the solids are obtained as 986.4 tons of wet cake after being washed with 354.4 tons of water every 24 hours. Efficient removal of the retained liquor is essential to prevent excessive loss of K_2SO_4 .

The 2,604.8 tons of concentrated liquor from the first-stage autoclaves, containing 25.2 grams of K_2SO_4 per 100 grams of H_2O , are pumped to vacuum evaporators at 356° F. On the removal of 354.4 tons of water from this solution approximately 290 tons of K_2SO_4 containing 1.6 tons of $CaSO_4$ as syngenite separates when cooling is applied to lower the temperature to 86° F.

The sensible heat of the liquors and the heat of crystallization of the K_2SO_4 separating from solution are such that in cooling the liquor from 356° to 86° F., 706,800,000 B.t.u. are removed, which would flash-evaporate about 350 tons of water if all the heat were available for evaporation purposes. However, such utilization is not feasible. Additional estimates supplemented with experimental pilot-plant testing would be necessary to determine a choice between vacuum coolers with possibly a lower final temperature than 86° F. or preliminary evaporation of some of the water before the thick liquors are introduced into the vacuum coolers. For preliminary estimates, the use of both evaporators and vacuum coolers is considered necessary.

The crystal crop of K_2SO_4 is recovered by means of salt traps and conical settlers and centrifuged with a water wash to produce 320.8 tons of wet crystals containing 287.2 tons of K_2SO_4 while the mother liquor (amounting to 1,961.6 tons daily) is pumped to the syngenite-formation step for use in washing the syngenite. Subsequently, the K_2SO_4 solution is employed to convert the syngenite-gypsum mixture to syngenite in the continuous agitators.

The crystal crop undergoes final dewatering in oil-fired rotary dryers that yield 288.8 tons of anhydrous final product, containing 287.2 tons of K_2SO_4 equivalent to 86.8 percent recovery from the polyhalite treated.

EQUIPMENT AND OPERATING COSTS

Process 5A comprises the two major steps involving the cold extraction (77° F.) of calcined polyhalite to produce syngenite, which is calcined and extracted in pressure autoclaves at 392° F. (200° C.) to make a concentrated solution of K_2SO_4 that will crystallize on cooling.

The magnitude of syngenite production and the quantity of potassium sulfate entering the syngenite formation operation so modify the equipment and operating costs that data obtained by analyzing the other syngenite processes do not provide an equitable basis for cost estimates. Therefore, the detailed-step analysis is necessary, as in the previous processes discussed. The detailed equipment and direct operating-cost estimates are given in appendix A, p. 206.

TABLE 24.—*Summarized equipment and direct operating costs for process 5A (1,600 tons of raw polyhalite per day)*

Operation	Equipment cost	No. of employees	Power	Labor	Steam	Fuel	Water	Repairs ⁽¹⁾	Totals ⁽¹⁾	Cost per ton ⁽²⁾
Salt washing.....	\$112,535	12	\$19.71	\$65.50			\$10.12	\$12.29	\$107.62	\$0.067
Calcining polyhalite.....	160,000	12	6.00	72.00		\$277.00		65.00	420.00	.265
Feeding polyhalite and calcined syngenite.....	3,950	2	.54	9.60				2.00	12.14	.008
Ball-milling syngenite-gypsum.....	45,000	3	24.30	18.00				15.00	57.30	.036
Classifying syngenite-gypsum.....	19,400	3	2.16	16.50				1.68	20.34	.013
Thickening syngenite-gypsum.....	37,500		1.13	1.50				1.88	4.51	.003
Filtering syngenite-gypsum.....	160,000		28.50	36.00				16.20	80.70	.050
Agitating syngenite.....	17,500	3	2.70	16.50	\$177.40			10.00	206.60	.129
Thickening syngenite.....	43,000		1.13	1.50				2.15	4.78	.003
Filtering syngenite.....	190,000		32.40	36.00				19.40	87.80	.055
Calcining syngenite.....	275,000	18	11.10	93.60		481.00		45.00	630.70	.394
Autoclaving syngenite.....	144,000	18	18.00	86.40	710.00		24.75	24.00	863.15	.539
Filtering pentasalt-anhydrite.....	145,000	18	3.00	86.40				30.00	119.40	.074
Autoclaving pentasalt-anhydrite.....	144,000	18	18.00	86.40	290.94		1.98	24.00	411.32	.257
Filtering pentasalt-anhydrite.....	119,000	18	2.46	86.40				24.54	113.40	.071
Evaporating K_2SO_4 liquors.....	32,000	3	18.00	18.00			25.50	2.70	64.20	.040
Crystallizing K_2SO_4 liquors.....	55,500	3	6.00	18.00			8.34	4.60	36.94	.023
Filtering K_2SO_4	42,500	3	7.50	18.00			.15	16.50	42.15	.026
Drying K_2SO_4	26,000	3	4.35	18.00		17.00		5.85	45.20	.028
Totals.....	1,771,885	151	206.98	784.30	1,168.34	775.00	70.84	322.79	\$3,328.25	2.08
Depreciation, 11.4 percent.....	201,994.89			(³)					673.31	.421
Revised totals.....									\$4,015.56	2.51

¹ Includes supplies.

² Per ton of raw polyhalite.

³ Subject to electric power surcharge of \$255.27.

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The equipment and direct operating costs for the treatment plant are summarized in table 24. From these data it will be noted that 151 men are required to operate the plant and that an expenditure of \$1,771,885 is necessary, not including the buildings. The direct operating costs are \$3,583.52, corresponding to \$2.24 per ton of raw polyhalite treated per day. Including a depreciation charge of 11.4 percent of the investment distributed upon the basis of a 300-day operating year, the combined costs will be \$4,270.83 per day and equivalent to \$2.67 per ton.

TOTAL PRODUCTION AND EQUIPMENT COSTS

Table 25 summarizes the complete equipment and production expenditures per 24-hour day and includes the costs of the mining, crushing, treating, direct and general supervision, general office expense, housing for all mine, crushing, and treatment plants,

TABLE 25.—*Total production and plant costs for process 5A*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Treatment.....	151	² \$2,126,262	\$ 784.30	\$2,543.95	\$3,328.25
Other ³	191	626,776	1,036.88	518.97	1,555.85
Total direct operating.....	342	2,753,038	1,821.18	3,062.92	4,884.10
Direct supervision.....	20		172.00	115.00	287.00
Total direct costs.....	362	2,753,038	1,993.18	3,177.92	5,171.10
Administration and general expense ³	48		343.00	229.00	572.00
Buildings:					
Camp site, etc.....		175,000			
Treatment plant.....		425,000			
Total costs.....		600,000			
Fixed charges:					
Depreciation:					
Buildings.....				100.00	100.00
Treatment.....				807.97	807.97
Other ³				188.31	188.31
Total depreciation.....				1,096.28	1,096.28
Taxes and insurance.....				167.65	167.65
Interest on investment.....				670.60	670.60
Total fixed costs.....				1,934.53	1,934.53
Amortization, preliminary mine costs.....				95.20	95.20
Electric power, surcharge.....				255.27	255.27
Total production costs.....	410	3,353,038	2,336.18	5,691.92	8,028.10

¹ See table 13, p. 54, for break-down.² 120 percent of values of actual estimates; see table 24, p. 84.³ See table 12, p. 53, for break-down.

and employees' living quarters. Fixed charges, comprising depreciation of all buildings and equipment, as well as insurance and taxes on the whole investment, have been included. Finally, the daily charge of \$95.20 to amortize the preliminary mine development has been added.

The basis for charges other than the direct operating costs, has been discussed in connection with process 1 (p. 52). However, it should be noted that the treatment-plant investment, which represents a 20-percent extra allowance for minor accessory equipment, would require a \$425,000 allotment for buildings.

Reference to the table will show that the total plant investment, exclusive of the power plant, is \$3,353,038, and the daily produc-

tion cost is \$8,028.10. This corresponds to a treatment cost of \$5.02 per ton of polyhalite mined or to \$27.95 per ton of K_2SO_4 (100-percent basis) produced; also to 51.7 cents per unit of K_2O .

CAPITAL REQUIREMENTS

The capital required to construct and operate this process is estimated at \$4,832,400 and the distribution of the capital has been indicated (with that for all the other processes) in table 36 (p. 105).

EXTRACTION AND RECOVERY OF POTASH FROM POLYHALITE BY PROCESS 6

GENERAL CONSIDERATIONS

This treatment process represents a departure from the previous methods of extraction discussed, in that the sulfates present in the polyhalite and associated anhydrite are reduced to their respective sulfides or oxides, which are leached with water at atmospheric temperature. A solution of relatively high concentration of K_2S , KHS , and K_2CO_3 , with minor amounts of other potassium salts such as thiosulfate and sulfite, is obtained which on treatment with flue gas results in the conversion of the K_2S and KHS to K_2CO_3 , with elimination of the sulfur as hydrogen sulfide. Either K_2S or K_2CO_3 can be produced as desired; however, the latter compound is a more acceptable potassium salt for most purposes. One advantage these products possess is a high K_2O content, which is 85.4 percent in the sulfide and 68.1 percent in the carbonate. Therefore, the potential saving in transportation costs is obviously an important economic consideration.

In spite of the fact that the process and the flow sheet offered to indicate the various operating steps are fundamentally sound and believed to be technically feasible, the type of equipment required, especially for reduction of the sulfates to sulfides, is such that an intermediate pilot-plant-scale study is necessary and is recommended before the outlined procedure can be applied successfully. However, very liberal estimates for equipment investment have been made intentionally, and it is believed that final estimates would show a downward revision in costs.

The reduction of the sulfates of potassium, calcium, and magnesium produces the extremely soluble potassium sulfide; but the calcium sulfide and the magnesium oxide, which are formed by the interaction of the sulfide with the water vapor present, are insoluble. Only the soluble salts present in the polyhalite and not affected by the gas-reduction treatment, notably $NaCl$, are obtained in the K_2S -extract solution. Therefore, a washed polyhalite especially low in $NaCl$ is desirable for treatment by this process.

POSSIBLE USES FOR POTASSIUM SULFIDE

The market for potassium sulfide is limited at present. Whether the product derived from process 6 might ever find direct outlets is questionable. One speculative possibility involves the use of the kraft or sulfate process for pulping wood as a means of converting potassium sulfide into a crude potassium sulfate suitable for incorporation in fertilizer mixtures. Instead of the standard cycle of the kraft process—in which the sulfate black liquor containing the lignin from the digestion step is concentrated and

burned to supply heat and to reduce the sulfate to sulfide for reuse in the digestion step—potassium sulfide might be used in the digestion step, and the black liquor containing largely potassium sulfate and lignin then concentrated to provide a fertilizer material. Direct conversion of the sulfide to the sulfate probably would be more practical.

Although potassium sulfide does not oxidize readily to the sulfate on heating in air, the conversion can be accomplished readily in a cyclic process in which potassium sulfide is treated with sulfuric acid, liberating hydrogen sulfide. The latter is burned to sulfur dioxide and converted into sulfuric acid by the customary catalytic process, the resultant acid then being returned for treatment of more potassium sulfide.

An alternative process would be the production of potassium phosphates by treating the potassium sulfide with phosphoric acid. The hydrogen sulfide liberated would be converted into sulfuric acid as before, and with additional acid used to treat phosphate rock to manufacture the phosphoric acid required in the process.

Potassium metaphosphate probably is the most desirable fertilizer material that might be obtained by such a procedure. A crude product could be made by direct reaction between P_2O_5 derived by thermal processes from phosphate rock and the moisture-containing K_2S -KHS product from the reduction of polyhalite.

If potassium nitrate were desired, it might be necessary to convert the potassium sulfide into potassium carbonate before treatment with nitric acid, since otherwise some oxidation of the sulfide and reduction of the nitric acid would occur.

Conversion to potassium carbonate would provide a product suitable as a starting material for a variety of industrial potassium chemicals. Estimates have accordingly been made only on this operation. As a first approximation, the cost of conversion to the other products previously noted might be assumed to equal the cost of conversion to the carbonate.

Aside from the economic problem of marketing of the potassium carbonate produced and the necessity of converting it into the chloride, sulfate, nitrate, or phosphate to supply a more commonly acceptable type of potash for the fertilizer trade, the question must be decided whether a single large installation or a number of small units would be more practical. It is believed that the latter alternative, though probably requiring a slightly larger equipment expense, would be more easily controlled and likewise, more flexible. Therefore, a series of units comprising a converter with a preheater and a rotary kiln is suggested and equipment and operating costs estimated on this basis. (See appendix A, p. 216.)

The reduction process has been founded on scientific data, including thermodynamic considerations, and has been tested in small laboratory apparatus. However, the ultimate selection of the furnace for reducing the polyhalite would require some additional pilot-plant investigation. The catalytic procedure for producing CO and H_2 is an accepted commercial process.

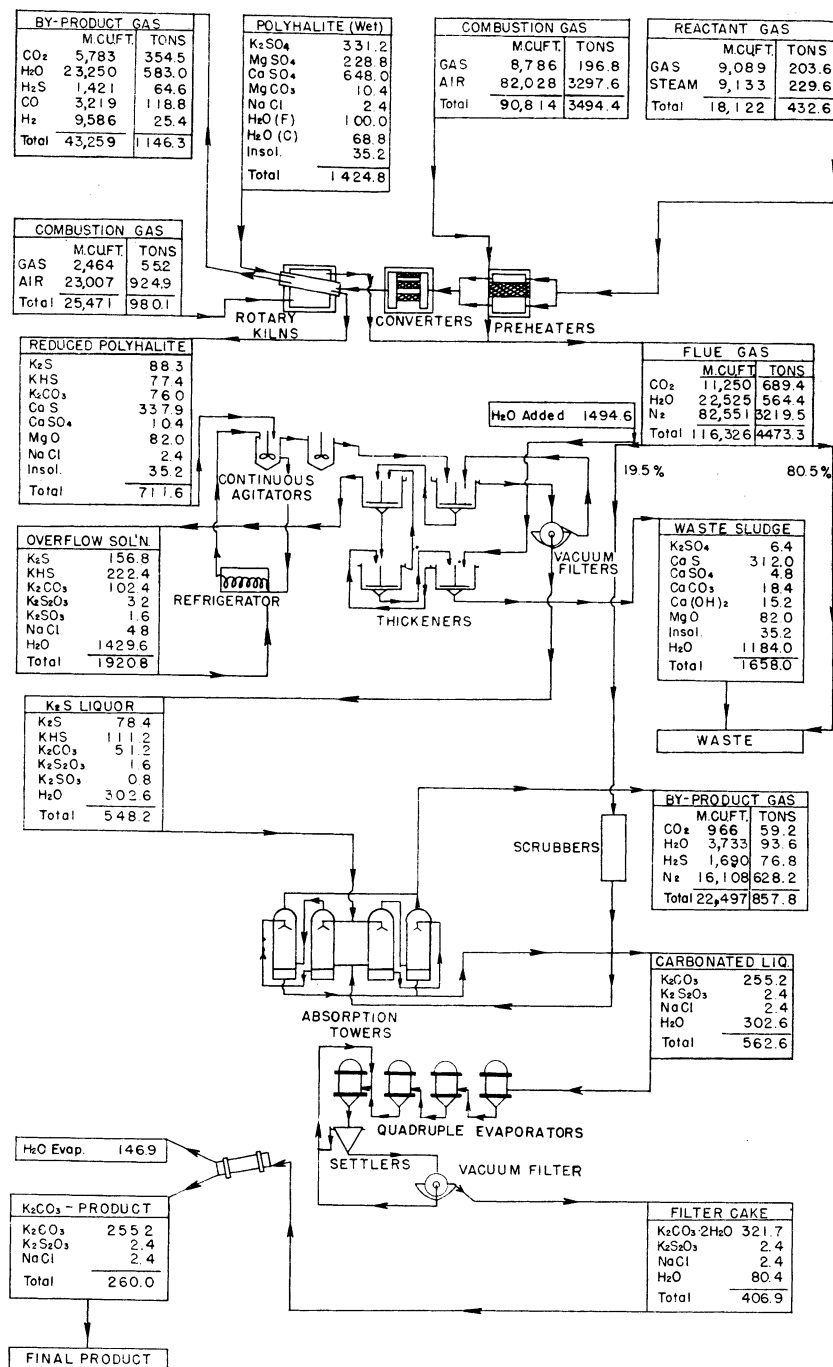


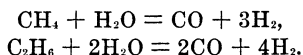
FIGURE 17.—Suggested flow sheet for treatment process 6.

DETAILS OF PROCESS

To facilitate comparisons upon the same basis as in other processes, 1,424.8 tons of washed polyhalite are charged daily to a battery of special rotary kilns heated by indirect means, through which 203.6 tons (9,089,000 cubic feet) of high-methane natural gas and 229 tons of water vapor—after conversion treatment to produce a mixture of carbon monoxide and hydrogen—are passed countercurrently every 24 hours. Reduction is effected by treating the polyhalite at 830° C. (1,526° F.) for not less than 43 minutes with a 50-percent excess of reducing gas present, as indicated in the flow sheet (fig. 17).

The solid products resulting from the rotary-kiln treatment consist of 711.6 tons of mixed sulfides and oxides and contain 88.3 tons of K_2S , 79.4 tons of KHS , and 76.0 tons of K_2CO_3 as extractable potash salts; the gaseous discharge consists of carbon dioxide, water vapor, hydrogen sulfide, and the excess carbon monoxide and hydrogen supplied and should total 1,146.3 tons with a volume of approximately 43 million cubic feet (standard conditions); this waste gas represents a potential source of by-product heat and sulfur.

To produce the reducing-gas mixture ($CO + H_2$, etc.) 9,089,000 cubic feet of natural gas and 229.6 tons of steam are required. The steam-gas mixture is preheated to 900° C. in a recuperative type of furnace. The fuel requirement of this furnace is estimated as 8,897,000 cubic feet of natural gas (900 B.t.u. per cubic foot). The preheated gas is passed through a bed of alumina-supported nickel catalyst to produce a mixture of CO and H_2 by reactions such as:



This "water gas" is then ready for use in the reduction kilns. The burned gas is available for carbonation of K_2S liquors.

The 711.6 tons of reduced solids are extracted in a series of continuous agitators discharging to countercurrent washing, the clarified overflow solution from the second thickener being added to the agitators. The heat of solution of the reduced solids is approximately 74,000,000 B.t.u. daily, and since it is preferable to keep the temperatures to 86° F. or less, refrigeration is applied at this step. To bring about this cooling, 260 tons of refrigeration⁷ are necessary, and this is applied by circulating the charge through heat-exchanger tubes cooled directly by the vaporizing refrigerant.

The 2,697 tons of agitator discharge, consisting of 592 tons of solids and 1,494.6 tons of water containing 610.4 tons of dissolved salts, will flow to No. 1 thickener, from which 548.2 tons of concentrated K_2S solutions overflow every 24 hours; and the settled solids, after being washed successively in the three remaining thickeners, are discharged as a thickened sludge from the final thickener, where all of the 1,494.6 tons of water, used in the entire extraction process, is added.

⁷ 1 ton of refrigeration = 12,000 B.t.u. per hour.

The clarified thickener-overflow solution is pumped directly to coke-filled absorption towers, through which the flue gases are passed countercurrent to the solution flow. Care is essential to prevent saturation with potassium bicarbonate so that only enough carbon dioxide to produce the normal carbonate is used. The theoretical yield of carbonated liquor is 562.6 tons daily, containing 255.2 tons of K_2CO_3 .

The solution of potassium carbonate is then fed to quadruple-effect evaporators with parallel steam and liquor flow where 194.8 tons of water must be evaporated daily. The potassium carbonate separates only in the last two effects and crystallizes as $K_2CO_3 \cdot 2H_2O$. The crystal crop is transferred to settling cones and the thickened sludge discharged to centrifugal filters which produce 368.1 tons of wet crystals. The overflow from the conical settling tanks and the filtrate from the centrifuges are returned to the evaporators, while the wet crystal crop is dehydrated and dried in oil-fired rotary kilns to expel 108.1 tons of free and combined water and produce 260.0 tons of 98-percent K_2CO_3 every 24 hours.

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The equipment and direct operating costs for the treatment plant are summarized in table 26. From these data it will be noted that 49 men are required to operate the plant and that an expenditure of \$1,024,405 is necessary, not including the buildings. The direct operating costs are \$2,171.84 per day, corresponding to \$1.36 per ton of raw polyhalite treated. Including a depreciation charge of 11.4 percent of the investment, distributed upon the basis of a 300-day operating year, the combined costs are \$2,560.91 per day and equivalent to \$1.60 per ton of polyhalite.

TABLE 26.—*Summarized equipment and direct operating costs for process 6 (1,600 tons of raw polyhalite per day)*

Operation	Equip- ment costs	No. of em- ployees	Power	Labor	Steam	Fuel	Water	Re- pairs ¹	Total ¹	Cost per ton ²
Salt washing.....	\$112,535	12	\$19.71	\$65.50			\$10.12	\$12.29	\$107.62	\$0.067
Calcining ³										
Converting natural gas.....	314,000	18	32.40	108.00	\$183.20	\$545.30	109.80		1,722.70	1.076
Reducing washed polyhalite.....	310,000					\$745.00				
Scrubbing flue gas.....	35,000									
Feeding reduced polyhalite.....	1,750	$\frac{3}{8}$.27		2.25			1.00	3.52	.002
Extracting reduced polyhalite.....	2,620	$2\frac{5}{8}$	1.08	15.75			3.72	1.50	22.05	.014
Cooling agitator charge.....	26,000	$\frac{1}{4}$	17.58	1.50			5.28	2.25	26.61	.017
Thickening extracted residue.....	60,000	$\frac{1}{4}$	3.24	1.50			14.20	3.00	21.94	.014
Carbonating extract liquor.....	100,000	6	5.40	32.40				20.00	57.80	.036
Evaporating extract liquor.....	17,500	3	5.40	18.00	48.70		7.00	1.50	80.60	.050
Filtering $K_2CO_3 \cdot 2H_2O$ -crystal crop.....	15,000	3	2.70	18.00				5.00	25.70	.016
Drying $K_2CO_3 \cdot 2H_2O$ -crystal crop.....	30,000	3	4.80	18.00		73.00		6.50	102.30	.064
Totals.....	1,024,405	48 $\frac{1}{2}$	92.58	278.65	234.15	1363.30	40.32	162.84	2,171.84	1.357
Depreciation at 11.4 percent.....									389.07	.243
									2,560.91	1.600

¹ Includes supplies.

² Based upon 1,600 short tons of raw polyhalite.

³ Calcination accomplished during reduction.

⁴ Cost of natural gas at \$0.06 M cu. ft.

⁵ Cost of fuel oil.

TOTAL PRODUCTION AND EQUIPMENT COSTS

Table 27 summarizes the complete equipment and production expenditures per 24-hour day and includes the costs of mining, crushing, treating, direct and general supervision, general office expense, housing for all mine, crushing, and treatment plants, and employees' living quarters. Fixed charges, comprising depreciation of all buildings and equipment, as well as insurance and

TABLE 27.—*Total production and plant costs for process 6*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Treatment.....	49	² \$1,229,286	\$278.65	\$1,893.19	\$2,171.84
Other ³	191	626,776	1,036.88	518.97	1,555.85
Total direct operating.....	240	1,856,062	1,315.53	2,412.16	3,727.69
Direct supervision.....	20		172.00	115.00	287.00
Total direct costs.....	260	1,856,062	1,487.53	2,527.16	4,014.69
Administration and general expense ³	48		343.00	229.00	572.00
Buildings:					
Camp site, etc.....		175,000			
Treatment plant.....		250,000			
Total cost.....		425,000			
Fixed charges:					
Depreciation:					
Buildings.....				70.83	70.83
Treatment.....				466.88	466.88
Other ³				188.31	188.31
Total depreciation.....				726.02	726.02
Taxes and insurance.....				114.05	114.05
Interest on investment.....				456.20	456.20
Total fixed costs.....				1,296.27	1,296.27
Amortization, preliminary development costs.....				95.20	95.20
Total production costs.....	308	2,281,062	1,830.53	4,147.63	5,978.16

¹ See table 13, p. 54, for break-down.

² 120 percent of values for actual estimates in table 26, p. 90.

³ See table 12, p. 53, for break-down.

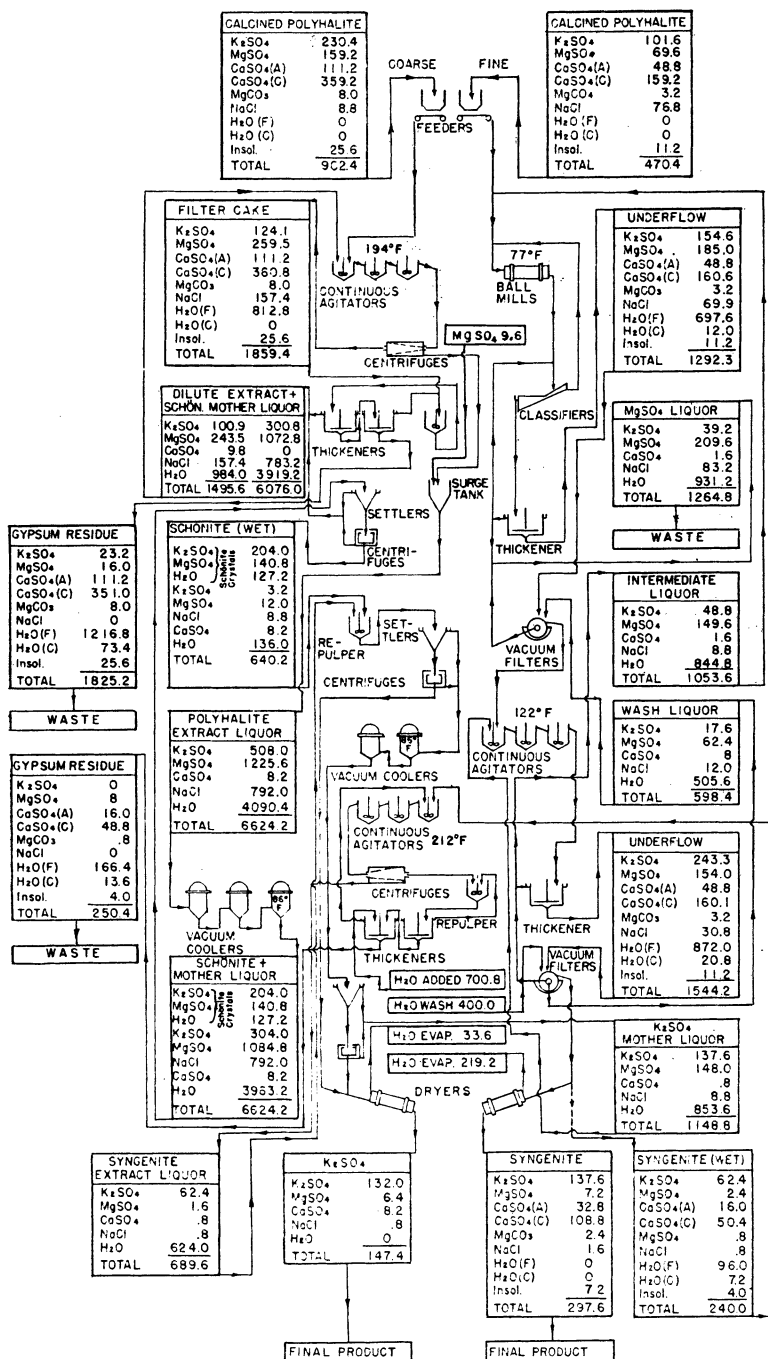
taxes on the whole investment, have been included. Finally, the daily charge of \$95.20 to amortize the preliminary mine development has been added.

The basis for charges other than the direct operating costs has been discussed in connection with process 1 on page 52. However, it should be noted that the treatment-plant investment, which represents a 20-percent extra allowance for minor accessory equipment, would require a \$250,000 allotment for buildings.

Reference to the table will show that the total plant investment, exclusive of the power plant, is \$2,281,062, and the daily production cost is \$5,978.16. This corresponds to a treatment cost of \$3.70 per ton of polyhalite mined or to \$23.42 per ton of K_2CO_3 produced; also to 34.4 cents per-unit of K_2O .

CAPITAL REQUIREMENTS

The amount of capital required to construct and operate this process is estimated at \$3,855,070, and the distribution of the capital has been indicated (with that of all other processes) in table 35 (p. 105).



EXTRACTION OF CALCINED POLYHALITE FOR RECOVERY OF POTASH AS SULFATE BY PROCESSES 7 AND 7A

GENERAL CONSIDERATIONS

Process 7 represents an innovation for the production of schönite from calcined polyhalite without any evaporation of extract liquors. The objective is accomplished by extracting the polyhalite with a hot solution of potassium and magnesium sulfates containing the maximum concentration of sodium chloride that will not cause saturation with this compound when increased by the salt in the calcined feed and when subsequently cooled. Conditions are selected that do approach saturation with schönite, which separates on cooling the clarified extract liquors.

The basic principle of this process has been incorporated in a more general scheme by the addition of certain steps of the other processes discussed, to obtain the more complex process 7A illustrated in figure 18.

The salient features of this latter process may be outlined by the following separate steps:

1. Hot extraction of a portion of the total polyhalite treated by means of a solution of potassium and magnesium sulfate high in sodium chloride to obtain a solution that will yield schönite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) on cooling and a mother liquor that is recycled to extract more calcined material.
2. Hot dissolution ($176^\circ F.$) of the schönite produced in (1) by the solution obtained in (4) to yield a solution approaching saturation with K_2SO_4 , which separates on cooling to make the final product, sulfate of potash.
3. Cold extraction of the remainder of the calcined polyhalite to produce syngenite from the potassium sulfate mother liquors obtained under (2).
4. Hot extraction ($212^\circ F.$) of a portion of the undried syngenite produced under (3) to obtain a solution of potassium sulfate that can be used to extract the schönite produced in (1).

The potential types of final products that can be made by this plan are:

1. Sulfate of potash.
2. Sulfate of potash-magnesia (kali-magnesia).
3. Syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$).
 - (a) Dried.
 - (b) Calcined.

A study of the flow sheet (fig. 18) will disclose that step 1 represents process 7; step 2 is similar to process 2; and steps 3 and 4 are from processes 4, 4B, 5, and 5A. However, the schönite-crystal crop is obtained without evaporation, as is required in process 2, and the potassium sulfate solution is made by extracting syngenite rather than calcined polyhalite directly. This latter modification permits production of the extra syngenite as a final product.

DETAILS OF PROCESS

A detailed outline of all operations involved in this process will not be presented at this point, as the individual unit processes are discussed in appendix A (p. 223) in connection with the selection of equipment. It should be emphasized, however, that successful operation of the process depends largely on production

of the hot solution of schönite and sodium chloride as outlined in step 1.

The satisfactory application of step 1 depends on hot filtration of the concentrated liquors with little drop in temperature and a subsequent countercurrent-decantation washing treatment of the extracted residue at elevated temperatures. A continuous centrifugal filter presumably could be used in the filtration step. Insulated thickeners and heat exchangers to restore temperature losses of the clarified overflow will be necessary.

A further operating difficulty of this process is the unbalancing arising from the loss of a certain amount of MgSO_4 from the solutions being recycled. This occurs when the schönite obtained by crystallization from the hot polyhalite extract carries with it a portion of the retained liquor that cannot be displaced entirely by washing. When the schönite is dissolved and again cooled to crystallize K_2SO_4 , the mother liquors carry the retained MgSO_4 into the syngenite-production step, where it is ultimately discarded as waste. The obvious method of overcoming this difficulty is to add 9.6 tons of MgSO_4 at some point in the circulating liquors. This addition is made just before cooling of the hot extract liquors to deposit the schönite as indicated in figure 18. Waste-plant liquors carrying this quantity of MgSO_4 in excess of the 1 : 1 molar ratio of K_2SO_4 : MgSO_4 presumably would be used for this purpose instead of pure MgSO_4 .

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The equipment and direct operating costs for the treatment plant are summarized in table 28. From these data it will be noted that 81 men are required to operate the plant and that an expenditure of \$929,835 is necessary, not including the buildings. The direct operating costs are \$2,346.90 per day, corresponding to \$1.47 per ton of raw polyhalite treated. Including a depreciation charge of 11.4 percent of the investment distributed upon the basis of a 300-day operating year, the combined costs are \$2,700.23 per day, equivalent to \$1.69 per ton of polyhalite.

TOTAL PRODUCTION AND EQUIPMENT COSTS

Table 29 summarizes the complete equipment and production expenditures per 24-hour day and includes the costs of mining, crushing, treating, direct and general supervision, general office expense, housing for all mine, crushing, and treatment plants, and employees' living quarters. Fixed charges, comprising depreciation of all buildings and equipment, as well as insurance and taxes on the whole investment, have been included. Finally, the daily charge of \$95.20 to amortize the preliminary mine development has been added.

The basis for charges other than the direct operating costs has been discussed in connection with process 1 (p. 52). However, it should be noted that the treatment-plant investment, which represents a 20-percent extra allowance for minor accessory equipment, would require a \$225,000 allotment for buildings.

Reference to the table will show that the total plant investment, exclusive of the power plant, is \$2,142,578, and the daily produc-

TABLE 28.—*Summarized equipment and direct operating costs for process 7A (1,600 tons of raw polyhalite per day)*

Operation	Equipment costs	No. of employees	Power	Labor	Steam	Fuel	Water	Repairs	Total	Cost per ton
Salt washing.....	\$112,535	12	\$19.71	\$65.50	\$10.12	\$12.29	\$107.62	\$0.067
Calcining polyhalite.....	160,000	12	6.00	72.00	\$277.00	65.00	420.00	.265
Feeding calcined polyhalite.....	3,500	¾	.54	4.50	1.00	6.04	.004
Extracting calcined polyhalite (hot).....	4,500	2½	2.16	15.75	\$475.20	2.50	495.61	.310
Filtering gypsum.....	80,000	6	21.60	32.40	13.33	67.33	.042
Washing gypsum.....	67,500	3	2.71	18.00	169.60	16.68	3.50	210.49	.132
Cooling polyhalite extract liquors.....	140,000	6	13.50	36.00	12.00	41.10	11.67	114.27	.071
Filtering schönite.....	19,500	3	3.45	18.00	1.10	4.35	26.90	.017
Dissolving schönite.....	3,000	3	1.08	18.00	76.8025	96.13	.060
Filtering K ₂ SO ₄	7,500	1½	1.35	9.0040	2.00	12.75	.008
Drying K ₂ SO ₄	12,000	1½	6.30	9.00	18.00	2.67	35.97	.022
Cooling schönite extract liquors.....	31,000	1½	3.60	9.00	8.60	9.10	2.60	32.90	.021
Ball-milling syngenite-gypsum.....	11,250	1½	6.48	9.00	3.75	19.23	.012
Classifying syngenite-gypsum.....	4,850
Thickening syngenite-gypsum.....	15,000	1½	.70	9.00	1.17	10.87	.007
Filtering syngenite-gypsum.....	45,000	4	8.70	24.00	4.50	37.20	.023
Agitating syngenite.....	7,200	3	8.70	18.00	52.36	4.00	83.06	.052
Thickening syngenite.....	15,000	¼	.43	1.5075	2.68	.002
Filtering syngenite.....	45,000	4	8.70	24.00	3.53	4.50	40.73	.025
Drying syngenite.....	115,000	9	6.00	46.80	112.00	20.00	184.80	.116
Extracting syngenite (hot).....	4,500	3	2.16	18.00	77.20	6.34	2.50	106.20	.067
Filtering extracted syngenite.....	10,000	1½	1.80	9.00	1.67	12.47	.008
Washing extracted syngenite.....	15,000	1¼	.54	1.50	2.10	.75	4.89	.003
Totals.....	929,835	807½	126.21	467.95	871.76	407.00	90.47	164.75	1,218.14	1.33
Depreciation at 11.4 percent.....	106,001	135.33	.221
Combined totals.....	2,481.47	1.55

¹ Subject to electric power surcharge of \$218.76.TABLE 29.—*Total production and plant costs for process 7A*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Treatment.....	81	² \$1,115,802	\$467.95	\$1,660.19	\$2,128.14
Other ³	191	626,776	1,036.88	518.97	1,555.85
Total direct operating.....	272	1,742,578	1,504.83	2,179.16	3,683.99
Direct supervision.....	20	172.00	115.00	287.00
Total direct costs.....	292	1,676.83	2,294.16	3,970.99
Administration and general expense ³	48	343.00	229.00	572.00
Buildings:					
Camp site, etc.....	175,000
Treatment plant.....	225,000
Total cost.....	400,000
Fixed charges:					
Depreciation:					
Buildings.....	66.67	66.67
Treatment.....	423.99	423.99
Other ³	188.31	188.31
Total depreciation.....	678.97	678.97
Taxes and insurance.....	107.13	107.13
Interest on investment.....	428.75	428.75
Total fixed costs.....	1,214.85	1,214.85
Amortization, preliminary development costs.....	95.20	95.20
Electric power surcharge.....	218.76	218.76
Total production costs.....	340	2,142,578	2,019.83	4,051.97	6,071.80

¹ See table 13, p. 54, for break-down.² 120 percent of values of actual estimates of table 28.³ See table 12, p. 53, for break-down.

tion cost is \$6,071.80. This corresponds to a treatment cost of \$3.79 per ton of polyhalite mined, or to \$22.52 per ton of K₂SO₄ (100-percent basis) produced; also to 41.6 cents per unit of K₂O.

CAPITAL REQUIREMENTS

The amount of capital required to construct and operate this process is \$3,506,580, and the distribution of the capital has been indicated (with that of all the other processes) in table 35 (p. 105).

EXTRACTION AND RECOVERY OF POTASSIUM SULFATE FROM CALCINED POLYHALITE AND SYLVITE BY PROCESS 8

GENERAL CONSIDERATIONS

This process is a departure from previous methods discussed in that only 30 percent of the amount of calcined polyhalite is converted to a mixture of syngenite and gypsum, which is decomposed by ammonium carbonate to liberate the sulfate content of the gypsum for subsequent reaction with potassium chloride to yield potassium sulfate. The potassium sulfate is recovered by adding ammonia to "salt out" the sulfate, which is separated essentially as potassium sulfate but also contains about 10 percent of $(\text{NH}_4)_2\text{SO}_4$. The ammonia remaining in the mother liquors is recovered for reuse by stripping in an ammonia-recovery plant after addition of quicklime. This arrangement eliminates any evaporation other than that required in the ammonia stripping operation.

The smaller consumption of polyhalite means increased mining and calcination costs, if the sylvite is not produced from the same mine. Obviously, the logical procedure is to mine both the polyhalite and sylvinite necessary to supply the amounts of sulfates and refined KCl (sylvite) required by the process, thus assuring low cost of raw material.

DETAILS OF PROCESS

As indicated in the flow sheet (fig. 19), 390.5 tons of washed and calcined polyhalite containing 99.6 tons of K_2SO_4 are treated with 208.5 tons of muriate containing 204.2 tons of KCl to produce 322.5 tons of finished product containing 290.6 tons of K_2SO_4 carrying 30.2 tons of $(\text{NH}_4)_2\text{SO}_4$.

The essential steps of the process are as follows:

1. Cold extraction (77°–86° F.) of the calcined polyhalite to remove the magnesium sulfate and residual sodium chloride as a virtually saturated solution of the former and to recover the potassium and calcium sulfates as a mixture of syngenite and gypsum.
2. Treatment of the syngenite-gypsum mixture with ammonia and carbon dioxide or ammonium carbonate to convert the calcium sulfate in the syngenite and gypsum to calcium carbonate and the sulfate to the ammonium salt.
3. The sulfate converted in (2) is then treated with KCl to yield potassium sulfate and ammonium chloride by double decomposition, which results in crystallization of the K_2SO_4 , when concentrated ammonia is added. Filtration of the mixture serves for recovery of the crystallized salts.
4. Treatment of the concentrated ammonical mother liquor with quicklime to recover the ammonia to be used again to "salt out" a second batch of potassium sulfate.

Economic feasibility of the process depends largely on the efficiency of the recovery of the ammonia used. Unavoidable losses occur in the stripping treatment and in the finished product and are estimated to amount to 5.5 tons and 8.2 tons, respectively;

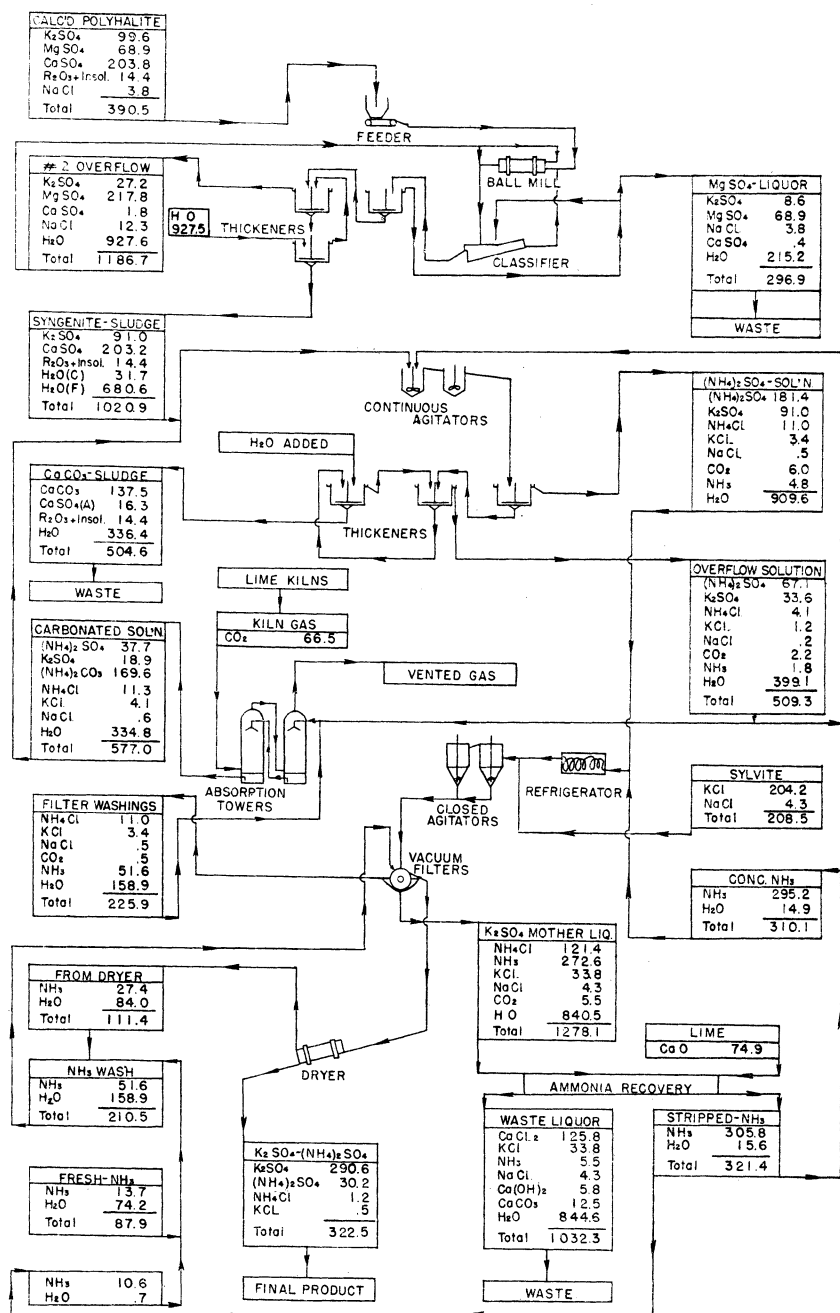


FIGURE 19.—Suggested flow sheet for treatment process 8.

other small unpredictable losses also might occur. These losses necessitate daily addition of 13.7 tons of NH_3 to the process; this is done by employing aqua ammonia for washing the final K_2SO_4 crystal crop, with subsequent use of the washings, supplemented by a portion of the overflow liquors from the No. 2 thickener being employed to wash the carbonated sludge, to produce the ammonium carbonate solutions. This solution is then used to convert the calcium sulfate in the syngenite-gypsum to carbonate.

Actually, the principal loss of ammonia is represented by the 5.5 tons of NH_3 discharged in the ammonia-still waste liquors, since the ammonia present as sulfate and chloride in the K_2SO_4 crystalline product possesses a potential value of approximately 80 percent of its original cost. Due allowance should be made for the quantity of ammonia present in the potash product when marketed as a fertilizer.

REMOVAL OF MAGNESIUM SULFATE

The magnesium sulfate will be removed from the calcined polyhalite and the syngenite produced by wet-grinding in ball mills in closed circuit with classifiers discharging to thickeners. The process operates satisfactorily with a slurry containing as much as 2 parts of water to each part of syngenite, so that the 340.3 tons of syngenite can be discharged with 680.6 tons of water directly from thickeners without the necessity of filtering. This arrangement requires 927.5 tons of water to be added to the final thickener to yield 1,020.9 tons of washed syngenite slurry and provide 1,186.7 tons of overflow solution from No. 2 thickener to extract the 390.5 tons of polyhalite in the ball mills, as indicated in figure 19. The 296.9 tons of magnesium sulfate solution overflow every 24 hours from the No. 1 thickener at approximately 32 parts of MgSO_4 with 4 parts of K_2SO_4 per 100 parts of water and discharge to waste or recovery of magnesia.

SPECIAL CONDITIONS PERTAINING TO PROCESS 8

The estimated equipment and direct operating costs with added depreciation charge have been summarized in table 30 to permit comparison with the other proposed processes. However, the different amount of polyhalite treated and the use of refined sylvite (KCl) make direct comparison more uncertain.

The amount of raw materials required daily is 480 tons of polyhalite and 567.2 tons of sylvinite (60 percent NaCl , 40 percent KCl). This means that 1,047.2 tons of potash salts are mined each day instead of 1,600, as needed in all of the other processes. Obviously a new cost analysis upon this lower tonnage basis is necessary to determine probable production costs, since, in addition to mining costs, the expenditures for grinding and crushing, salt washing of the ground polyhalite, and calcination of the washed polyhalite are increased on the "per-ton" basis.

To obtain an approximation of these various costs, credits for the over-all decreased costs of mining and crushing the polyhalite have been made upon a pro rata basis and would result in a daily deduction of \$1,748.80 and \$85.18, respectively, for these two

operations. In addition, the salt washing and calcination costs have been prorated and penalized by an extra 10 percent.

The \$2,085 daily charge for refined sylvite and the \$1,235 ammonia cost are the two major items of expense and warrant careful scrutiny. Furthermore, the \$10 per ton price assumed for the 98-percent KCl used is possible only if produced from the same mine as the polyhalite. Therefore, the cost of a refining plant to supply the 208.5 tons of KCl must be added to the estimated equipment costs presented in the table.

The probable cost of a treatment plant to handle the 567.2 tons of sylvinites and produce the 208.5 tons of product containing 204.2 tons of KCl is about \$300,000. This means that the \$659,250 representing the equipment costs for processing the polyhalite and refined KCl should be increased to approximately \$960,000 to correspond to full treatment-plant-equipment investment.

It should be noted also that the $(\text{NH}_4)_2\text{SO}_4$, amounting to 30.2 tons daily, which is recovered in the final K_2SO_4 product possesses an extra potential sales value in that the price of $(\text{NH}_4)_2\text{SO}_4$ for fertilizer purposes is approximately \$30 per ton. Assuming an average return of \$20 per ton for the 30.2 tons associated with the K_2SO_4 , \$600 would be realized. This return should be placed as a credit to the production costs, but is considered in the final summarized data (see table 36, p. 105), which give the market values of the daily production of all of the processes.

SUMMARIZED EQUIPMENT AND DIRECT OPERATING COSTS

The equipment and direct operating costs for the treatment plant are summarized in table 30. From these data it will be noted that 57 men are required to operate the plant and that an expenditure of \$659,250 is necessary, not including the buildings. The direct operating costs are \$5,667.43 per day, corresponding to \$5.41 per ton of mined product^{*} treated per day. Including a depreciation charge of 11.4 percent of the investment, distributed upon the basis of a 300-day operating year, the combined costs are \$5,917.93 per day, equivalent to \$5.65 per ton of mined product.

TOTAL PRODUCTION AND EQUIPMENT COSTS

Table 31 summarizes the complete equipment and production expenditures per 24-hour day and includes the costs of mining, crushing, treating, direct and general supervision, general office expense, housing for all mine, crushing, and treatment plants, and employees' living quarters. Fixed charges, comprising depreciation of all buildings and equipment, as well as insurance and taxes on the whole investment, have been included. A daily charge of \$66.64 to amortize the preliminary mine development has been added also.

The basis for charges other than the direct operating costs, has been discussed in connection with process 1, on pages 52 to 55. However, it should be noted that the treatment-plant investment, which represents a 20-percent extra allowance for minor accessory equipment, would require a \$160,000 allotment for buildings.

^{*} Only 480 tons of polyhalite and 567.2 tons of sylvanite treated.

100 POTASH SALTS FROM TEXAS-NEW MEXICO POLYHALITE DEPOSITS

TABLE 30.—*Summarized equipment and direct operating costs, process 8 (480 tons raw polyhalite and 208.5 tons of refined sylvite* per day)*

	Equipment cost	Number of employees	Power	Labor	Fuel	Steam	Water	Repairs (1)	Totals (1)
Salt washing.....	\$37,500	4	\$6.57	\$21.85			\$3.37	\$4.10	\$35.89
Calcining polyhalite.....	53,500	4	2.00	24.00	\$93.00			22.00	141.00
Feeding calcined polyhalite.....	1,750		.27	1.50				1.00	2.77
Ball-milling calcined polyhalite.....	11,250	3	8.10	7.50				3.75	19.35
Classifying syngenite-gypsum.....	4,850		.54	1.50				.42	2.46
Thickening syngenite-gypsum.....	60,000		1.73	7.50			11.13	3.00	23.36
Agitating syngenite-gypsum.....	4,500	2½	1.08	15.75			.75	2.00	19.58
Thickening carbonated syngenite-gypsum.....	25,500	¾	1.08	2.25			4.04	1.28	8.65
Carbonating ammonia liquors.....	92,400	6	4.20	36.00				15.00	55.20
Agitating (NH ₄) ₂ SO ₄ -K ₂ SO ₄ liquors.....	6,000	3	2.16	18.00				2,087.00	2,107.16
Filtering K ₂ SO ₄ -crystal crop.....	19,500	3	3.45	18.00				1,242.50	1,263.95
Drying K ₂ SO ₄ -crystal crop.....	32,500	1½	4.80	9.00	52.00			6.50	72.30
Recovering ammonia.....	250,000	6	2.88	36.00		\$1,440	\$26.88	35.00	1,540.76
Lime plant.....	60,000	4 26	3.00	125.00	202.50			44.50	375.00
Totals.....	659,250	57	38.86	313.85	347.50	1,440	46.17	3,468.05	5,667.43
Depreciation, 11.4 percent.....	75,154.50								250.50
Combined totals.....									5,917.93

¹ Includes supplies.

² Includes \$2,085 for estimated direct production costs of 208.5 tons of sylvite.

³ Includes \$1,235 for daily consumption of ammonia.

⁴ Based on an estimated 33½ percent labor cost at an average of \$0.60 per hour.

* Derived from 567.2 tons of sylvinitite (60 percent NaCl, 40 percent KCl).

TABLE 31.—*Total production and plant costs for process 8*

	Number of employees	Equipment costs	Labor	Other items ¹	Total
Direct operating costs:					
Treatment.....	57	² 791,100	\$ 313.85	\$5,353.58	\$5,667.43
Other ³	64	209,000	345.62	173.00	518.62
Total operating, direct.....	121	1,000,100	659.47	5,526.58	6,186.05
Direct supervision ⁴	14		120.40	80.50	200.90
Total direct costs.....	135	1,000,100	779.87	5,607.08	6,386.95
Administration and general expense ^{3 4}	34		240.10	160.30	400.40
Buildings:					
Camp site, etc.....		125,000			
Treatment plant.....		160,000			
Total costs.....		285,000			
Fixed charges:					
Depreciation:					
Buildings.....				44.17	44.17
Treatment.....				² 300.60	² 300.60
Other ^{2 4}				131.82	131.82
Total depreciation.....				476.59	476.59
Taxes and insurance.....				64.26	64.26
Interest on investment.....				257.02	257.02
Total fixed costs.....				797.87	797.87
Amortization, preliminary mine costs ⁴				66.64	66.64
Total production costs.....	169	1,285,100	1,019.97	6,631.89	7,651.86

¹ See table 13, p. 54, for break-down.

² 120 percent of values of actual estimates in table 30.

³ See table 12, p. 53, for break-down.

⁴ Assumed at 70 percent of other processes.

Reference to the table will show that the total plant investment, exclusive of the power plant, is \$1,285,100 and the daily production cost is \$7,651.86. This corresponds to a treatment cost of \$7.31 per ton of potash salts mined,⁹ or to \$26.33 per ton of K₂SO₄ (100-percent basis) produced; also to 48.9 cents per unit of K₂O.

⁹ See footnote reference 7, p. 89.

CAPITAL REQUIREMENTS

The amount of capital required to construct and operate this process is estimated at \$2,657,150, and the distribution of the capital has been indicated together with all the other processes in table 35, page 105.

POWER-PLANT ESTIMATES

GENERAL CONSIDERATIONS

In checking the electric power and process-steam requirements of the various processes it has been found that daily power consumption ranges from 31,560 kw.-hr. and a peak load of 1,572 kw. for process 8 to 104,140 kw.-hr. and a peak load of 4,710 kw. for process 5A; the steam demand varies from 832,000 pounds per day in process 4 to 4,764,000 pounds per day in process 6. Obviously each process requires a carefully designed power plant to assure maximum efficiency and minimum power and steam costs.

However, in examining the possible types of power- and steam-generating equipment best-suited for the purpose, it was deemed advisable to divide the processes into two groups, one comprising plants that consume large quantities of steam and relatively smaller amounts of electric power and the other comprising those that consume more electric power than steam. The former group represents type I and the latter type II, as listed in table 32. Type I has the advantage over type II of potentially lower power costs because all of the steam, usually supplemented by extra

TABLE 32.—*Estimated costs of power plants*

Process No.	Class ¹	Steam plant			Electric plant			Building cost	Total plant cost	Peak load, kw.
		Number of boilers	Total b.-hp.	Cost	No. and type of turbines ²	Kw. total	Cost			
1	I	4	3,200	\$320,000	3A	4,500	\$160,000	\$60,000	\$540,000	3,000
2	I	4	4,000	400,000	3A	4,500	160,000	70,000	630,000	3,040
3	I	6	6,000	600,000	3A	4,500	160,000	70,000	830,000	3,840
4	II	3	2,250	225,000	3 (A,B,C)	4,500	160,000	60,000	445,000	2,680
4B	II	3	3,000	300,000	3 (A,B,C)	4,500	160,000	70,000	530,000	3,011
5	I	4	4,000	400,000	3A	4,500	160,000	70,000	630,000	3,562
5A	II	4	4,000	400,000	3 (A,B,C)	7,500	260,000	75,000	735,000	4,710
6	I	6	6,000	600,000	3A	4,500	160,000	70,000	830,000	2,803
7A	II	4	4,000	400,000	3 (A,B,C)	4,500	160,000	60,000	620,000	3,364
8	I	4	4,800	480,000	3A	2,400	84,000	60,000	624,000	1,572

¹ I refers to steam demand in excess of power demand; II refers to power demand in excess of steam demand.

² A is noncondensing turbogenerator; B is bleeder condensing; C is condensing.

steam from the boiler plant, can be utilized in turbines to generate electric power, then conducted to the chemical plant for heating purposes. Thus the electric power assumes the byproduct role of the steam-generating plant. When the steam necessary to generate the required electric power exceeds the thermal consumption in the treatment plants, the electric power plant must bear the full burden of steam-generating costs.

ELECTRIC PLANT

Type of equipment.—To obtain exhaust steam from the prime movers, it was decided to select turbogenerators arranged to

operate on 200-pound (gage) steam with 100° F. superheat exhausting at 30 pounds. In those processes of type I, the steam is delivered directly to the chemical-plant supply mains, but a modification is necessary for type II plants.

To obtain flexibility, three turbogenerators of suitable size have been specified so that two can carry the load, even at peak demand, and the third unit be for standby emergency service. Where an excess of steam (type I) is required, the turbines should all be of like size and design, but for excess power (type II) one turbine operates noncondensing (30-pound gage exhaust); one operates as a bleeder turbine (30-pound steam); and the third is of the condensing type. In the latter arrangement the noncondensing and bleeder turbines must each have the necessary exhaust-steam capacity to operate the chemical plant.

Basis of estimates.—Steam consumption by the turbines is estimated as follows:

Noncondensing—30-pound exhaust:

45 pounds of 200-pound (100° F. S.H.) steam per kilowatt-hour.

Condensing (vacuum)—no exhaust steam:

15 pounds of 200-pound (100° F. S.H.) steam per kilowatt-hour.

Operation of the mine and grinding plant for 16 hours and the chemical plant for 24 hours results in a heavy demand for power from 8 a.m. to midnight, and two of the turbines can carry this load safely. Estimates of the number and type and of the combined kilowatt capacity are given in columns 6 and 7 of table 32. Column 8 indicates the electric-plant equipment costs, and column 9 includes housing costs for both the boiler and electric plants.

BOILER PLANT

Type of equipment.—A modern steam-generating plant burning oil fuel and designed to operate at 200 to 250 pounds (gage) pressure and deliver the steam with 100° F. superheat should be installed. The number of boiler units specified ranges from two to five, each installation having an additional spare boiler for standby service.

Basis of estimates.—The boiler capacities are based upon 30 pounds evaporation per hour per horsepower and with operation at 180 percent of rated boiler-horsepower equivalent to the maximum power-plant steam demands at peak load. Ten pounds of steam per pound of fuel oil burned is used in fuel-cost estimates.

The numbers of boiler units are given in column 3 of table 32, and the total installed boiler-horsepower and estimated full plant-equipment costs are tabulated in columns 4 and 5 respectively. Housing is included with the electric plant and is given in column 9.

An excess of 20 percent of both power and steam above the estimated process consumption has been used in the electric-plant and boiler-plant capacity to provide for operation of minor equipment in the mine and treatment plant and to supply light and heating for the offices and warehouses. Miscellaneous auxiliary and accessory equipment in the boiler plant and in the electric plant also consume extra steam.

OPERATING COSTS

The operating costs for the power plant, inclusive of the steam- and power-generator units, comprise: Expenditures for supervisory and operating labor, the cost of fuel oil, the cost of miscellaneous supplies, and a general charge for administration and fixed charges, such as depreciation, taxes, and insurance.

Salary expenditures.—The salaries paid for directing and operating personnel have been based upon the following staff:

1 chief engineer, at \$5,000 per year.....	\$ 5,000
1 assistant engineer, at \$3,600 per year.....	3,600
3 stationary engineers, at \$2,400 per year.....	7,200
4 firemen, at \$2,000 per year.....	8,000
4 laborers, at \$1,500 per year.....	6,000

Total salary account.....	\$29,800
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This charge for salaries was placed against the power plant for process 1; and an additional allowance was made for the extra firemen, laborers, and in special instances, an extra stationary engineer, if it appeared to be warranted by the size of plant suggested for the other power plants.

Supplies.—This cost has been assumed to be $1\frac{1}{2}$ percent of the total plant-investment cost in all instances.

General expense.—Administrative costs and supplies, with depreciation, taxes, and insurance, are included in the plant-burden costs and are estimated at 20 percent of the investment.

The data in table 33 have been prepared upon this basis, and the operating expenses (annual), exclusive of fuel costs, are recorded in column 6 and on a "per day" basis in column 7.

Fuel.—The fuel-oil consumption of the boiler plants has been calculated by assuming steam and power to be 20 percent greater than the estimated consumption in the complete plants as recorded in the tables giving the direct operating costs for the respective processes. Forty-five pounds was then allowed per kilowatt-hour generated in the noncondensing turbines and 15 pounds of steam per kilowatt-hour generated in the condensing turbines (see p. 102). One gallon of 19,000-B.t.u. fuel oil was then allowed for every 10 pounds of steam generated. Column 8 in table 33 gives the fuel-oil costs, calculated according to this plan.

Excess steam costs in the type I power plants were then determined by crediting the total process steam consumed in the plant (not inclusive of the 20-percent excess allowance) at 40 cents per 1,000 pounds and the electric power at 3 mills per kilowatt-hour. The cost per 1,000 pounds for the excess steam was then found by dividing by the amount of steam available to give the data recorded in the last column.

Power costs in the plants (type II) utilizing a noncondensing turbine were determined by crediting all of the steam generated (120 percent of process requirements) at 40 cents per 1,000 pounds and charging the balance of the costs against all of the power generated (120 percent of whole plant estimates). This method resulted in indicated costs of 8.0, 8.1, 6.7, and 8.2 mills per kilowatt-hour in processes 4, 4B, 5A, and 7A, respectively, as

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given in column 11 of table 33. The difference between these respective amounts and the 3-mill preliminary power cost were then added as surcharges where necessary.

TABLE 33.—*Production costs for power and steam*

Process No.	Annual costs				
	Class	Labor	Supplies	Burden	Total
(1)	(2)	(3)	(4)	(5)	(6)
1.....	I	\$29,800	\$8,100	\$108,000	\$145,900
2.....	I	29,800	9,500	126,000	165,300
3.....	I	40,000	12,000	164,000	216,000
4.....	II	29,800	7,000	89,000	125,800
4B.....	II	29,800	8,000	106,000	143,800
5.....	I	33,300	9,500	126,000	168,800
5A.....	II	33,300	11,000	147,000	191,300
6.....	I	40,000	12,000	166,000	218,000
7A.....	II	29,800	9,300	124,000	163,100
8.....	I	29,800	8,000	124,800	162,600

Process No.	Daily costs						
	Other ¹	Fuel	Total	Electric power total, kw.-hr.	Production ² cost, kw.-hr., mills	Steam	
(1)	(7)	(8)	(9)	(10)	(11)	Surplus ³ 1,000 lb. (12)	Cost, 1,000 lb. (13)
1.....	\$486.33	\$968.00	\$1,454.33	61,132	3.0	516	\$0.46
2.....	551.00	1,246.00	1,797.00	64,020	3.0	664	.42
3.....	720.00	2,030.00	2,750.00	83,748	3.0	1,082	.31
4.....	419.33	525.00	944.33	55,488	8.0	208	.40
4B.....	479.33	834.00	1,313.33	63,348	8.1	334	.40
5.....	562.67	1,106.00	1,668.67	76,584	3.0	590	.39
5A.....	637.67	1,460.00	2,097.67	104,140	6.7	584	.40
6.....	726.67	2,248.00	2,974.67	58,370	3.0	1,191	.35
7A.....	543.67	1,091.00	1,634.67	71,820	8.2	436	.40
8.....	542.00	1,406.00	1,948.00	31,560	3.0	900	.40

¹ Obtained by dividing figures in previous column by 300.
² 120 percent of estimated mining- and treating-plant consumption.
³ Process steam is 4 times these quantities.

SUMMARY OF UTILITIES CONSUMED IN THE VARIOUS PROCESSES

To correlate the data on the utility requirements of the various processes, the amounts of the power, steam, fuel, and water consumed and the cooling water circulated have been recorded in

TABLE 34.—*Utilities consumed in the different processes*

Process number	Power		Steam		Fuel oil		Water, M gallons	
	Kw.-hr.	Cost	M pounds	Cost	Barrels	Cost	Cooling	Consumed
1.....	50,943	\$152.83	2,581	\$1,032.44	1,381	\$1,381.00	5,048	1,596
2.....	53,350	160.05	3,323	1,329.24	1,560	1,560.00	8,208	1,998
3.....	69,790	211.37	5,411	2,164.40	2,352	2,352.00	9,325	2,659
4.....	46,240	309.81	1,041	416.40	1,034	1,034.00	1,102
4B.....	52,790	427.60	1,670	668.00	1,075	1,075.00	2,306	1,213
5.....	63,820	191.46	2,948	1,179.20	1,914	1,914.00	4,950	1,854
5A.....	86,780	580.43	2,920	1,168.00	2,235	2,235.00	3,542	938
6.....	48,640	145.92	5,953	2,381.20	1,297	2,976.00	614	635
7A.....	59,850	490.77	2,180	872.00	1,498	1,498.00	2,510	947
8.....	26,300	78.90	3,600	1,440.00	1,735	1,735.00	1,344	480

¹ Also requires 9,090 thousand cubic feet of natural gas at a cost of \$545.40.

table 34. Incidentally, an indicated daily consumption of 9,090,000 cubic feet of natural gas also is listed under process 6.

SUMMARY OF CAPITAL COSTS FOR ALL PROCESSES

Table 35 summarizes the total capital costs for the mining, crushing, treatment, and power plants and for housing employees. The treatment-plant estimates include buildings for the chemical plant and for the development of the camp site and construction of living quarters for the employees. The figures in column 4 comprise the estimated costs for current mining equipment, preliminary mine development, and the crushing plant.

TABLE 35.—*Summary of total capital costs for all processes*

Process No.	Power plant ¹	Treatment plant ²	Mine and crushing plant ³	Total
1.....	\$540,000	\$1,316,340	\$1,545,780	\$3,402,120
2.....	630,000	1,444,030	1,545,780	3,619,810
3.....	830,000	1,591,670	1,545,780	3,967,450
4.....	445,000	1,094,100	1,545,780	3,084,880
4B.....	530,000	1,203,850	1,545,780	3,279,630
5.....	630,000	1,780,480	1,545,780	3,956,260
5A.....	735,000	2,551,260	1,545,780	4,832,040
6.....	830,000	1,479,290	1,545,780	3,855,070
7A.....	620,000	1,340,800	1,545,780	3,506,580
8.....	624,000	951,100	1,082,050	*2,756,150

¹ Steam and electric plants.

² Includes buildings.

³ Comprising \$1,387,780 for mine inclusive of preliminary development and \$158,000 for crushing plant.

⁴ Does not include \$300,000 estimate for sylvite production plant.

DAILY PRODUCTION AND VALUES OF PRODUCTS MADE
BY THE VARIOUS PROCESSES

All of the production costs have been calculated upon the basis of operation of the mine and crushing plants for two shifts per day (16 hours) and of continuous operation of the treatment plant for an average of 300 days per year (24 hours per day). The amounts of potash products produced per day therefore have been used in estimating the market values of the finished products and the potential profits and losses.

In table 36 the amounts and types and estimated market values of the products from each of the 10 processes are presented.

TABLE 36.—*Daily amounts and market values ¹ of products of the different processes*

Process number	K ₂ SO ₄		Sulfate of potash-magnesia		Calcined syngenite		Total potash, tons		Total gross market value
	Tons	Value	Tons	Value	Tons	Value	K ₂ SO ₄	K ₂ O	
1.....	131.2	\$4,382.21	323.2	\$8,749.94	284.0	153.5	\$13,132.15
2.....	263.4	9,278.20	245.6	132.8	9,278.20
3.....	339.2	11,937.75	316.0	170.8	11,937.75
4.....	522.9	\$9,217.59	244.0	131.9	9,217.59
4B.....	94.0	3,207.33	396.8	7,222.96	276.1	149.3	10,430.29
5.....	316.0	10,668.42	282.4	152.7	10,668.42
5A.....	288.8	10,849.76	287.2	155.8	10,849.76
6.....	² 260.0	33,800.00	² 255.2	173.9	*23,800.00
7A.....	147.4	4,986.66	297.6	5,198.12	269.6	145.7	10,184.78
8.....	322.5	11,582.20	290.6	157.1	11,582.20

¹ K₂SO₄ = \$34.00 ton, 90 percent K₂SO₄; K₂SO₄ + MgSO₄ = \$25.00 ton, 48 percent K₂SO₄; syngenite—basis of K₂SO₄ contained.

² K₂CO₃.

Potassium sulfate, sulfate of potash-magnesia, calcined syngenite, potassium carbonate, and mixed potassium-ammonium sulfate are

included. The market values have been calculated according to the current quotations for potash salts, which are as follows:

Compound:	Basis, percent K_2SO_4	Price per short ton
Sulfate of potash.....	90	\$34.00
Sulfate of potash-magnesia.....	48	25.00
Calcined syngenite	48	¹ 18.13

¹ Price = $\frac{48}{90}$ of 34 or \$18.13.

Compound:	Basis	Price per short ton
Ammonium-potassium sulfate	90 percent K_2SO_4	¹ \$ 34.00
Potassium carbonate	\$0.65 per lb.	130.00

¹ With premium of \$20 per net ton of $(NH_4)_2SO_4$ contained.

Upon this basis it will be noted that the value of the daily production of sulfate compounds ranges from approximately \$9,200 to \$13,000 (\$11,036), depending on the method of calculation. Process 1 apparently gives a greater market value than any process but 6. However, both of these figures warrant special attention.

In process 1, the full market price of the sulfate of potash-magnesia has been employed in determining the total value of the products, but it is questionable whether all of this material could be sold for fertilizer uses at the present prices; the 323.2 tons of this compound manufactured daily represent about 6.5 times the average daily consumption for fertilizer uses, in the United States, in that sulfate of potash-magnesia containing only 21.6 tons of K_2SO_4 was consumed during 1939. This indicates that the balance of the potash produced as the 48-percent sulfate of potash-magnesia must be sold at a lower price per unit, presumably even as low as that for the 90-percent K_2SO_4 product. However, the consumption of the double sulfate might be expanded under the stimulus of a lower market price, especially since there is a definite demand for calcined kieserite ($MgSO_4 \cdot H_2O$) to supply the additional magnesium-sulfate requirements in fertilizers. In 1939 the calcined magnesium sulfate imported by the United States amounted to 2,472 tons.¹⁰

Based upon the potential sale of the amount equal to normal consumption, the market value of the daily production of potash salts would be \$11,036 instead of the \$13,132.15 given in the table.

The \$33,800 market value assigned to the 260 tons of K_2CO_3 produced daily in process 6 likewise is misleading because the domestic consumption for 1938 was only about 6,000 tons, or less than 8 percent of the hypothetical amount manufactured by this process. If half of the market could be supplied, the remaining 96-percent excess of this compound must be disposed of for other purposes. These uses doubtless would include the manufacture of other potassium chemicals for which a good return would be realized. However, the bulk must be sold to the fertilizer market.

Potassium carbonate is unsuitable for use as a potash fertilizer, especially in appreciable concentrations, owing to its causticity, so that it probably would require conversion to nitrate, chloride, phosphate, or sulfate before finding ready sale. There are many possibilities, but for purposes of comparison it is assumed that the

¹⁰ Minerals Yearbook, 1940, p. 1440.

carbonate would be converted to sulfate. The 3,000 tons of carbonate per year (10 tons per day) at \$130 per ton would return \$1,300, and the remaining 250 tons of crude K_2CO_3 would be equivalent to approximately 308.7 tons of 100 percent K_2SO_4 , worth \$11,660, or a total of \$12,960. Obviously, the conversion costs for making K_2SO_4 from the K_2CO_3 must be deducted.

SUMMARIZED PRODUCTION AND MARKETING COSTS

Consideration of the costs of transporting the potash to consuming centers (more specifically, to fertilizer-mixing plants) and the selling costs must be added to the estimated production costs to determine the potential profits or losses from the proposed

TABLE 37.—*Estimated daily gross profits from sale of products from various processes*

Process number	1	2	3	4	4B
Costs:					
1. Production.....	\$5,871.44	\$6,211.25	\$7,980.28	\$5,155.44	\$5,703.16
2. Freight allowance ¹	3,180.80	1,843.80	2,374.40	3,660.30	3,435.60
3. Total.....	9,052.24	8,055.05	10,354.68	8,815.74	9,138.76
4. Unit of K_2O60	.68	.59	.67	.61
Credits:					
5. Products ex-vessel at seaports.....	11,036.00	9,278.20	11,937.75	9,217.59	10,430.29
6. Units of K_2O	15,350.00	13,280.00	17,080.00	13,190.00	14,930.00
7. Unit value ²	\$.72	.70	.70	.70	.70
Gross profits ⁴	1,983.76	1,223.15	1,583.07	401.85	1,291.53

Process number	5	5A	6	7A	8
Costs:					
1. Production.....	\$6,940.53	\$8,028.10	\$5,978.16	\$6,071.80	\$7,651.86
2. Freight allowance ¹	2,212.00	2,021.60	1,820.00	3,115.00	2,257.50
3. Total.....	9,152.53	10,049.70	7,798.16	9,186.80	9,909.36
4. Unit of K_2O60	.65	.45	.63	.63
Credits:					
5. Products ex-vessel at seaports.....	10,668.42	10,849.76	12,960.00	10,184.78	11,582.20
6. Units of K_2O	15,270.00	15,530.00	17,390.00	14,570.00	15,710.00
7. Unit value ²70	.70	.75	.70	.74
Gross profits ⁴	1,515.89	800.06	⁵ 5,161.84	997.98	1,672.84

¹ \$7.00 charge per short ton for transportation to base points; this is approximately the same as 11.2 cents per unit for muriate (60 percent K_2O).

² Based upon \$34.00 per ton of 90 percent K_2SO_4 .

³ Higher values result from presence of magnesia, nitrogen, or carbonate.

⁴ Subject to sales expense and trade discounts.

⁵ This indicated profit would be reduced to \$2,074.84 if charges of \$10.00 per ton of K_2SO_4 were made for conversion.

potash-manufacturing ventures. Such costs are summarized in table 37.

Item 1 in the table represents the total production costs and item 5 the market values as given in table 36, but corrected for processes 1 and 6. Item 2 corresponds to the freight costs, allowing \$7.00 per ton to cover transportation charges in accordance with current sales practice with respect to the muriate produced in the New Mexico region.¹¹

The selling costs of potassium compounds are difficult to estimate because a variable expenditure for advertising would involve a corresponding change in sales expense; however, it is reasonably

¹¹ Thorp, Willard L., and Tupper, Ernest A., The Potash Industry (a report submitted to the U. S. Department of Justice by the U. S. Department of Commerce), May 1940.

certain that the full selling costs would fall in the range from 4 to 8 percent of the selling price.

The net daily spread or margin represents gross potential profits before deduction of selling costs and trade discounts. Process 6 shows the largest profit and process 4 the smallest. Also, in connection with all processes, it should be remembered that a 6-percent interest charge has already been placed against the full plant investment.

In process 6 the cost of converting 96 percent of the K_2CO_3 to K_2SO_4 should be deducted, and if this cost is assumed to be \$10.00 per ton of K_2SO_4 produced the daily margin would still be \$2,074.84. Actually, the conversion cost should be less than this.

In analyzing the different proposed processes, the indicated larger returns for process 1 attracts attention to an important point. The larger potential profit from this process is due to the high unit cost for the potash associated with the magnesium sulfate in the "kali-magnesia". Obviously, advantage should be taken of this condition wherever possible. It is feasible to modify virtually every one of the proposed processes to produce enough sulfate of potash-magnesia to supply the normal demands for the material. Process 7A, especially, is adapted to such a modified plan.

PART II. PERTINENT FACTORS CONTROLLING EXTRACTION AND RECOVERY OF POTASSIUM AND MAGNESIUM SULFATE FROM POLYHALITE

During the laboratory and pilot-plant investigations detailed studies were made of the major factors controlling the extraction and recovery operations. Although extremely important as bases for recommended treatment procedures, such details burden a reader who is interested in evaluating only the over-all results and proposed flow sheets. However, presentation of the supporting data and an interpretation of the results are warranted for the special benefit of the more technically minded reader. Such detailed supporting data, therefore, are presented in this part of the bulletin.

For a graphic picture of possible procedures for treating polyhalite the five methods presented in figure 20 should be noted.

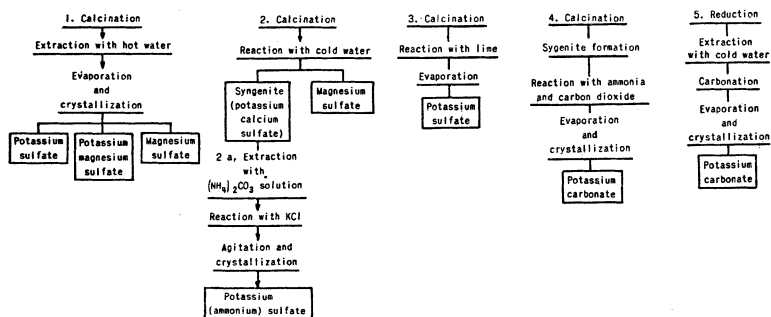


FIGURE 20.—Outline of possible methods for treating polyhalite.

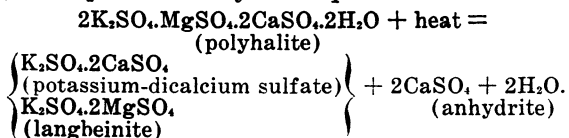
EFFECT OF CALCINATION OF POLYHALITE

From a practical standpoint, the changes produced by calcination may best be evaluated by the behavior of the calcined product during subsequent treatment with water. Some fundamental knowledge of what happens to polyhalite during heating—supplied by studies of the optical properties, the X-ray diffraction patterns, and density—has, however, proved helpful in understanding the phenomena of extraction.

When polyhalite was examined under the polarizing microscope after heating to successively higher temperatures (36) no change was observed in samples held at 110° and 215° C., but in the range from 270° to 500° C. increasing quantities of a new, granular, nearly amorphous phase were observed, the indexes of which varied somewhat, the lowest index passing through a minimum in the range between 325° and 375° C. In the sample heated at 550° C., another new phase appeared in the form of crystal plates with refractive indexes close to those of langbeinite. This phase—which was thought to be a solid solution of potassium-dicalcium

sulfate, langbeinite, and anhydrite—comprised most of the sample heated at 575° C. and was also present after complete fusion at about 950° C.

Alteration of the original polyhalite into a granular polycrystalline mass in the range from 270° to 500° C. might be attributed to simple dehydration. That a more complex change occurs has been shown by the X-ray studies of Ramsdell (25). He found that removal of the water of hydration from polyhalite resulted in a complete break-down of the structure to form anhydrite and an equimolar-solid solution of potassium-dicalcium sulfate in langbeinite, as represented by the equation:



Each particle of the porous calcined polyhalite is apparently an

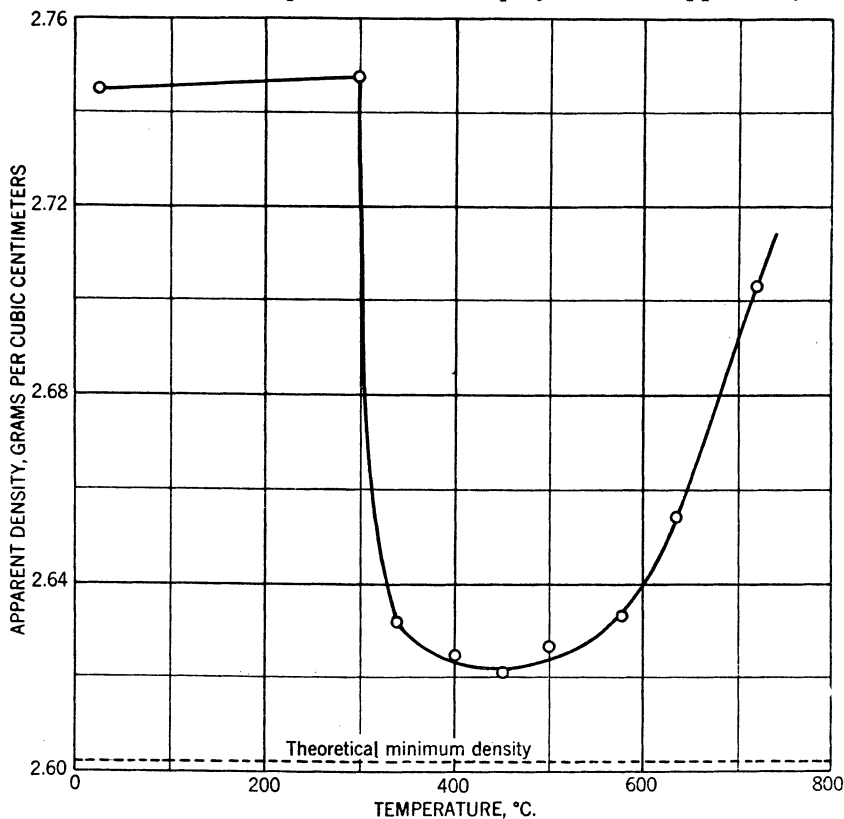


FIGURE 21.—Effect of temperature of calcination on apparent density of polyhalite.

intimate mixture of submicroscopic crystallites of the two decomposition products.

Although microscopic examination indicated that some change was taking place in the polyhalite when heated at 270° C., the

thermal studies of Storch and Clarke (36) showed that rapid dehydration did not take place until about 300° C. A second slight thermal effect observed at 550° C. may have been due to a rapid increase in the rate of growth of crystals of the solid solution.

The heat of decomposition was determined by Storch and Clarke (36) upon the basis of direct measurements over the range from 250° to 400° C. to be $66,000 \pm 5,000$ calories per mole (197.0 ± 14.7 B.t.u. per pound).

The change in apparent density produced by calcining polyhalite for a given period at different temperatures supports the view that a significant change takes place in the solid in addition to the loss of water. For example, with heating periods of 1 hour, Conley, Fraas, and Davidson¹² obtained the results shown in figure 21. Temperatures up to 300° C. caused no appreciable dehydra-

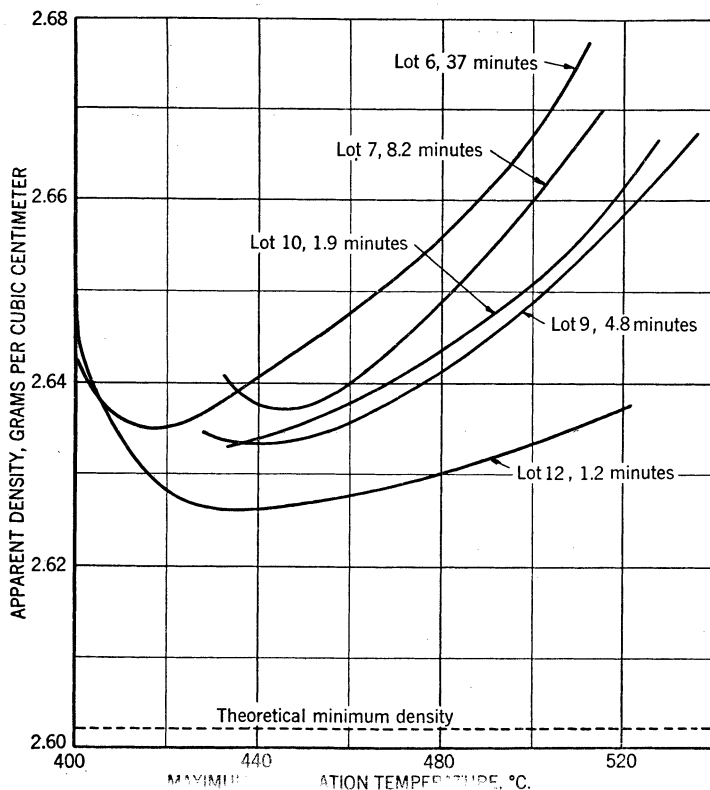


FIGURE 22.—Effect of time and temperature of calcination on apparent density of polyhalite.

tion, but the density of the sample heated at 340° C. dropped well toward the hypothetical minimum value calculated on the assumptions of complete dehydration without change in volume of particle and nonpenetration of the dehydrated particles by the kerosine used as the reference liquid. Further increase in the temperature

¹² See reference 7 in list of Bureau of Mines publications (p. 248).

of calcination resulted first in a slight further decrease in density and then in a progressive increase.

The density of the calcine is a function of the time of heating as well as of the temperature. The curves of figure 22 show this clearly by their displacement upward and to the left with increase in the time of calcination.

RELATION BETWEEN CALCINATION CONDITIONS AND EXTRACTION BEHAVIOR

Although the conditions under which polyhalite has been calcined determine, to a great extent, the behavior during treatment with water, other factors also affect this operation profoundly. Among these are particle size, concentration of sodium chloride in the system, and temperature. Although it is necessary to consider all of these variables in relation to each other, a logical division may be made upon the basis of the temperature employed, since the end products obtained at temperatures approaching the boiling point differ greatly from those obtained by the use of cold water. In the first case, which is much the more complex of the two, decomposition of the calcine by hot water produces a liquor containing moderately high concentrations of potassium sulfate and magnesium sulfate and a solid residue of calcium sulfate, but this mixture is unstable and tends to re-form polyhalite. In the second case, which is fundamentally more simple, decomposition of the calcine by cold water moves toward a condition of stable equilibrium between solid phases of syngenite and gypsum and a liquor containing all of the magnesium sulfate, but only a small part of the potassium sulfate originally present in the calcine.

TREATMENT OF CALCINED POLYHALITE WITH WATER AT ELEVATED TEMPERATURES

Properly calcined polyhalite dispersed in hot water yields liquors containing from 15 to 18 parts of dissolved salts per 100 parts of water, predominantly potassium and magnesium sulfates, with a small amount of calcium sulfate and any sodium chloride present in the polyhalite as an impurity. The practical objective is to attain the highest possible concentration of potassium and magnesium sulfates in the liquor without leaving an appreciable quantity of these substances in the solid residue. When the composition of the liquor is followed by analysis, it is found that this objective is not easy to attain, for the concentration, after rising for a period of time, reaches a maximum and then starts to decrease.

This behavior is more readily understandable when viewed against the background of the system K_2SO_4 - $MgSO_4$ - $CaSO_4$ - H_2O , as worked out by Conley, Gabriel, and Partridge (7).

As a substitute for a space model, figure 23 shows the curves representing the various equilibria projected upon the K_2SO_4 - $MgSO_4$ and K_2SO_4 - $CaSO_4$ faces. The dashed lines show how the composition of the liquor would change if the respective simple salts represented by calcined polyhalite were to go into solution

in the ratios in which they are present in the calcine. The dotted lines represent the actual changes in solution composition observed during an experiment in which polyhalite calcined at a maximum of 475°C . for 37 minutes (27.2 minutes above 300°C .) was agitated in contact with water at the atmospheric boiling point.

Correlation of the solution data with examination of the solid phases under the polarizing microscope at intervals during the

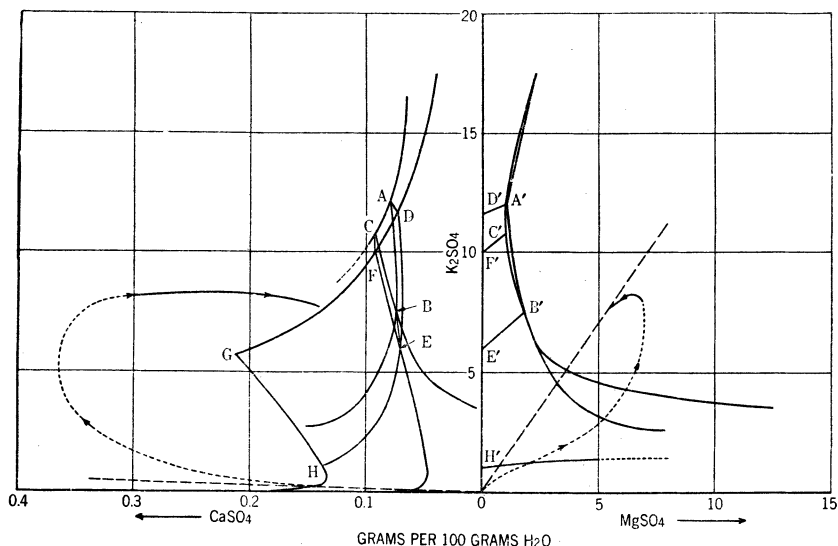


FIGURE 23.—Equilibrium diagram for system $\text{K}_2\text{SO}_4\text{--MgSO}_4\text{--CaSO}_4\text{--H}_2\text{O}$ at 100°C .

extraction shows that almost instantaneously when the calcine is brought in contact with the hot water, the concentration of calcium sulfate exceeds saturation with respect to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which begins to crystallize from solution while the concentrations of potassium sulfate and magnesium sulfate increase. The next solid phase to appear is syngenite ($\text{K}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot \text{H}_2\text{O}$), which continues to form while the gypsum disappears. Finally, polyhalite ($\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot \text{H}_2\text{O}$) begins to crystallize, and the syngenite slowly redissolves as this ultimate stable phase grows. The maximum concentration of potassium sulfate in the liquor occurs when the loss by re-formation of polyhalite just balances the gain from decomposition of the calcine and of the unstable syngenite.

Examination under the polarizing microscope shows that, as dissolution of the calcine proceeds, the particles which were originally opaque, because of their minutely polycrystalline nature, become progressively more transparent, while their optical properties approach those of anhydrite. Since only relatively small amounts of syngenite and re-formed polyhalite are present when the liquor has reached its maximum concentration, most of the calcium sulfate carried into solution as the calcined polyhalite dissolved must have recrystallized on the anhydrite skeleton of the particles of calcine.

Owing to formation of syngenite, which technically ties up an appreciable fraction of the potassium sulfate, concentration of magnesium sulfate in the liquor arrives at its maximum value first, then decreases only slightly as a result of incipient reformation of polyhalite while the concentration of potassium sulfate is increasing to its maximum as a result of the decomposition of syngenite. Finally, the concentrations of both salts decrease in equimolar ratio as the last of the syngenite disappears and the crystallization of polyhalite becomes the dominant reaction. These progressive changes may be followed in the dotted curves of figure 23.

During the early work on polyhalite it was realized that particle size, calcination conditions, and temperature of extraction probably would affect the results. What was not anticipated was the very significant improvement produced by the presence of sodium chloride during extraction, the adverse effect of absorption of moisture by calcined polyhalite in the interval between calcination and extraction, and the necessity for agitation adequate to disperse the calcine thoroughly as it came into contact with the extracting water.

In retrospect, it is possible to interpret some of the puzzling discrepancies in the exploratory work and therefore some of the conclusions originally drawn concerning the effect of calcination conditions and particle size must be modified. In general, however, the picture outlined in the early publications¹³ has been amplified and clarified rather than changed by the subsequent investigations. The importance of having sodium chloride present in the extracting solution was demonstrated by Conley and Fraas,¹⁴ and the interrelation of the various factors that affect extraction has since been discussed in some detail by Davidson, Berk, Conley, and Partridge.¹⁵ Much of the succeeding discussion is based upon the more recent studies.

Keeping in mind this general view of the somewhat complex changes taking place during the treatment of calcined polyhalite with hot water, the specific factors that influence the degree of extraction and the maximum concentration of the liquor may be considered in greater detail.

TEMPERATURE OF EXTRACTION

Studies by Conley and Fraas¹⁶ of the change in concentration during extraction of calcined polyhalite at 80° and 90° C., and at the boiling point, presented in figure 24, show that higher maximum concentrations of potassium sulfate and a more rapid approach thereto are obtained with increase in temperature up to the atmospheric boiling point. These experiments were made with polyhalite ground to — 30 + 150 mesh and calcined 20 minutes with a maximum temperature of 485° C. The calcine, which contained 30.37 percent of potassium sulfate and only 0.35 percent of sodium chloride, was extracted with 9.5 parts of water per part of potassium sulfate so that complete extraction would have

¹³ See references 3, 23, 24, and 25 in list of Bureau of Mines publications (pp. 248 and 249).

¹⁴ See reference 5 in list of Bureau of Mines publications (p. 248).

¹⁵ See reference 12 in list of Bureau of Mines publications (p. 249).

¹⁶ See reference 6 in list of Bureau of Mines publications (p. 248).

yielded a liquor containing 10.5 parts of potassium sulfate per 100 parts of water. Even at $101^{\circ}\text{C}.$, therefore, extraction was only 81 percent complete when the maximum liquor concentration

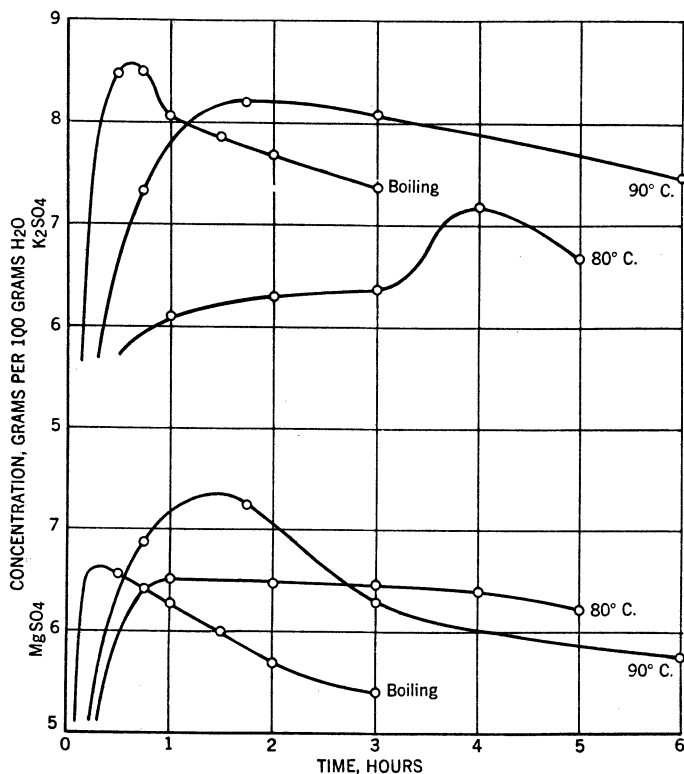


FIGURE 24.—Effect of temperature on extraction of K_2SO_4 and MgSO_4 from calcined polyhalite.

was reached—a typical result for an extraction in the substantial absence of sodium chloride, as will be shown in greater detail in a later section.

The rate at which the maximum concentration is attained might be still greater above $100^{\circ}\text{C}.$ than at that temperature, but the corresponding increase in the rate of recrystallization of polyhalite would necessitate very rapid separation of liquor from the solid residue to achieve good recoveries. In general, the atmospheric boiling point seems to be the optimum temperature for the extraction of calcined polyhalite.

AGITATION

In the earlier extraction experiments the mixture of polyhalite and water was energetically agitated. Improved results were later obtained when gentle boiling under a reflux condenser supplied the only agitation,¹⁷ but much of the observed difference may have been due to higher concentrations of sodium chloride during extraction. There is nothing to indicate any advantage

¹⁷ See reference 3 in list of Bureau of Mines publications (p. 248).

of agitation during extraction beyond the minimum necessary to insure continuous mixing of the liquid and solid.

In contrast to the slight agitation required during extraction, very efficient initial dispersion of the calcine in the hot water or dilute liquor is essential to prevent balling-up of the particles into masses that are only slowly extracted. The tendency to agglomerate is, of course, less marked with relatively coarse than with finely ground calcine, but even in this case, effective mixing at the point and during the time of addition of the calcine to the water is desirable.

EFFECT OF SODIUM CHLORIDE

Before a supply of natural polyhalite from New Mexico became available, laboratory work could be carried out only on very limited samples of core drillings, on synthetic polyhalite, or on imported material from foreign potash deposits. Most of the early experiments were conducted on natural polyhalite from Poland, which contained amounts of sodium chloride ranging from about 4 to 7 percent, but in a few instances selected core drillings of relatively pure domestic minerals were used. Some puzzling

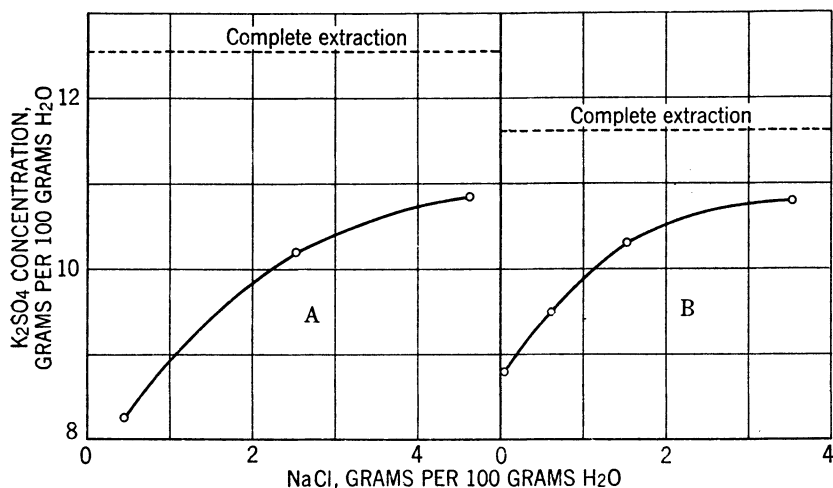


FIGURE 25.—Effect of NaCl on concentration of K₂SO₄.

discrepancies between the results of different tests were not understood until Conley and Fraas¹⁸ demonstrated that the quantity of sodium chloride present in the liquor during extraction very materially affected the quantity of potassium sulfate held in solution. The key experiments were made with polyhalite 97.4 percent pure, containing only 1.05 percent of sodium chloride. The original 10-mesh material,¹⁹ which was calcined in an experiment rotary kiln with a time of retention of 16 minutes and a maximum temperature of 460° C., was extracted with a quantity of water that would have yielded a concentration of 12.6 parts of potassium sulfate per 100 parts of water if all of this constituent had been transferred from the solid to the solution. The actual concentra-

¹⁸ See reference 6 in list of Bureau of Mines publications (p. 248).

¹⁹ See reference 7 in list of Bureau of Mines publications (p. 248).

tion attained was only 8.26, but when 5 grams of sodium chloride were added to a parallel extraction, the potassium sulfate content of the extract liquor increased to 10.2, and 10 grams of sodium chloride yielded a still higher value of 10.84. The effect of sodium chloride concentration on the potassium sulfate in the extract liquor in these experiments is shown in the left part of figure 25.

Similar data for some batch-extraction tests with — 30- + 150-mesh polyhalite calcined for about one-half hour at a maximum temperature of 460° C. are shown in the right part of figure 25. In

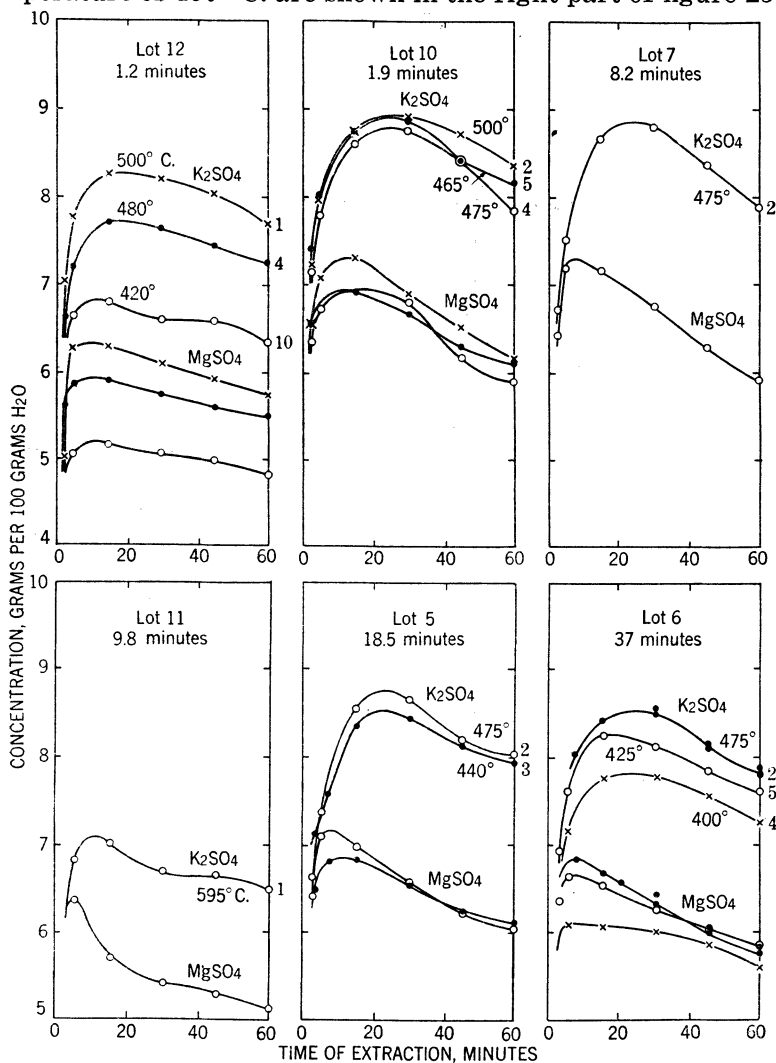


FIGURE 26.—Effect of calcination conditions on hot-extraction behavior of minus 10-mesh polyhalite containing 0.8 percent NaCl.

these experiments a higher ratio of water to potassium sulfate was employed, so that complete extraction would have yielded a liquor containing 11.63 parts of potassium sulfate per 100 parts of water.

The rather pronounced effect of sodium chloride indicated by these batch extractions for an arbitrary period of 45 minutes was subsequently confirmed during the detailed study of the four batches of polyhalite mentioned on page 124. Comparison of

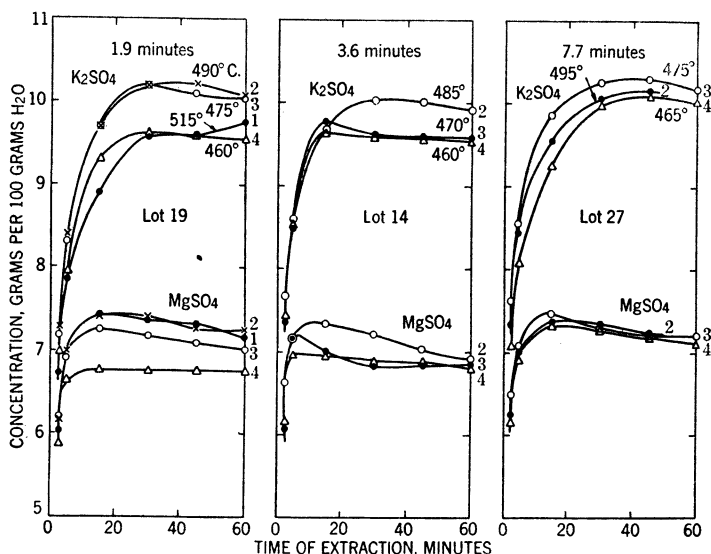


FIGURE 27.—Effect of calcination conditions on hot-extraction behavior of minus 10-mesh polyhalite containing 5.0 percent NaCl.

figures 26 and 27, representing the behavior of minus 10-mesh calcine containing respectively 0.8 and 5 percent of sodium

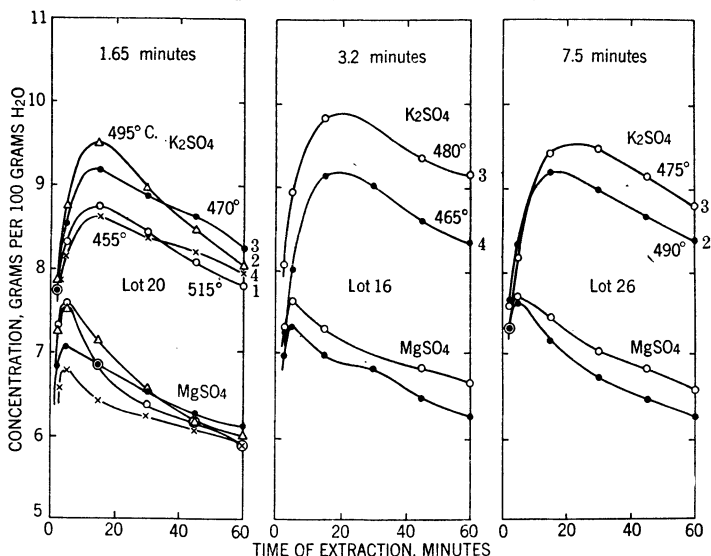


FIGURE 28.—Effect of calcination conditions on hot-extraction behavior of minus 20-mesh polyhalite containing 1.33 percent NaCl.

chloride, corresponding to average concentrations of 0.32 and 2.32 parts of this constituent per 100 parts of water in the extract

liquor, show that not only are higher concentrations of potassium sulfate attained but that these concentrations are maintained over a much longer period.

The same improvement in extraction is produced in the case of 20-mesh material, as may be seen by comparison of the curves in figures 28 and 29 for polyhalite containing, respectively, 1.33

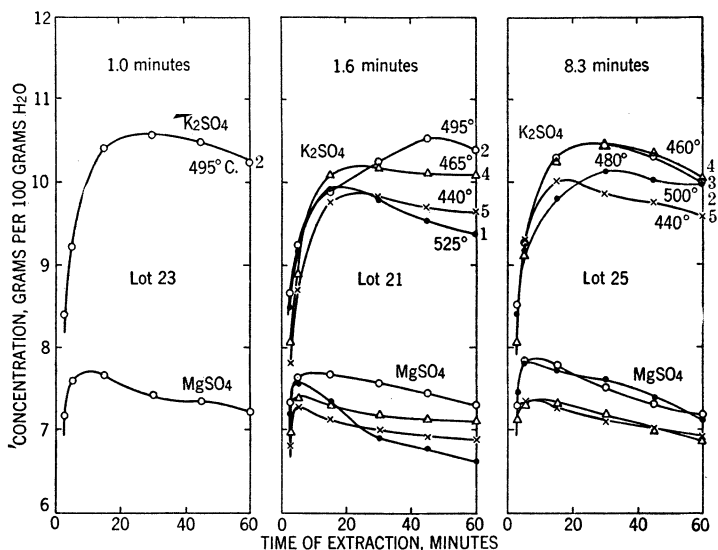


FIGURE 29.—Effect of calcination conditions on hot-extraction behavior of minus 20-mesh polyhalite containing 5.11 percent NaCl.

and 5.11 percent of sodium chloride. A slightly greater tendency for the concentrations to drop after attaining maximum values is shown by the 20-mesh material represented in figure 29 than by the 10-mesh material in figure 27, owing perhaps both to the higher concentrations reached and to the greater area of contact between the solid phase and the solution.

The extraction experiments consistently showed that all of the sodium chloride present in the calcined polyhalite was dissolved almost immediately after addition of the water. Since the beneficial effect of sodium chloride upon the extraction process is apparently due to the fact that it decreases the tendency for syngenite and polyhalite to form from solution, equally good results might be anticipated whether the sodium chloride entered as an impurity in the polyhalite or was added to the water used for extraction. The effect of the latter treatment upon different types of calcine is shown in figure 30. The highly overcalcined lot 11-1 showed a much greater improvement in concentration than the undercalcined lots 12-11, 12-10, and 6-4. Material A was a composite derived from several lots, one of which was undercalcined. Lots 18-3 and 20-3 were both slightly undercalcined; 19-3 and 21-4 represent material nearer the optimum condition. The double-end arrows indicate the range of concentrations obtained in the three or four best extractions for each of the four original batches of polyhalite. It seems reasonable to conclude

from the combined data in the figure that sodium chloride present during extraction in a concentration of 2 parts per 100 parts of water will yield a maximum concentration of potassium sulfate higher by 0.5 to 1 part per 100 parts of water than would be

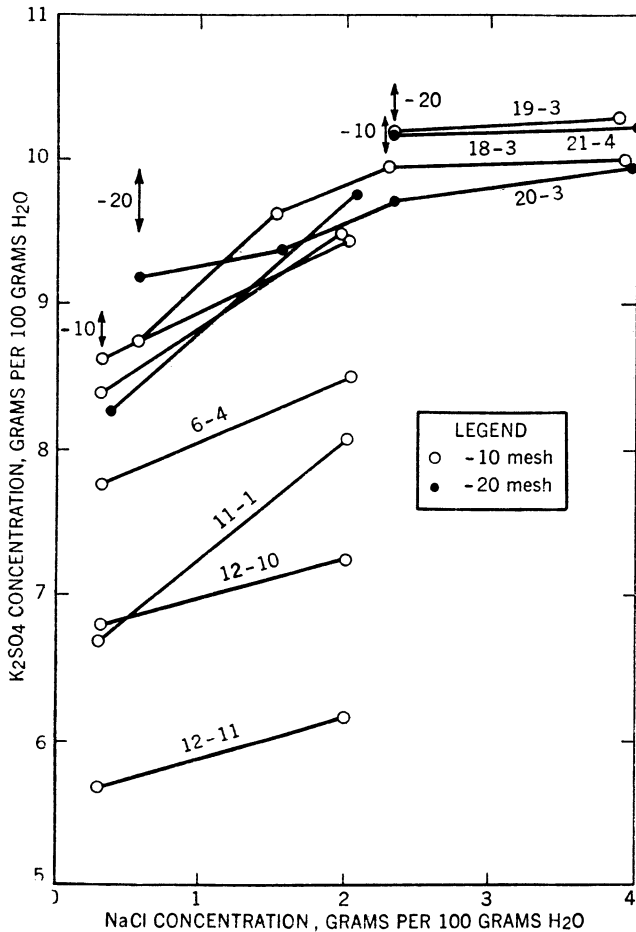


FIGURE 30.—Comparison of optimum concentrations of K_2SO_4 from 10- and 20-mesh calcined polyhalite with varying concentrations of NaCl.

obtained in the substantial absence of sodium chloride and that little further gain is to be expected by using a sodium chloride concentration greater than 2 parts per 100 grams of water.

EFFECT OF PARTICLE SIZE

If the particles of polyhalite are too large, it will be difficult to calcine them rapidly without either overburning the exterior or leaving the interior incompletely calcined. Even if slowly and uniformly calcined, such particles would, moreover, be slow to extract. On the other hand, fine grinding means added expense and greater difficulty in handling. In the earlier experiment,²⁰ before the considerable effect of sodium chloride upon the extrac-

²⁰ See references 23 and 24 in list of Bureau of Mines publications (p. 249).

tion step was recognized, investigation of the range from 10- to 200-mesh led to the conclusion that material not coarser than 65-mesh would yield maximum liquor concentrations with high percentage of extraction.

Later tests, considering the effects of the sodium chloride, showed that sizes as coarse as minus 10-mesh or minus 20-mesh, properly calcined, would yield concentrations closely approaching those obtained by extraction of the finer-size material. A slightly longer time is necessary to obtain maximum extraction of the potassium sulfate with the coarser sizes, but this applies also to the rate of formation of the secondary polyhalite—a fact that in itself had technologic advantage.²¹

The advantages in being able to treat a minus 10- or minus 20-mesh calcined polyhalite were deemed important enough to warrant a detailed study of extractions with these two sizes. The results of these studies, made and published by staff members,²² cover this information in detail. The differences in extraction behavior of minus 10- and minus 20-mesh polyhalite with corresponding percentages of sodium chloride may be noted by comparison of figures 25 and 27 with figures 28 and 29, respectively.

Comparison of figures 26 and 28 shows at once that higher concentrations and hence (from the method of the test) correspondingly higher recoveries were obtained from the minus 20-mesh material containing 1.3 percent sodium chloride than from minus 10-mesh material with the lower salt content (0.8 percent). Although part of the improvement shown by the finer polyhalite probably was caused by the higher concentration of sodium chloride during extraction, as discussed in the preceding section, this should have amounted to an increase in the maximum potassium sulfate concentration of only about 0.3 gram per 100 grams of water. Direct comparison of individual curves in figure 26 with those in figure 28 is scarcely justified, but the three highest concentrations actually measured in the series of tests with the minus 20-mesh material actually exceed the three highest found with the minus 10-mesh material by two to three times the amount ascribable to the difference in sodium chloride content.

Figures 27 and 29, representing data from batches of polyhalite with the same sodium chloride content (approximately 5 percent), show only a small effect of particle size. The three highest concentrations actually measured for the minus 20-mesh material exceed the three highest for the minus 10-mesh material by approximately 0.3 part of potassium sulfate per 100 parts of water.

In the preceding studies of calcined polyhalite with different upper limits of particle size, much of the material in all cases was in the range of finer sizes. A comparison of minus 10- plus 20-mesh and of minus 20-mesh fractions with the composite lot of minus 10-mesh calcined polyhalite from which they were screened is presented in figure 31, in a manner which indicates the course of the changes in composition of the solution. When the sodium

²¹ See reference 6 in list of Bureau of Mines publications (p. 248).

²² See reference 12 in list of Bureau of Mines publications (p. 249).

chloride concentration was approximately 0.3 part per 100 parts of water, the coarse fraction yielded a slightly higher, and the fine fraction a slightly lower, maximum concentration of potassium sulfate than the original composite. In the presence of 2 parts of sodium chloride per 100 parts of water the case was just reversed, the finer fraction yielding the highest extraction of potassium sulfate, with the coarse fraction barely below the composite. The approach to a common solution composition after 60 minutes is probably fortuitous.

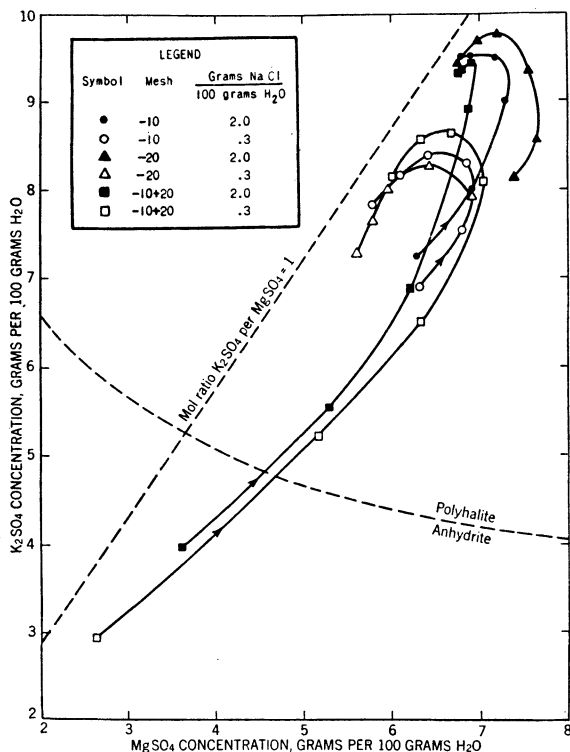


FIGURE 31.—Extract-solution compositions projected on K_2SO_4 - $MgSO_4$ plane, illustrating effects of particle size and NaCl concentration.

The best estimate based upon the available data is that reduction of the upper size limit from minus 10- to minus 20-mesh will increase the maximum concentration attained during extraction by less than 5 percent. The optimum conditions of calcination seem to be about the same for the two sizes. That even as short a time of retention as 1 minute may be adequate for minus 20-mesh polyhalite is indicated in figure 29 by the results for lot 23-2, which was heated to a maximum temperature of 495° C.

COMPARISON OF EFFECTS

Figure 32 shows four pairs of extraction curves for samples of well-calcined material from each of the four batches of polyhalite. Although these are intended particularly to compare the results obtained by calcination for 2 minutes with maximum tem-

peratures slightly below 500° C. and for 8 minutes with temperatures some 20° lower, they also illustrate the small effect of particle size and the much more important effect produced by sodium chloride.

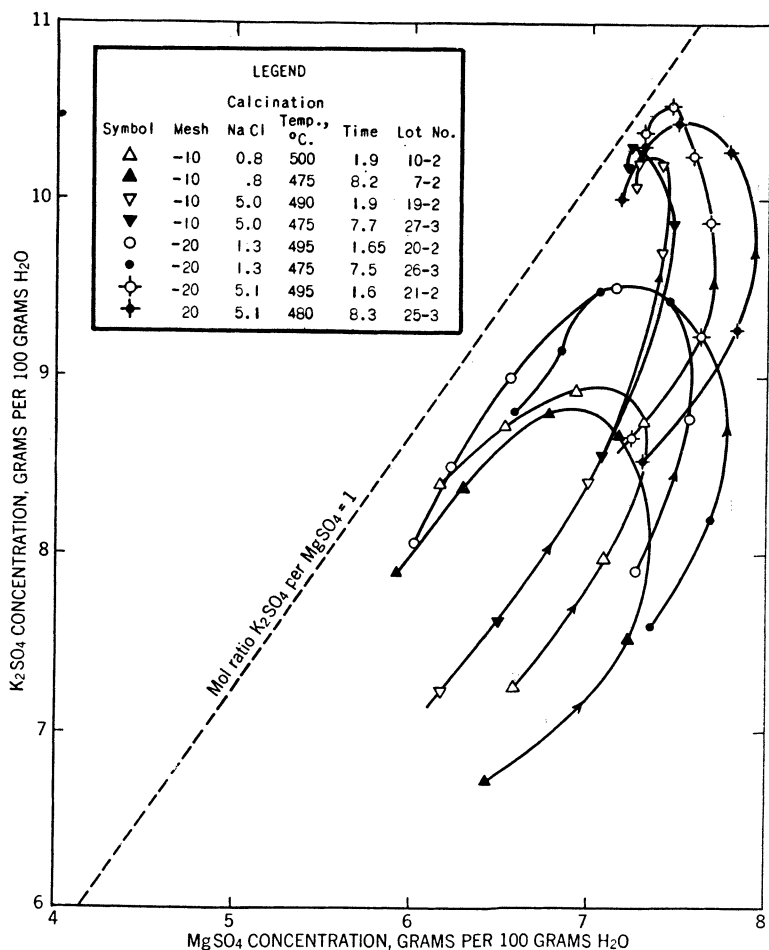


FIGURE 32.—Effects of calcination conditions on extract-solution compositions projected on K_2SO_4 - $MgSO_4$ plane.

The major difference between the two calcination conditions is a greater tendency toward early formation of syngenite in materials calcined for the longer period with the lower maximum temperature. This is indicated by the displacement downward and to the right of the curve for this material in each pair in figure 32. The effect of sodium chloride in decreasing the rate of polyhalite formation is illustrated clearly by the limited reversal of the two upper pairs of curves after attainment of the maximum concentration of potassium sulfate, as compared with the manner in which the two lower pairs of curves turn downward parallel to the line representing a mole ratio of unity. In this

figure all curves are displaced somewhat to the right as a result of including calcium sulfate with magnesium sulfate.

TIME AND TEMPERATURE OF CALCINATION

Because particle size and sodium chloride content influence the extraction process, the effect of time of retention and maximum temperature during calcination must be considered separately for various types of material. Four batches of polyhalite with the chemical compositions and size analyses given in tables 38 and 39 investigated systematically ²³ have yielded definite information concerning the individual effect of these variables and have substantiated the suggestion of Conley, Fraas, and Davidson ²⁴ that a period of only 2 or 3 minutes in passing through the temperature range from 300° to a maximum somewhat below 500° C. would yield optimum results.

The background of calcination data for the four batches of polyhalite has previously been presented on pages 119 to 124. The behavior on extraction of the various lots calcined under different conditions was tested by experiments in which 200 grams of calcine, the potassium sulfate content of which had been determined by analysis, were agitated for 60 minutes in contact with

TABLE 38.—*Chemical composition of four batches of polyhalite*

Batch	Screen Size		Composition, percent				Apparent density, per cubic centimeter	
	Meshes per inch	Opening, mm.	K ₂ SO ₄	MgSO ₄	CaSO ₄	NaCl	Original (measured)	Dehydrated (calcined) ¹
A.....	Through 10	1.651	26.14 26.08	19.18 19.15	0.80 .80	2.751	2.603
B.....	Through 20	.833	25.37 25.41	18.96 18.91	47.99 47.93	1.32 1.33	2.746	2.601
C.....	Through 10	1.651	24.61 24.65	18.32 18.28	46.32 46.11	5.02 5.02	2.729	2.590
D.....	Through 20	.833	24.58 24.53	18.27 18.30	46.09 46.11	5.09 5.12	2.731	2.592

¹ On assumptions that initial polyhalite contained no free moisture, and that water of hydration could be removed without change in volume of solid.

TABLE 39.—*Size distribution of four batches of polyhalite*

Screen size		Material on screen, percent			
Meshes per inch	Opening, mm.	A	B	C	D
20.....	0.833	42.8	1.7	39.0	0.8
28.....	.589	13.2	20.8	12.4	16.8
35.....	.417	16.9	8.8	17.1
65.....	.208	22.2	20.7	13.0	25.5
100.....	.147	4.1	9.1	6.7	9.9
150.....	.104	2.7	2.7	1.3	3.0
Through 150.....	15.0	28.1	18.8	26.9

enough water, boiling gently under a reflux condenser, to produce a liquor containing 11 parts of potassium sulfate per 100 parts of water if all the potassium sulfate dissolved. The change in composition of the liquor was followed by the analysis of samples removed at intervals, while the corresponding change in character

²³ See reference 12 in list of Bureau of Mines publications (p. 249).

²⁴ See reference 7 in list of Bureau of Mines publications (p. 248).

of the solid residue was checked by observation under the polarizing microscope.

What took place during the various extractions may best be visualized by two different types of diagrams. In the first type, the measured concentrations of potassium sulfate and magnesium sulfate are plotted against time, as in figure 24, which shows clearly the respective maxima and the subsequent drop in concentration. In the second type, the simultaneous values for the two sulfates are plotted against each other, as in figures 31, 32, and 33, and illustrate the deviation of the molar ratio of potassium

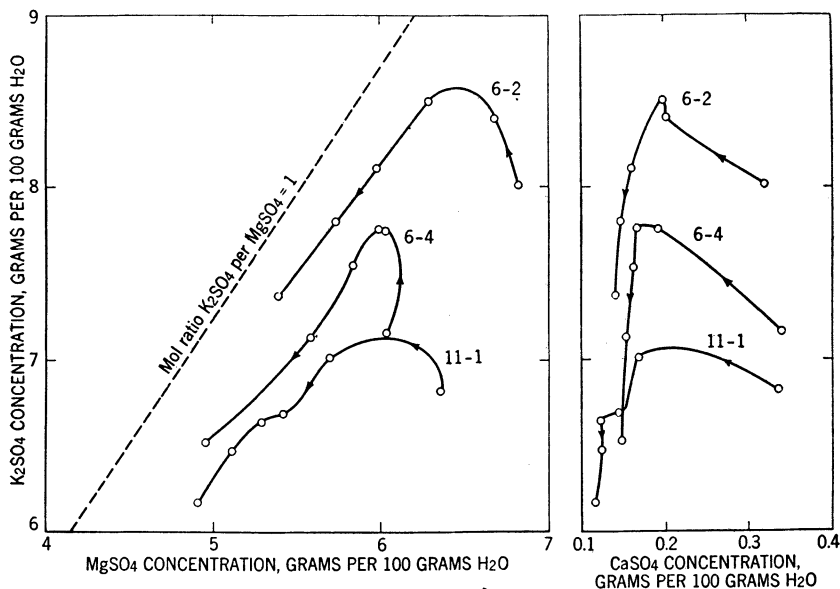


FIGURE 33.—Extract-solution composition changes plotted on K_2SO_4 - $MgSO_4$ and K_2SO_4 - $CaSO_4$ planes.

sulfate to magnesium sulfate from the value of 1, which would be obtained if syngenite did not form during the extraction.

As calcium was not separated from magnesium in the analyses of the liquor samples, the concentrations of magnesium sulfate in both types of diagram are higher than the true values. As may be seen from figure 33, the quantity of calcium sulfate in solution during the early part of an extraction may exceed 0.3 but probably does not rise above 0.4 part per 100 parts of water, dropping slowly thereafter to a value of about 0.15 at the end of 60 minutes.

The curves of the first type in figure 26 represent the extraction behavior of minus 10-mesh polyhalite containing approximately 0.8 percent of sodium chloride calcined under a wide range of conditions.

Because particle size and sodium chloride content influence the extraction process, the effect of time of retention and maximum temperatures must be considered individually with respect to each of the four batches of material put through the calcination tests. A wide range of calcination conditions is represented by the

curves in figure 26 for minus 10-mesh polyhalite containing approximately 0.8 percent of sodium chloride. If under-, over-, and optimum-calcination are defined in terms of the maximum concentrations of potassium sulfate and magnesium sulfate obtained during extraction, it is apparent that lots 10-2 and 7-2 were the best-calcined of the group. The short time of 1.9 minutes in the kiln, combined with a maximum temperature of 500° C., produced nearly the same results as 8.2 minutes with a maximum of 475° C. At this latter temperature, the effect of increasing the time of retention may be seen by comparing the extraction curves for lots 12-4, 10-4, 7-2, 5-2, and 6-2, which represent the range from undercalcination to overcalcination, with lot 7-2 close to the optimum condition. A similar comparison for lots 12-1 and 10-2 with a maximum temperature of 500° C. indicates that the former was inadequately calcined during 1.2 minutes in the kiln.

Extreme overcalcination is evident in the case of lot 11-1 in figure 26, which attained a maximum temperature of 595° C. during its period of 9.8 minutes in the kiln. The low maximum concentration of magnesium sulfate reached during extraction and the rapid decrease in concentration with time indicate an accelerated formation of polyhalite from solution, as compared with the behavior of lot 7-2, which was in the kiln for a period only slightly shorter but was not heated above 475° C.

The relative effects of time and temperature of calcination on the extraction behavior of calcined minus 20-mesh polyhalite low in sodium chloride are shown in figure 28. It is evident from the eight curves in this group that a time of retention of 3.2 minutes, with a maximum temperature of 480° C. (lot 16-3), gave optimum results during extraction. A longer time with a slightly lower maximum temperature (lot 26-3) and a shorter time with a higher maximum of 495° C. (lot 20-2) yielded the next highest concentrations.

The fact that even a brief exposure of minus 20-mesh material to a temperature above 500° C. will result in overcalcination is brought out by comparison (in fig. 28) of the extraction behavior of the various lots from run 20 in the kiln. Lots 20-4 and 20-3 are obviously undercalcined with respect to lot 20-2, which reached a temperature of 495° C.; lot 20-1, which was heated to 515° C., can owe its comparatively poor extraction only to overcalcination. As in the case of overcalcined lot 11-1 in figure 26, the magnesium sulfate concentration for lot 20-1 drops sharply after its early maximum, indicating excessive formation of polyhalite from solution.

Trends similar to those already discussed may also be observed in figures 27 and 29 for polyhalite containing approximately 5 percent of sodium chloride. It seems safe to conclude that polyhalite as coarse as minus 10-mesh may be adequately calcined by a heating cycle lasting only 2 or 3 minutes with a maximum temperature of 470° to 490° C., as suggested by Conley, Fraas, and Davidson.²⁵ A temperature of 500° C., instead of being the

²⁵ See reference 7 in list of Bureau of Mines publications (p. 248).

lower limit as recommended by Schoch (30, 32), appears to be the upper limit for the best results.

Two different problems are presented in connection with designating the optimum conditions for calcination. For the purpose of removal of the potassium and magnesium sulfates from the calcium sulfate by dissolution methods, it is important to have the calcium sulfate in as inactive or insoluble form as possible to decrease the tendency toward its going into solution and reacting with the other sulfates to form secondary less-soluble compounds. On the other hand, when the object is to extract only the magnesium sulfate and permit the interaction of the calcium and potassium sulfates to produce syngenite, a readily soluble type of calcium sulfate is beneficial.

Low-temperature dehydration only long enough to expel the combined water is indicated as satisfactory in syngenite-formation processes, and a higher-temperature treatment within the range given is better-adapted to those processes based upon extraction of both magnesium and potassium sulfates. As discussed in the previous sections, an optimum temperature exists which need not be maintained longer than a few minutes when material as coarse as minus 10- or minus 20-mesh is being treated.

A condensed comparison of calcination conditions with the composition of the extract liquor at highest measured concentration of potassium sulfate during each of 56 extraction tests is presented in table 40.

EFFECT OF STORAGE BETWEEN CALCINATION AND EXTRACTION

Immediate quenching of the hot calcine in the water used for extraction was recommended as a result of some of the early work.²⁶

In the later experiments samples of calcine taken hot from the kiln were stored for periods ranging from 20 to 150 days before their extraction behavior was tested. Correlation of all the data indicates no tendency for the degree of extraction to decrease on protracted storage, as long as the container remained tightly closed. In two instances, however, a second sample tested at an interval of several months after the first sample showed increased density and decreased extraction. This change probably was due to absorption of water vapor from the air during the period when the first sample was removed from the container.

It is safe to conclude that storage of itself does not lead to poorer extraction. In practice, however, it would be difficult to avoid absorption of moisture from the atmosphere if the calcine were held for some time before extraction.

Aside from the question of improving extraction by avoiding absorption of moisture by the calcine, quenching has the added advantages of promoting initial dispersion of the calcine in the water used for extraction and of conserving the heat carried out of the kiln by the calcine.

²⁶ See reference 25 in list of Bureau of Mines publications (p. 249).

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TABLE 40.—*Comparison of calcination conditions with composition of extract liquor*

Lot	Calcination conditions			Density of calcine, grams/cc.	Ext. liquor compn. at max. K ₂ SO ₄ concn., grams/100 grams H ₂ O			Max. extn. of K ₂ SO ₄ , percent
	Time of retention, min.	Time above 300° C., min.	Max. temp., C.		K ₂ SO ₄	MgSO ₄	NaCl	
BATCH A, MINUS 10-MESH, 0.8 PERCENT NaCl								
12-1	1.2	0.9	500	2.632	8.26	6.30	0.33	75
4		.8	480	2.633	7.65	5.76	.33	70
10		1.0	420	2.627	6.80	5.18	.31	62
11		.7	400	2.649	5.68	4.33	.31	52
10-2	1.9	1.4	500	2.649	8.92	6.92	.32	81
4		1.5	475	2.642	8.76	6.82	.32	80
5		1.4	465	2.639	8.88	6.68	.33	81
13-1	3.5	2.2	515	2.661	7.99	5.55	.32	73
4		2.2	455	2.643	8.51	6.63	.32	77
8-2	8.3	5.8	510	2.663	8.10	6.97	.33	76
7-2	8.2	5.8	475	2.647	8.80	6.77	.31	80
11-1	9.8	9.1	595	2.730	7.01	5.70	.30	64
5-2	18.5	14.5	475	2.654	8.65	6.56	.32	79
3		13.6	440	2.646	8.43	6.54	.33	77
6-2	37.	27.2	475	2.653	8.50	6.56	...	77
5		26.2	425	2.636	8.25	6.53	.32	71
4		24.9	400	2.642	7.76	5.99	.32	75
BATCH B, MINUS 20-MESH, 1.3 PERCENT NaCl								
22-2	1.1	0.9	495	2.637	9.44	7.28	0.57	86
20-1	1.7	1.3	515	2.674	8.75	6.84	.57	80
2		1.3	495	2.654	9.51	7.15	.57	86
3		1.3	470	2.637	9.19	6.87	.57	83
4		1.1	455	2.626	8.65	6.43	.56	79
16-3	3.2	3.1	480	2.637	9.93	7.28	.58	90
4		2.9	475	2.636	9.15	7.00	.58	83
26-2	7.8	5.8	490	2.653	9.22	7.20	.58	84
3		5.6	475	2.646	9.48	7.06	.59	86
28-3	11.6	8.3	465	2.650	9.16	7.35	.58	83
4		8.0	440	2.642	9.44	7.22	.58	86
5		7.8	425	2.636	9.54	7.22	.58	87
BATCH C, MINUS 10-MESH, 5 PERCENT NaCl								
19-1	1.9	1.7	515	2.653	9.76	5.85	2.32	89
2		1.6	490	2.626	10.21	7.27	2.25	93
3		1.8	480	2.622	10.19	7.18	2.27	93
4		1.8	460	2.613	9.61	6.76	2.25	88
14-2	3.6	2.7	485	2.640	10.03	7.22	2.27	92
3		2.5	470	2.640	9.76	7.01	2.21	89
4		2.5	460	2.627	9.64	6.95	2.16	88
27-2	7.7	5.4	495	2.637	10.17	7.24	2.19	93
3		5.3	475	2.627	10.30	7.23	2.35	94
4		5.3	465	2.622	10.11	7.20	2.35	92
BATCH D, MINUS 20-MESH, 5 PERCENT NaCl								
23-2	1.0	0.9	495	2.619	10.56	7.42	2.32	96
21-1	1.6	1.3	525	2.630	9.90	7.34	2.32	90
2		1.3	495	2.615	10.53	7.45	2.33	96
4		1.2	465	2.611	10.18	7.19	2.30	93
5		1.1	440	2.619	9.82	6.98	2.33	89
15-2	3.7	2.5	500	2.635	10.00	7.31	2.31	91
3		2.5	475	2.617	10.20	7.26	2.31	93
5		2.4	440	2.612	9.77	7.09	2.31	89
25-2	8.3	6.3	500	2.649	10.12	7.61	2.35	92
3		6.0	480	2.636	10.44	7.49	2.31	95
4		6.0	460	2.622	10.43	7.54	2.33	95
5		5.6	440	2.618	10.01	7.28	2.30	91
29-2	14.5	10.4	475	2.639	10.24	7.50	2.32	93
3		10.1	460	2.622	10.40	7.51	2.37	95
4		10.0	440	2.619	10.33	7.46	2.28	94
31-3	21.5	14.3	460	2.625	10.37	7.49	2.29	94
4		13.9	440	2.620	10.06	7.25	2.28	92

COUNTERCURRENT EXTRACTION

At first glance, it might appear that countercurrent extraction, either by batch or continuous operations, would be the logical method for extracting the magnesium and potassium sulfates from calcined polyhalite. Were no secondary double salts formed in the dissolution process and were relatively low temperatures suited for optimum extraction of the potassium sulfate, such extraction procedures would apply without question.

At the end of the most effective batch extraction comprising a single treatment, about 5 percent of the total potassium sulfate will still be locked up in the solid residue as re-formed polyhalite, syngenite, or pentasalt or as combinations of these salts. Also, at least 15 percent of the dissolved salts will be present in the liquor retained by the residue when the mixture is filtered. The obvious way to avoid loss is to wash the residue with water to obtain a dilute liquor, which could be reused in the next extraction. The early tests by Storch and Clarke (36) were conducted in this manner, and the initial two processes proposed (which were outlined by Wroth (44)) were based upon the use of a single washing treatment of the extracted residue before discharge by the filter. Later experiments showed the desirability of repulping the filter cake to improve the recoveries by effecting a more complete displacement of the retained liquors as well as further dissolution of the potash compounds in the residue.

The merits of a multiple-batch treatment with three extractions, followed by filtration at elevated temperatures closely approaching the atmospheric boiling point with a final extraction treatment at room temperature, were studied by Conley and Fraas.²⁷ Those investigations proved that high concentrations can be obtained by multiple-stage treatment, and the residues are low in potassium when water is used at room temperature in the final treatment.

The discussion on the mechanism of the extraction behavior of calcined polyhalite (p. 113) explains that gypsum, syngenite, polyhalite, and finally pentasalt is the order of appearance of the secondary compounds at high extraction temperatures approaching 100° C. All of these salts yield their potassium sulfate when present in small crystal size to a water extraction at room temperature up to approximately 4 to 5 parts per 100 parts of water, excepting the pentasalt. Even this complex sulfate dissolves, on prolonged treatment in water, to yield concentrations approaching 1.2 parts per 100 parts of water. The presence of sodium chloride and temperatures up to 50° to 60° C. likewise are beneficial.

The possibilities of a continuous countercurrent-extraction treatment in which no filtration would be necessary was also investigated.²⁸ Tests have demonstrated the feasibility of obtaining high extractions by this means but likewise showed that difficulties from slimes would arise. The settling of the fine material is complicated both by the density of the concentrated solution and by the convection currents set up in the hot solutions. The maintenance of boiling temperatures, except on a small laboratory

²⁷ See references 5 and 6 in list of Bureau of Mines publications (p. 248).

²⁸ See reference 9 in list of Bureau of Mines publications (p. 248).

scale, is another technologic difficulty to be overcome. The outcome of these various lines of investigation has been that the hot mixture of extracted solids and liquor should be separated with a minimum of delay either by continuous vacuum filtration or by centrifuging to assure clear solutions and high extraction. The residue, with retained liquor and unextracted potassium salts, then should be treated by continuous countercurrent leaching, with the last thickener operating at 45° to 50° C., if possible. Extractions by this procedure tend to minimize variations from optimum conditions and permit less rigid control. For example, if an occasional lot of polyhalite is slightly undercalcined, presumably more syngenite is formed in the hot extraction, but this syngenite and the proportional amount of pentasalt produced therefrom are decomposed subsequently in the dilute solution and water treatments of the early stages of the countercurrent leaching treatment. Efficient and thorough dissolution is assured, in any event. The limiting condition is the maximum attainable concentration of the liquor obtained in the continuous countercurrent-leaching step. This corresponds to the metastable syngenite-gypsum equilibria at the selected operating temperature and the sodium chloride concentration maintained, and is approximately at 5.0 parts of potassium sulfate per 100 parts of water. The minimum percentage extraction in the hot step that will assure high recoveries is therefore 54.6 (6/11 times 100) plus 8.2 (6/11 of 15), or 62.8, based upon the assumption that 15 percent of the potassium sulfate extracted from the calcined polyhalite remains as retained liquor in the filtered residue. To guarantee good results, conservative practice would require higher than the indicated 62.8-percent minimum decomposition in the hot step and a correspondingly lower concentration of potassium sulfate (probably not over 3 or 3.5 parts per 100 parts of water), in the low-temperature treatment. The time necessary to attain an 11-gram concentration of potassium sulfate by using a 3- to 4-gram solution as the extracting medium is 15 to 20 minutes. This time varies little if water is used, as tests have shown that concentrations of approximately 5 parts of K_2SO_4 in 100 parts of water are obtained in 2 to 3 minutes after the full charge of calcine is added to the hot water (see fig. 31, p. 122).

EXTRACTION OF CALCINED POLYHALITE WITH COLD WATER

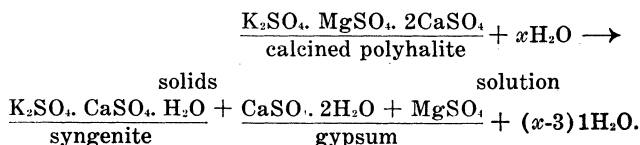
FORMATION OF SYNGENITE

The formation of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$) by a solution process offers a means of separating the magnesium sulfate of polyhalite from potassium sulfate and calcium sulfate.

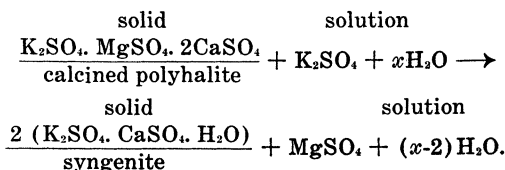
In the development of this process step, it is desirable to consider the solution equilibria involved, the mechanism by which the double salt is formed, and the effect of various factors on the rate of this reaction before examining the results obtained during the experimental production of syngenite or of syngenite-gypsum mixtures from polyhalite.

The calcium sulfate may be regarded as the reagent by means of which potassium sulfate is removed in the solid phase and

thereby separated from the magnesium sulfate that remains in solution. Polyhalite, on decomposing, supplies 2 moles of calcium sulfate for each mole of potassium sulfate, but the latter can combine with only 1 mole in forming syngenite. Neglecting the potassium sulfate left in the mother liquor, the over-all reaction of calcined polyhalite with water may be represented as:



In this process the second mole of calcium sulfate appears as gypsum admixed with the syngenite. This excess calcium sulfate might, however, be used to recover additional potassium sulfate from a liquor such as that obtained in the decomposition of calcined polyhalite by hot water. Whatever the source of the additional potassium sulfate, the over-all reaction for complete conversion of the calcium sulfate to syngenite may be written as:



The formation of a syngenite-gypsum mixture or of syngenite enters into a number of possible process outlines.

Proper application of this method of separating the magnesium sulfate from the potassium sulfate and thorough understanding of the underlying equilibrium data are desirable. A critical examination of the system $\text{K}_2\text{SO}_4\text{--CaSO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ at the temperatures to be employed is essential also. The effects of the presence of sodium chloride, rates of approach to equilibrium, possible utilization of metastable equilibria, and various pertinent factors such as particle size, rates of agitation, physical properties of the solid and mixtures, and solution phases are all important and will be discussed in more or less detail in some of the more important aspects. These factors apply both to the formation and decomposition of syngenite and syngenite-gypsum mixtures and to incorporation of these steps in proposed processes outlined in the previous sections of part I.

EQUILIBRIA IN THE SYSTEM

$\text{K}_2\text{SO}_4\text{--CaSO}_4\text{--MgSO}_4\text{--H}_2\text{O}$ AT 25°C .

The equilibrium conditions that should ultimately be attained when polyhalite is placed in contact with water at 25°C . are represented by the dashed lines in figure 34. The concentration of calcium sulfate, not indicated in this diagram, is very low throughout the system, with a determined value of 0.17 gram of CaSO_4 per 100 grams of water at point A. The first significant feature of figure 34 is the fact that polyhalite is only stable, if it can exist at all, when in contact with a solution high in magnesium

sulfate. The second important feature is that, at any lower concentration of magnesium sulfate, syngenite should appear as soon as the concentration of potassium sulfate reaches slightly more than 3 grams of K_2SO_4 per 100 grams of water. If the process of decomposition of pure polyhalite followed the equilibrium diagram, it would be represented by the solid line in figure 34.

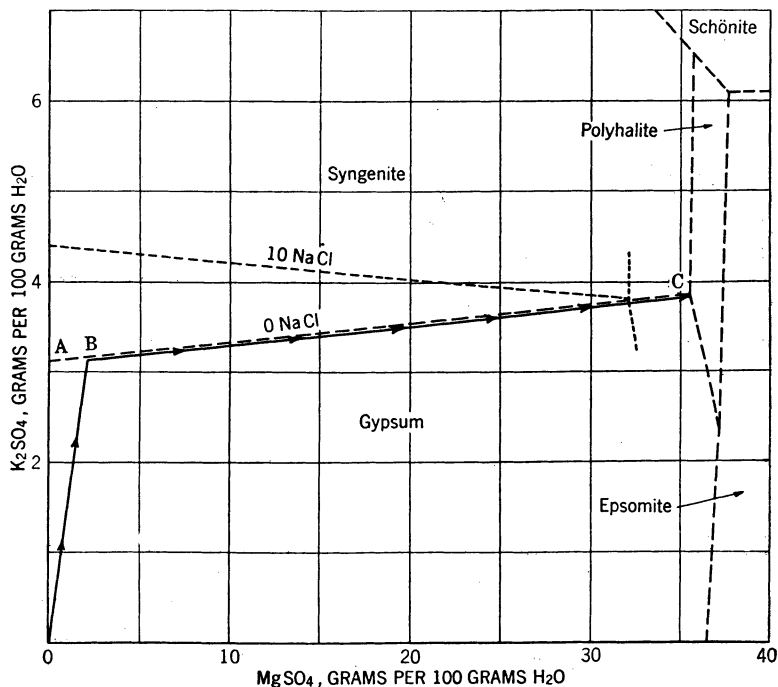


FIGURE 34.—Equilibrium diagram for system K_2SO_4 — $MgSO_4$ — $CaSO_4$ — H_2O at 25° C. (plotted on K_2SO_4 — $MgSO_4$ plane).

Polyhalite placed in water (represented by the lower left corner of the diagram) would decompose, sending potassium, magnesium, and calcium sulfates into solution. The last compound would almost immediately commence to deposit as gypsum ($CaSO_4 \cdot 2H_2O$), while the concentrations of the two former would increase in equimolecular ratio until the point B was reached. Here syngenite would begin to deposit along with the gypsum, and these two solid phases would continue to form as the polyhalite decomposed, while the solution composition would move toward point C. Only at this point would polyhalite become a stable-solid phase, thus ending the dissolution process.

Theoretically, from figure 34 it should be possible to proportion the quantities of polyhalite and water to cause the solution composition to just attain point C as the last particle of polyhalite was decomposed. This would produce a solid residue of syngenite and gypsum and an end liquor containing 35.6 grams of $MgSO_4$ and 3.85 grams of K_2SO_4 per 100 grams of H_2O . Two other factors affecting the equilibrium must, however, be considered—the presence of sodium chloride and the fact that atmospheric

temperatures somewhat above 25° C. probably would be encountered in practice.

The effect of sodium chloride on the equilibrium between syngenite and gypsum has been measured with precision only at point A for zero concentration of magnesium sulfate in figure 34. The data of D'Ans (9, p. 156) are shown in figure 35. Experiments for periods up to 24 hours²⁹ have indicated, however, that

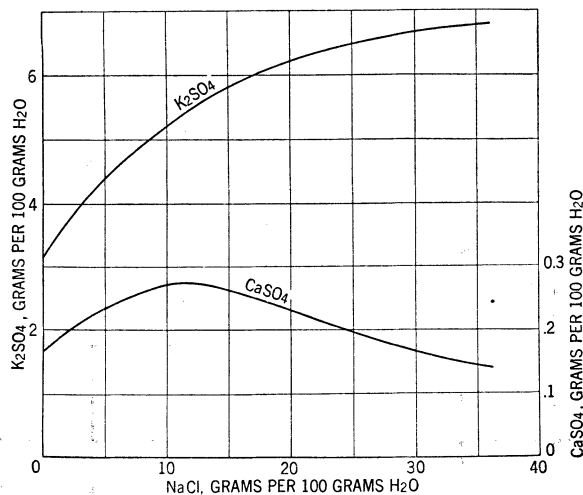


FIGURE 35.—Effect of NaCl on syngenite-gypsum equilibrium at 25° C. (after D'Ans).

when considerable concentrations of magnesium sulfate are present, the syngenite-gypsum boundary is displaced much less by sodium chloride than it is at point A. The probable approximate position of the boundary in the presence of 10 grams of sodium chloride per 100 grams of water is indicated by the dotted line in figure 34.

Sodium chloride not only tends to cause a generally higher concentration of potassium sulfate in solutions in equilibrium with syngenite and gypsum but also reduces the limiting concentration of magnesium sulfate that can be attained during the decomposition. Thus, as indicated in figure 34, if 10 grams of sodium chloride per 100 grams of water are present, the magnesium sulfate concentration can only be built up to approximately 32 instead of to 35.6 grams per 100 grams of water without leaving magnesium sulfate in the solid phase. Like an increase in the sodium chloride concentration, increase in temperature also has an unfavorable effect upon the theoretical limiting equilibrium. Figure 36 shows the variation in point A with change in temperature (2, 14). A similar increase may be assumed at any other point on the boundary AC in figure 34.

The effect of a moderate increase in temperature on the limiting concentration of magnesium sulfate has not been determined. Since polyhalite is stable, however, in relatively low concentrations of magnesium sulfate at 100° C. (see fig. 62, p. 246), it is

²⁹ See pp. 137 and 138.

probable that even an increase in temperature from 25° to 35° C. would reduce appreciably the concentration attainable during the decomposition step.

From the foregoing discussion it is evident that figure 34 represents equilibrium conditions more advantageous than those

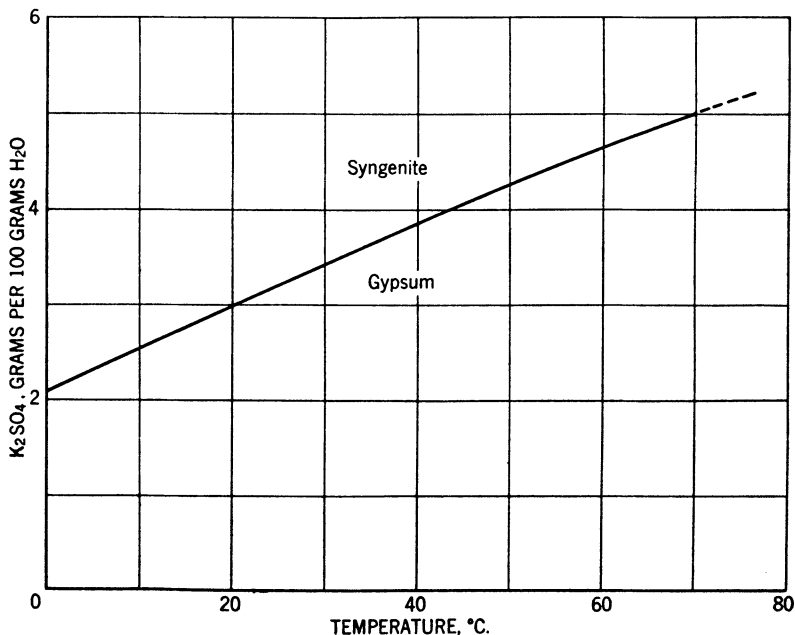


FIGURE 36.—Effect of temperature on the syngenite-gypsum equilibrium.

corresponding to probable practice, since both the presence of sodium chloride and any elevation of the temperature above 25° C. will tend to increase the fraction of the initial potassium sulfate retained in the final magnesium sulfate liquor and thus to reduce the recovery of potassium sulfate in the solid.

However, advantage may be taken of these conditions when the purpose of the treatment is to dissolve any syngenite present in the residues obtained from the hot extraction step.

RATE OF FORMATION OF SYNGENITE

In the formation of syngenite from polyhalite, the constituent simple salts must pass through the solution phase. The rate of formation of syngenite would therefore be expected to depend on either (1) the rate at which potassium sulfate and calcium sulfate are supplied to the solution by the decomposition of polyhalite; or (2) the rate at which these constituents are removed from solution by the crystallization of syngenite.

A third important consideration is the fact that the concentration of calcium is held, during the entire process of conversion, to the low value of 0.2 to 0.3 gram per 100 grams of water by the relative insolubility of gypsum. This low level of concentration acts to retard the transfer of calcium sulfate through the

solution phase from the decomposing original solid phase to the syngenite crystals in process of formation.

The over-all rate of approach to the equilibrium conditions described in the preceding section is increased by calcination of the polyhalite, increase in temperature, and the effect of mass action.

EFFECT OF CALCINATION

Uncalcined polyhalite is decomposed only at a slow rate by water at ordinary atmospheric temperature. Even when ground to pass a 325-mesh screen the rate at which it dissolves is too slow to allow its use directly in the production of syngenite.³⁰ When calcined, however, for a few minutes at 300° C. or above, polyhalite is dehydrated with an accompanying rearrangement of its crystal structure.³¹ The calcine, unstable in contact with water, decomposes rapidly when properly dispersed in it.

The temperature of calcination for polyhalite used in the production of syngenite need not be as high as the range of 475° to 490° C., which produces optimum extraction with hot water. In the latter case, establishment of anhydrite (CaSO_4) as the residual solid phase is essential. In the formation of syngenite, however, it is desirable to produce a calcine that will supply calcium sulfate to the solution at the maximum rate, and the process inevitably tends to approach ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) rather than anhydrite. A temperature of calcination as low as 400° C. apparently yields a satisfactory calcine, provided the time of calcination is long enough to insure complete decomposition.

EFFECT OF TEMPERATURE OF EXTRACTION

Increase in the temperature at which syngenite is formed apparently does not increase the rate of approach to ultimate equilibrium to any great extent, judging from the experimental work subsequently described. It does, however, increase the extent to which anhydrite, present as an impurity in the polyhalite, is dissolved. When the decomposition is carried out at 25° C., very little anhydrite reacts, while at 40° to 50° C. a large part disappears in a few hours. As noted previously, the use of a higher temperature throughout the process must inevitably result in an increased loss of potassium sulfate in the final liquor.

EFFECT OF MASS ACTION

The rate at which syngenite is formed in the early stages of the process might presumably be increased by increasing the concentration of potassium sulfate. Similarly, the rate of decrease toward a desirably low final concentration of potassium sulfate might be hastened by the presence of an excess of calcium sulfate. These effects are observable in figure 37, where the three full curves represent the process for converting calcined polyhalite completely into syngenite by the use of liquors containing additional potassium sulfate, and the two broken curves the process where a mixture of syngenite and gypsum is produced.

³⁰ See reference 25 (p. 3) in list of Bureau of Mines publications (p. 249).

³¹ See reference 25 (p. 4) in list of Bureau of Mines publications (p. 249).

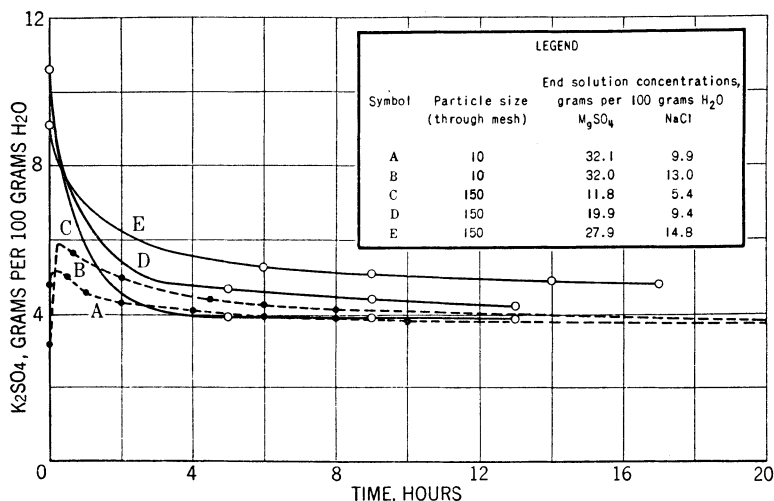


FIGURE 37.—Solution-composition changes on production of syngenite (curves C, D, E) and of syngenite-gypsum (curves A and B) from calcined polyhalite and K_2SO_4 solutions.

OTHER FACTORS

Within rather wide limits, variation in the particle size of the polyhalite and degree of agitation do not markedly alter the rate of syngenite formation. Polyhalite as coarse as minus 10-mesh, when thoroughly calcined, yields results as satisfactory as those obtained with much finer material. This may be due to the lessened tendency of the coarser material to ball up on contact with water.

Although only mild agitation is necessary during most of the process, effective dispersion of the particles of calcined polyhalite as they enter the liquor is essential; otherwise large aggregates are formed which are not subsequently broken down.

PRODUCTION TESTS

Hitherto unpublished results of experimental work on both a laboratory and a semiplant scale to produce both syngenite-gypsum mixtures and syngenite are discussed in this section against the background of information outlined in the preceding sections.

PRODUCTION OF SYNGENITE-GYPSUM MIXTURE

Apparently, all that is necessary to produce a mixture of syngenite and gypsum from calcined polyhalite is thoroughly to disperse the latter in water, agitate the mixture gently for a number of hours, and separate the solid product from the mother liquor and wash it. Actually the operation is more complicated owing to difficulties in the handling of the materials.

In the first place, a mixture of water and calcined polyhalite that would produce a mother liquor containing 32 grams of magnesium sulfate per 100 grams of water would have an initial ratio of solid to liquid of 1.8, which is much too high for practical handling. By recirculating mother liquor, a mixture of any desired consistency can be obtained; but to avoid increased cost, the amount recirculated should be limited to that which just

produces the requisite fluidity. Practical tests have demonstrated a solid : liquid ratio of 0.33 to be adequate.

A second complication is introduced by the fact that both syngenite and gypsum remove water from the liquor as water of hydration, thereby increasing the concentration of dissolved salts. Allowance must be made for this loss of water in calculating the materials charged to the process.

Ultimate separation of the mixture of syngenite and gypsum from the concentrated magnesium sulfate liquor presented still another problem. Attempts at direct filtration consistently resulted in plugging of the filter cloth, apparently by crystallization from the liquor during filtration. When separation by settling and decantation was tried, it was found that the syngenite-gypsum mixture settled so slowly that less than 25 percent of the mother liquor could be drawn off after 24 hours standing. However, by decanting a portion of this liquor and diluting the residual mixture with water a slurry was obtained that could be readily filtered and washed.

This dilution of the mother liquor before filtration fortunately fitted in well with the necessity for recirculating mother liquor to the process. The practical procedure would involve the reaction of calcined polyhalite with three times its weight of a magnesium sulfate liquor of such a concentration that, after decomposition of the polyhalite and formation of syngenite and gypsum with the accompanying removal of water, the mother liquor would closely approach the limiting concentration of magnesium sulfate. The mixture would be allowed to stand until a quantity of clear mother liquor, containing as much magnesium sulfate as was originally introduced in the calcined polyhalite, could be decanted. Water would then be added to the residual mixture, it would be filtered, and additional water would be used to wash the cake on the filter. As much water could be introduced in these operations as was removed in the concentrated mother liquor decanted after settling and in the form of moisture and water of hydration in the syngenite-gypsum product.

This procedure was tested on a semiplant scale in a 100-gallon agitator, the contents of which could be discharged to a 12-inch plate-and-frame filter press by means of a pressure-diaphragm pump with a rated capacity of 5 gallons per minute. Two series of tests were run, with polyhalite crushed to pass a 10-mesh screen and calcined, the first with crude polyhalite containing enough sodium chloride to produce a concentration of 10 to 15 grams per 100 grams of water in the mother liquor and the second with washed polyhalite which yielded a final concentration of less than 1 gram of sodium chloride per 100 grams of water.

The changes of the potassium sulfate and magnesium sulfate concentrations with time during four of the tests in which the sodium chloride concentration was high are shown in figure 38. The first significant feature is the hump in the curves for magnesium sulfate for runs 4 and 5 at 25° C. Obviously, an appreciable amount of magnesium sulfate must have been deposited from solution after the first 2 hours, due to proportioning of the initial

materials to produce a concentration of magnesium sulfate in the mother liquor above the allowable limit. In runs 6 and 7, with proper proportioning, the calculated concentrations of 32.4 and 31.8 grams of magnesium sulfate per 100 grams of water for the respective test temperatures of 25° and 30° C. were closely approximated.

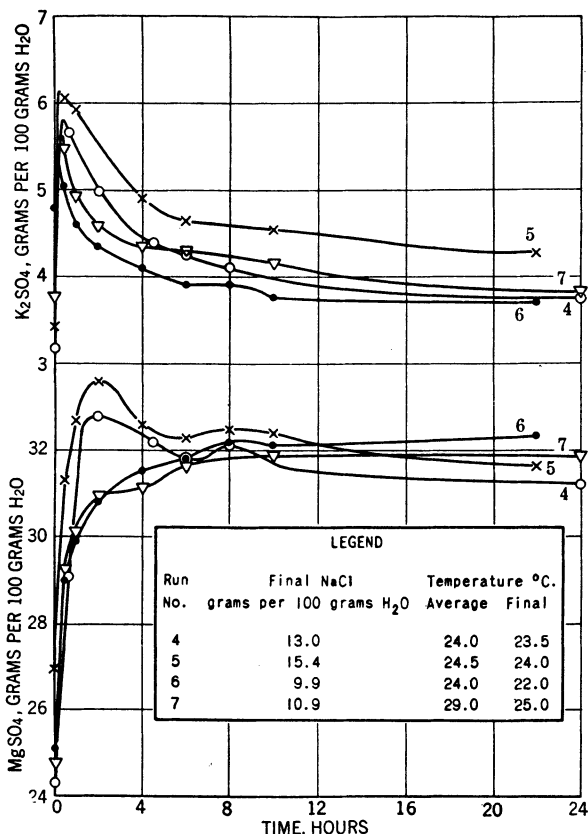


FIGURE 38.—Solution-composition changes during production of syngenite from calcined polyhalite and K_2SO_4 solutions in presence of high concentrations of NaCl.

It is evident from figure 38 that decomposition of the calcined polyhalite in runs 6 and 7 must have been essentially complete by the end of 8 hours, since little change in the magnesium sulfate concentration occurred after this point. The concentration of potassium sulfate at this time had also dropped well toward its final value. It should be noted that the further decrease between 8 and 10 hours on the curve for run 6 was probably due largely to a drop in temperature from 24.5° to 22° C. Similarly, the course of the curve for run 7 probably reflects the progressive drop in temperature from 29.5° at 6 hours to 28.5° at 10 hours and then to 25° C. at 24 hours.

Three tests from a second series in which the concentrations of sodium chloride were low—between 0.8 and 1.0 gram per 100

grams of water—are represented in figure 39. The final composition of the mother liquor in run 9 approaches closely the value given by Van Klooster (42) for equilibrium between syngenite, gypsum, and polyhalite at 25° C. in the absence of sodium chloride. The lower final concentrations of magnesium sulfate in runs 10

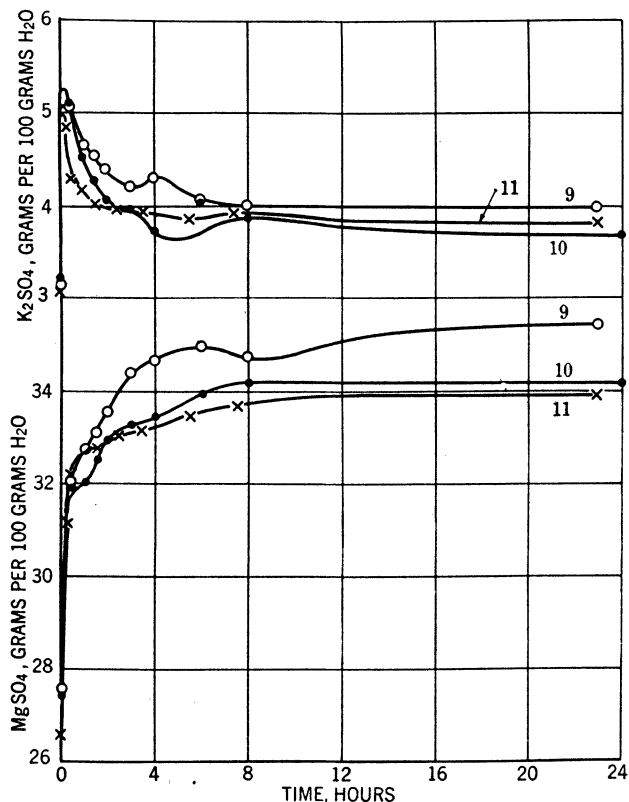


FIGURE 39.—Solution-composition changes during separation of syngenite with low concentrations of NaCl at room temperatures.

and 11 resulted from incomplete decomposition of the polyhalite, the syngenite-gypsum product after filtration, washing, and drying still containing 8 percent of magnesium sulfate. This failure to obtain all of the magnesium sulfate in solution probably was due to incomplete dehydration during calcination. The polyhalite used in these tests was calcined at high rate with a time of retention of only 1.9 minutes in the rotary kiln and a maximum temperature of only 435° C. Either a longer time of calcination at these low temperatures or a higher maximum temperature for the short time of calcination probably would have produced a completely reactive product.

In spite of the fact that the calcined polyhalite was not completely decomposed, it is evident from figure 39 that the reactive portion of the material had been almost completely converted by the end of 8 hours, as in all three tests of the second series the

concentration of potassium sulfate had dropped to or below 4 grams per 100 grams of water in this same period.

PRODUCTION OF SYNGENITE

The complete conversion of calcined polyhalite into syngenite in two stages comprises production of a syngenite-gypsum mixture in the first stage in much the manner described in the preceding section and complete conversion of this to syngenite in the second stage by reaction with a liquor containing an adequate concentration of potassium sulfate. This two-stage process presented a series of new problems.

The most obvious of these, from an experimental standpoint, was proper balancing of the potassium sulfate passing from the first stage to the second stage in the solid mixture of syngenite and gypsum against the potassium sulfate passing in the opposite direction in the syngenite mother liquor. In actual production this would adjust itself automatically, provided conditions were kept reasonably constant and enough time was allowed in each step. The second question was how much the second stage could be shortened by the use of increased temperature. The necessity for further study of handling of materials and separation and washing of solids was also anticipated.

As a result of the difficulty previously encountered in pumping the final mixture from tests in which minus 10-mesh polyhalite had been used, the following tests were all made with material that had been ground to minus 10-mesh, calcined in the rotary kiln, and then reground to minus 60-mesh. In passing, it should be noted that the exposure to moderately humid air during re-grinding, which would definitely have spoiled the calcined polyhalite for hot extraction,³² had no observable deleterious effect upon the process of syngenite formation.

In all of the tests reported, the supplementary potassium sulfate entering the top stage was introduced as a liquor containing approximately 14 grams of K_2SO_4 , 17 grams of $MgSO_4$, and 0.6 gram of $NaCl$ per 100 grams of H_2O , corresponding to the mother liquor from the crystallization of potassium sulfate in processes 4B and 7A.

After a preliminary test had shown that the syngenite-gypsum mixture from the first stage would settle only 15 percent in 2 hours, positive separation on a rotary filter was decided upon. The preliminary test also demonstrated that a considerable part of the anhydrite carried into the second stage would be converted into syngenite during 2 hours at 40° C.

Of the four subsequent tests, three were run in a 50-gallon drum with a clamp-on stirrer and the last in a standard 100-gallon jacketed agitator. The changes in composition of liquor during the preliminary laboratory test and the four larger-scale tests are indicated in figure 40. In studying this diagram, it should be remembered that as the concentration of potassium sulfate decreases during the first stage, calcined polyhalite is being decomposed and the mixture of syngenite and gypsum is forming.

³² See reference 12 (p. 479) in list of Bureau of Mines publications (p. 249).

Similarly, in the second stage, as the potassium sulfate concentration decreases, the gypsum in the syngenite-gypsum mixture is being converted to syngenite.

In figure 40 the magnesium sulfate concentration in the second stage is seen to increase in tests 1 and 2 but to decrease in the three later tests. This change is due to development of the washing procedure. In the first two tests the wet syngenite-gypsum mixture from the bottom stage was mixed directly with the starting liquor in the second stage without washing. Since the

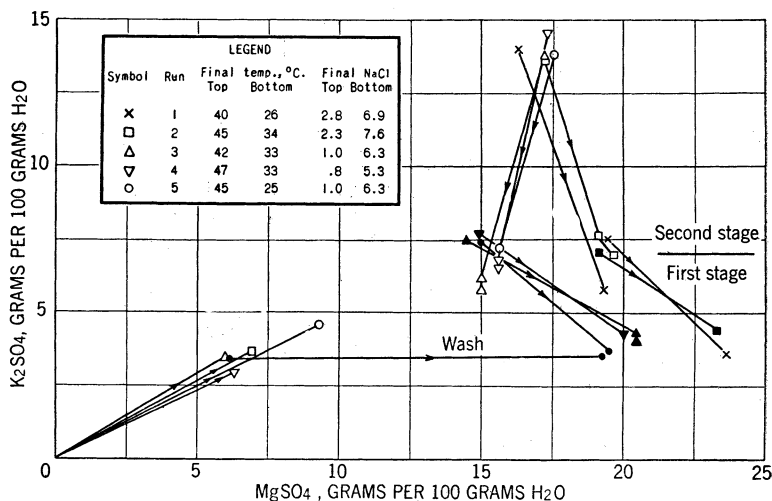


FIGURE 40.—Solution-composition changes during two-stage production of syngenite.

syngenite-gypsum mixture contained approximately 50 percent of moisture upon the wet basis, a considerable quantity of mother liquor high in magnesium sulfate was carried into the second stage. In the three later tests illustrated by the filled-in points, the syngenite-gypsum mixture was washed on the rotary filter with a liquor containing relatively low concentrations of potassium and magnesium sulfates. Since the washed solid still carried about 50 percent of moisture upon the wet basis into the second stage, the starting liquor would, in effect, be diluted by this retained wash liquor.

The syngenite product from the second stage was washed in each case with water, in test 2 by repulping the wet product and refiltering, and in the later tests by washing on the rotary filter with water sprays. The progressive improvement in the quality of the syngenite product and in the estimated recovery of potassium sulfate shown in table 41 reflects the development of the washing technique. In the last test, using a two-row spray wash, the soluble impurities in the dry syngenite were reduced to less than 2 percent, with a loss to the wash water of less than 1 percent of the potassium sulfate content of the syngenite.

Owing to the small size of the rotary filter the mother liquor and wash liquor could not be separated to the extent that would be possible on a full-size unit. In figure 40 the mother-liquor

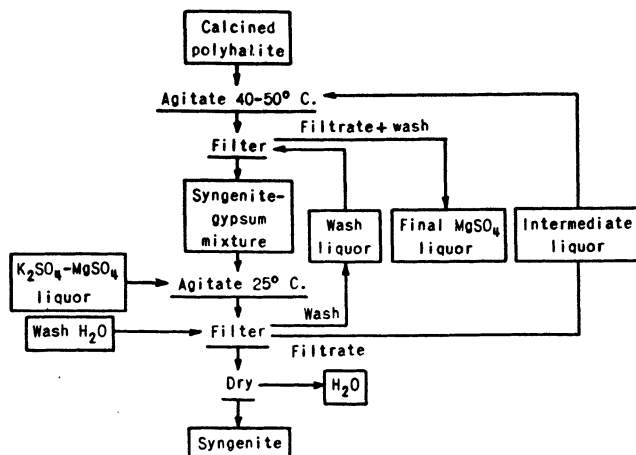
TABLE 41.—*Composition of syngenite product and estimated recovery of potassium sulfate*

Test	Stage	Composition of dry product, percent			Moisture in wet product (wet basis), percent	Estimated recovery of K ₂ SO ₄ in syngenite product	
		K ₂ SO ₄	MgSO ₄	NaCl		Materials in	Materials out
1.....	2	42.8	12.1	1.75	39
2.....	2	44.4	3.9	.26	35	67	74
3.....	1	37.8	8.3	1.29	52		
	2	48.5	2.6	.16	40	68	75
4.....	1	39.7	7.4	.63	52		
	2	48.6	3.3	.2	42.5	72	76
5.....	1	40.0	5.9	1.26	48		
	2	50.7	1.2	.13	40	75	77

concentrations have been corrected for this dilution upon the basis of samples removed before filtration.

Both the syngenite-gypsum mixture and the final syngenite product formed filter cakes that were extremely permeable, because syngenite crystallizes as long needles. It was found that a layer of syngenite nearly 1 inch thick could readily be formed and washed. The discharged cake contained about 40 percent of moisture upon the wet basis and dried readily to a friable mass. When the dried product was passed through rolls, it disintegrated to a fine, light powder.

Upon the basis of the tests just described, it is possible to calculate the flow diagram of figure 41 for a two-stage process,

FIGURE 41.—Flow sheet showing two-stage production of syngenite from calcined polyhalite and K₂SO₄-MgSO₄ liquor.

with the first stage operated for 2 hours at atmospheric temperature and the second for 1 hour at 40° to 50° C.

This figure illustrates the essential steps of the two-stage production of syngenite and corresponds closely to the final procedures recommended for processes 4B and 7A as discussed on pages 71 and 93. Slight modification of the proposed washing operations was made for processes 4 and 5A to meet the special

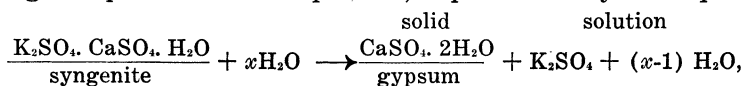
requirements of those specific flow sheets. Potassium sulfate-magnesium sulfate solution is used in these last two processes to convert the syngenite-gypsum mixture to syngenite to displace the retained liquor in the syngenite rather than water. The excess wash filtrate is then added to the agitators, with the unused portion of K_2SO_4 - $MgSO_4$ liquor.

DECOMPOSITION OF SYNGENITE

The production of syngenite represents a half-way step in the recovery of potassium sulfate from polyhalite according to several of the proposed flow sheets. Although syngenite should be acceptable as a fertilizer constituent, the transportation charges on its content of calcium sulfate from the polyhalite deposits to the existing fertilizer-mixing plants presumably would be high enough to render desirable further refining to produce potassium sulfate. Possible procedures are discussed in the following sections.

SINGLE-STAGE PROCESS—GYPSUM RESIDUE

At first glance, the decomposition of syngenite by means of water to produce a solution of potassium sulfate and a solid residue of calcium sulfate would appear to be a simple means of solving the problem. This process, represented by the equation,



might be carried out at 25° C., as indicated by the arrow A in figure 42. The liquor separated from the solid phase can, how-

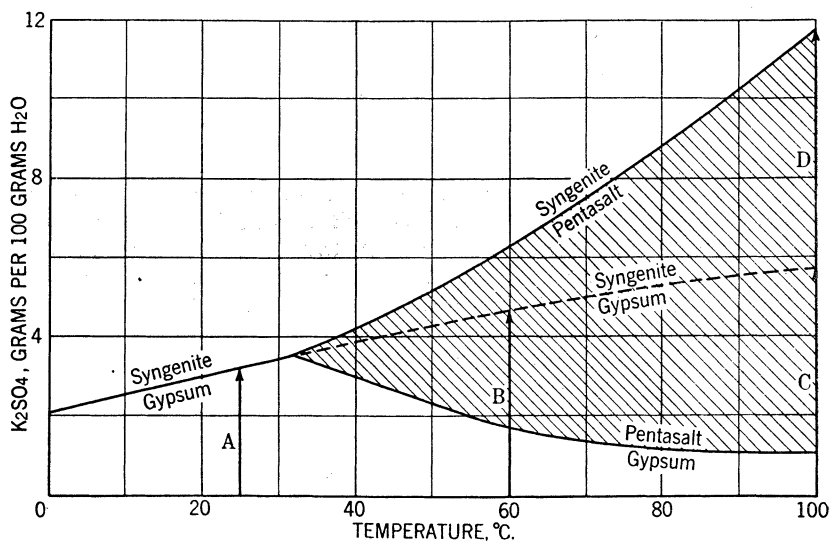


FIGURE 42.—Polytherm for system K_2SO_4 - $CaSO_4$ - H_2O .

ever, contain no more than 3.2 grams of potassium sulfate per 100 grams of water—a concentration much too low to be attractive for a commercial process. A slightly higher concentration of 4.7 grams of potassium sulfate per 100 grams of water might be

reached by carrying out the same process at 60° C., as indicated by arrow *B* in figure 42. Although pentasalt is the stable solid phase at this temperature and composition, its rate of formation is very slow compared to that of gypsum. The metastable equilibrium between syngenite and gypsum, indicated by the broken line in figure 42, will persist at 60° C. for several hours, at least. With increase in temperature, the tendency to form pentasalt increases. Thus, at 100° C., as shown in figure 43, the concentration of potassium sulfate, after pausing at the value corresponding to equilibrium between syngenite and gypsum in figure 42, soon rises, indicating the formation of pentasalt.

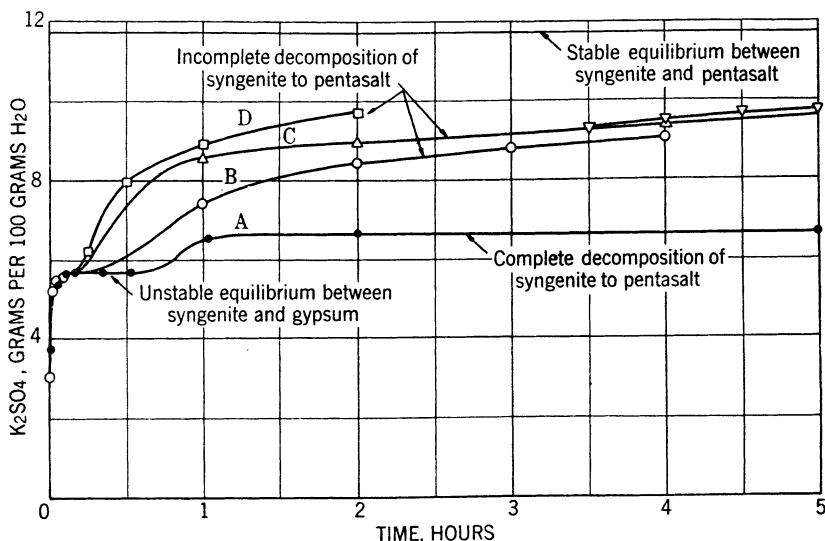


FIGURE 43.—Rate of approach to equilibrium in system K_2SO_4 — $CaSO_4$ — H_2O at 100°C.

In the experiment represented by curve *A* of figure 43, the quantities of syngenite and water were so chosen that the final concentration of potassium sulfate, after complete formation of pentasalt, was not far above the unstable equilibrium between syngenite and gypsum. Under these conditions, observation with the polarizing microscope showed less than 1 percent of pentasalt in the solid phase after 21 minutes, but approximately 25 percent after 32 minutes, even though the concentration of potassium sulfate had not yet started to shift from the value for unstable to that for stable equilibrium. It is probable that, if the initial ratio of syngenite to water were lowered still farther, the process represented by arrow *C* in figure 42 might be carried out to yield a liquor containing 5.7 grams of potassium sulfate per 100 grams without appreciable formation of pentasalt over periods of up to half an hour. This concentration is, however, scarcely high enough to justify the requisite special effort in the rapid separation of the gypsum residue.

If the concentration of potassium sulfate corresponding to the syngenite-gypsum equilibrium could be appreciably increased by the introduction of another salt in the mixture, the process just

outlined might be more attractive. Sodium chloride, already known to have the desired effect at 25° C. (see p. 137), could conceivably be employed for this purpose. The curves in figure 44

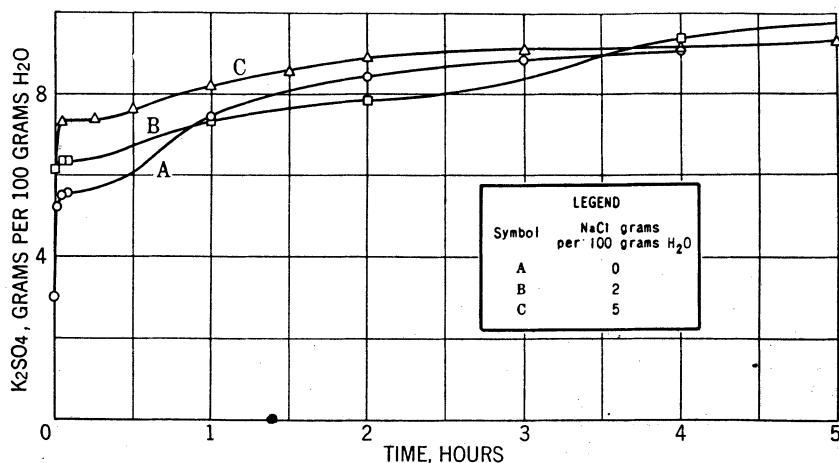


FIGURE 44.—Effect of sodium chloride on metastable syngenite-gypsum equilibrium at 100° C.

indicate, however, that additions of 2 and 5 grams of sodium chloride, respectively, per 100 grams of water used for the decomposition of syngenite at 100° C. raised the values for the unstable

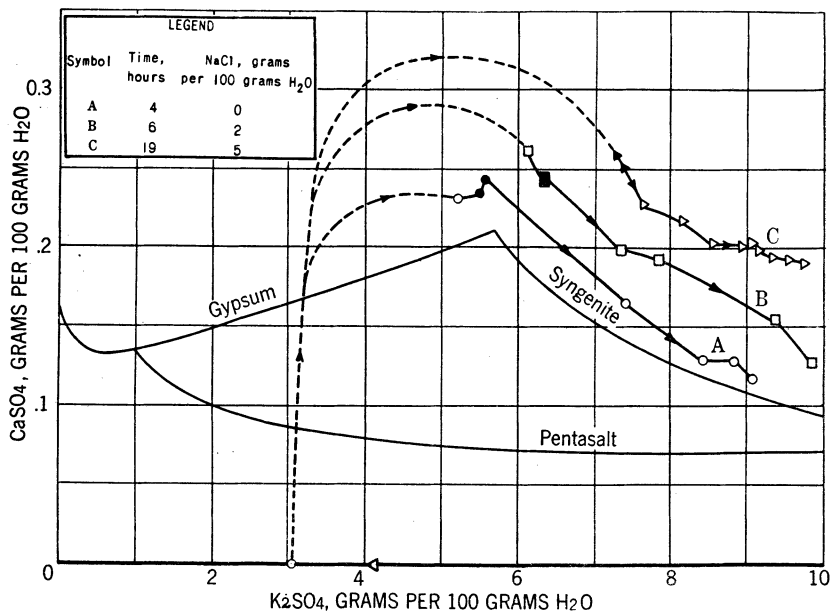


FIGURE 45.—Liquid-phase changes on hot extraction of syngenite with a 3-gram solution of K₂SO₄, plotted on the 100° C. isotherm.

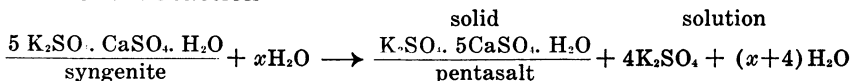
syngenite-gypsum equilibrium only to approximately 6.4 and 7.4 grams of potassium sulfate per 100 grams of water and did not greatly affect the subsequent formation of pentasalt.

The actual changes in the composition of the liquid phase during the experiments just cited may be viewed against the background of the 100° C. isotherm for the system $\text{K}_2\text{SO}_4\text{--CaSO}_4\text{--H}_2\text{O}$ in figure 45. The probable course of the process immediately after the addition of the syngenite to the dilute solution of potassium sulfate used as the starting liquor is indicated by the broken curves. In experiment A, to which no sodium chloride was added, the changes in solution composition paralleled the syngenite boundary of the equilibrium diagram at slightly higher concentrations of calcium sulfate. The presence of 2 and 5 grams of sodium chloride per 100 grams of water in experiments B and C resulted in displacing the solution composition toward higher values for both potassium sulfate and calcium sulfate.

From the preceding data, the single-stage decomposition of syngenite to yield a potassium sulfate liquor and a solid residue of gypsum substantially free of potassium-containing compounds does not appear particularly attractive, since the liquor concentrations are limited to relatively low values and the tendency toward formation of pentasalt, with resultant decreased recovery of potassium sulfate, is always present at temperatures appreciably above the ordinary level.

TWO-STAGE PROCESS—GYPSUM RESIDUE

If instead of attempting to avoid the formation of pentasalt at 100° C. the reaction



were allowed to go to completion, it is apparent that not more than 80 percent of the potassium sulfate initially present in the syngenite could be obtained in the liquor, the remaining 20 percent being retained in the pentasalt residue. The concentration of potassium sulfate in the liquor would, however, be relatively high if the theoretical limiting value of 11.7 grams of potassium sulfate per 100 grams of water could be attained, as represented by arrow *D* in figure 42. This concentration is slightly more than twice the limiting value for the process involving the approach to the unstable syngenite-gypsum equilibrium. Moreover, it is theoretically possible from figure 42, after separating the potassium sulfate liquor from the pentasalt residue, to decompose the latter by contact with water at 25° C., as represented by arrow *A*, to yield a dilute liquor with a limiting content of 3.2 grams of potassium sulfate per 100 grams of water. This makes possible the two-stage process originally visualized by Storch and Fragen³³ in which the pentasalt produced by the decomposition of syngenite at 100° C. is decomposed in turn by water at 25° C. to yield a dilute liquor which is then employed as the starting liquor in the decomposition of more syngenite at 100° C.

Although the equilibrium between syngenite and pentasalt at 100° C. corresponds to the presence of 11.7 grams of potassium sulfate per 100 grams of water, the rate of approach to this

³³ See references 26 and 28 in list of Bureau of Mines publications (p. 249).

equilibrium is, unfortunately, very slow. This is illustrated by curves *B*, *C*, and *D* in figure 43, which indicate that it would not be possible to exceed a concentration of 10 grams of potassium sulfate per 100 grams of water in a commercially practical period of time. Such a value as this, moreover, can only be attained by using an appreciable excess of syngenite, so that, instead of the theoretical 80 percent, somewhat less than 70 percent of the potassium sulfate is transferred from the solid syngenite to the liquor. As a conservative basis for calculating an industrial process, it is assumed that a liquor containing 9.5 grams of potassium sulfate per 100 grams of water may be obtained, with a 20-percent transfer of potassium sulfate, from the initial solid to the liquor when syngenite is agitated for 4 hours with a dilute potassium sulfate liquor at 100° C.

The mixture of syngenite and gypsum obtained from calcined polyhalite by simply reacting the latter with water at atmospheric temperature cannot be treated advantageously by the foregoing procedure. The additional calcium sulfate present in the form of gypsum doubles the quantity of pentasalt formed and reduces to 60 percent the maximum theoretical recovery of potassium sulfate in the liquor from the process at 100° C. If, however, the syngenite-gypsum mixture is calcined before treatment with water, greatly improved results may be obtained. During calcination, the gypsum is converted into anhydrite, which is relatively nonreactive, and the syngenite is probably converted into a mixture of potassium-dicalcium sulfate ($K_2SO_4 \cdot 2CaSO_4$) and potassium sulfate. When treated with water at 100° C., the latter dissolves immediately, while the potassium-dicalcium sulfate goes into solution more slowly. Some of the calcium sulfate entering the solution separates initially as gypsum; but, as in the case of the decomposition of syngenite, pentasalt soon begins to form from solution. The final solid residue is a mixture of pentasalt and anhydrite, the latter having behaved substantially as an inert constituent throughout the process.

The relative behavior of the uncalcined mixture of syngenite and gypsum and of the mixture calcined at various temperatures when treated with a dilute solution of potassium sulfate at 100° C. may be compared in figure 46. That a higher concentration of potassium sulfate in the final liquor may be obtained at this temperature than at any lower one is evident from the additional comparative tests at 80°, 85°, and 95° C.

The temperature of calcination is apparently not a critical factor, at least in the range from 355° to 640° C., covered by the four experiments collectively labeled *A* in figure 46. Calcination at 465° or 535° C. led, however, to higher concentrations in the extract liquor at the end of 4 hours than did calcination at considerably higher or lower temperatures. The time of calcination in each case was not more than 30 minutes.

Although a concentration of 10 grams of potassium sulfate per 100 grams of water in the final liquor has been attained or slightly exceeded in individual tests at the expense of decreased recovery, the average results only justify an estimate of 9.5 grams of

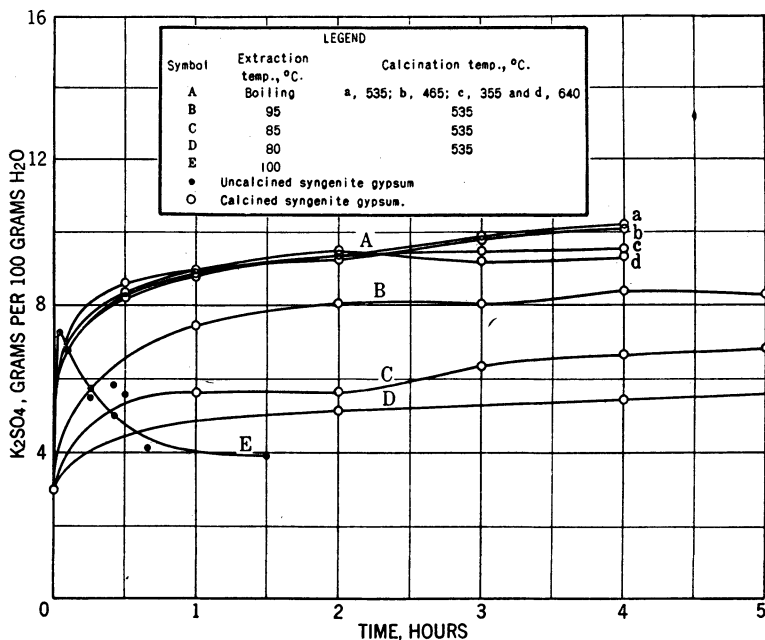


FIGURE 46.—Comparison of time extractions of calcined and uncalcined syngenite under different conditions.

potassium sulfate per 100 grams of water, with 70-percent transfer of potassium sulfate from the solid to the liquor at the end of 4 hours—the same limits previously given for the treatment of

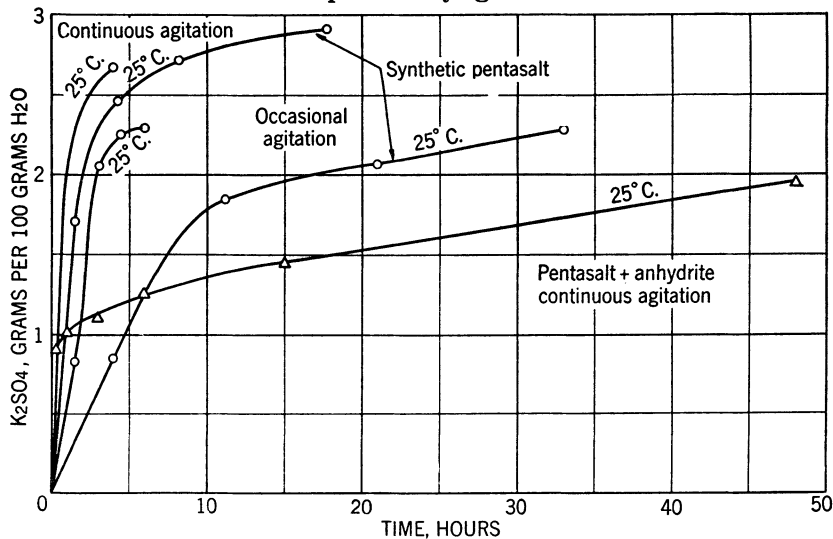


FIGURE 47.—Effect of agitation on extraction of pentasalt at 25° C.

syngenite alone. To achieve these results, it will be necessary to calcine the mixture of syngenite and gypsum at a temperature above 400° C. for several minutes.

Whether syngenite or the mixture obtained by calcining syngenite and gypsum is used, the decomposition with water at 100° C. leaves approximately 30 percent of the potassium sulfate in the solid residue in the form of pentasalt and undecomposed syngenite. The second step of recovering this potassium sulfate as a dilute liquor by treatment with water at atmospheric temperature may or may not be desirable. The time required for the decomposition of pure pentasalt by water at 25° C. is long, as indicated by the curves in figure 47. This slow process is still further retarded when anhydrite is present, as it will be in actual practice, either as an impurity derived from the original crude polyhalite, or as a product of the calcination of a mixture of syngenite and gypsum.

Anhydrite presumably slows the decomposition of pentasalt by maintaining the concentration of calcium sulfate at a relatively high level. In water alone at 25° C. the concentration of calcium sulfate corresponding to unstable equilibrium with respect to anhydrite is approximately 0.45 gram per 100 grams of water, or 100 percent above the stable equilibrium with respect to gypsum.

TWO-STAGE PROCESS—ANHYDRITE RESIDUE

During the course of the investigations described in the preceding sections, it became evident that the concentration of potassium sulfate corresponding to the equilibrium between syngenite and

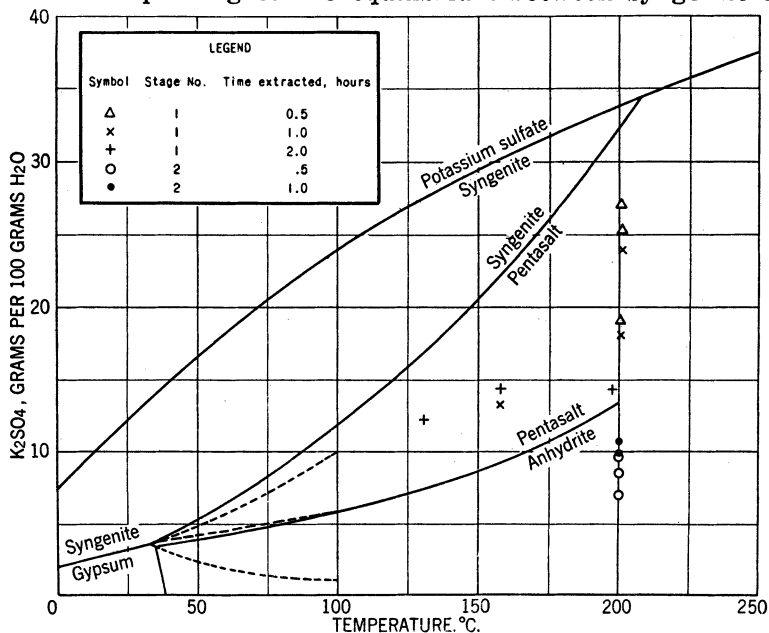


FIGURE 48.—High-temperature extraction concentrations plotted on polytherm for system $K_2SO_4-CaSO_4-H_2O$.

pentasalt must increase continuously with temperature up to 100° C. instead of passing through a maximum between 83° and 100° C., as concluded by Anderson and Nestell (1). Clarke²⁴ was

²⁴ See reference 2 (p. 898) in list of Bureau of Mines publications (p. 248).

the first to predict that this trend would continue above 100° C. and to measure both the syngenite-pentasalt and pentasalt-anhydrite equilibria up to 200° C. Figure 48 represents his results combined with those of earlier investigators. Stable equilibria are represented by solid lines, unstable or metastable equilibria by broken lines.

The upward sweep of the syngenite-pentasalt line in figure 48 leads to a possible limiting concentration of 32 grams of potassium sulfate per 100 grams of water when syngenite is treated with water at 200° C. to form pentasalt. This is nearly three times the limiting concentration for 100° C. Moreover, as might be expected, the rate of decomposition of syngenite at the higher temperature is much more rapid than at 100° C. Final liquors containing more than 25 grams of potassium sulfate per 100 grams of water have been obtained after only 30 minutes at 200° C. following a 45-minute period of heating up from room temperature.

The concentrations of a number of liquors obtained at lower temperatures as well as at 200° C. are indicated in figure 48. Although the advantage of high temperature is obvious, even in this step of decomposing syngenite to form pentasalt, it is not until subsequent decomposition of this pentasalt that operation at 200° C. really becomes essential.

The problem in decomposition of the pentasalt is to cause the calcium sulfate entering the solution phase to be removed therefrom as anhydrite rather than as gypsum. A glance at figure 48 shows that the curve representing stable equilibrium between pentasalt and anhydrite, like that for syngenite and pentasalt, rises continuously with temperature. The curve for metastable equilibrium between pentasalt and gypsum drops, however, toward progressively lower concentrations over the range up to 100° C. for which measurements are available. It is this less desirable condition that is approached whenever pentasalt is heated in contact with water, even at temperatures well above 100° C.

For example, 4 hours' treatment of pentasalt with water at 165° C. produced a liquor containing only 1.7 grams of potassium sulfate per 100 grams of water as compared with the theoretical limiting value of 9.6 if anhydrite had been formed from solution.

To cause rapid removal of calcium sulfate from solution in the form of anhydrite, a temperature of approximately 200° C. appears to be necessary. On heating pentasalt in contact with water from room temperature to 200° C. during 45 minutes and holding it at this level for 1 hour, substantially complete conversion of the pentasalt to anhydrite has been obtained, with concentrations exceeding 10 grams of potassium sulfate per 100 grams of water, as indicated in figure 48. The data of Schoch (32) yield the same general picture, although he recommends a temperature of at least 220° C. in his process of decomposing polyhalite with lime to produce a potassium sulfate liquor and a solid residue of anhydrite and magnesium hydroxide (31). Still higher temperatures are mentioned in several foreign patents (4, 24), describing processes in which the formation of pentasalt was to be avoided.

The choice of the optimum temperature for each of the two stages in the process of recovering potassium sulfate from syngenite will depend on an economic balance between the advantage of high concentration in the final liquor on the one hand and the disadvantage of operation at high pressure on the other. Since a temperature of 200° C. is about the minimum for the satisfactory decomposition of pentasalt, and since the concentration attainable in the decomposition of syngenite at this temperature is adequately high, it seems probable that an actual industrial process would operate at or near 200° C. in both stages.

Implicit in the upward trend of the pentasalt-anhydrite curve in figure 48 is the possibility that a liquor containing 20 grams of potassium sulfate per 100 grams of water might be obtained in a single-stage decomposition of syngenite to anhydrite at 250° C. or above. If further study should verify this, an efficient process might be devised in spite of the relatively high pressure involved.

One of the major operating difficulties anticipated in the processes just discussed would be the formation of scale on the heat-transfer surfaces, although no scale formed in the small test made. By using a piece of equipment alternately in the two stages, the effect of scale might be minimized, since any pentasalt deposit formed during the first stage would tend to be decomposed during the second, while any anhydrite formed during the second would tend to react with the liquor during the first to form pentasalt. There is a fair chance that this repeated shift in equilibrium will cause scale to crack off from the heat-transfer surfaces in much the same way that a scale of anhydrite in a steam boiler disintegrates after proper conditioning of the water is established to make calcium phosphate the stable solid phase.

In the preceding discussion it has been assumed that the syngenite to be decomposed in the two-stage process at 200° C. would be substantially free of impurities. Actually, syngenite made from polyhalite will contain residual magnesium sulfate and sodium chloride derived from mother liquor which cannot be removed completely during washing, with appreciable amounts of anhydrite and small amounts of magnesite and other minerals carried through from the original crude polyhalite. Of these, the magnesium sulfate and the anhydrite are the only ones that need be given serious consideration.

If the total magnesium content of the syngenite, when calculated as magnesium sulfate, is more than about 1.5 percent, appreciable formation of polyhalite will occur in the first stage at 200° C., and this polyhalite will pass through the second stage without being decomposed, causing a corresponding loss of potassium sulfate in the solid discarded from the process. On the other hand, if the magnesium sulfate in the syngenite is kept down to 1.2 percent, experiment has indicated that only 1.9 percent of the potassium sulfate will be lost in the solid residues.³⁵

Anhydrite present in the syngenite reacts rapidly during the first stage at 200° C. to form pentasalt, thereby increasing the quantity of potassium sulfate carried over in the solid to the

³⁵ See reference 3 (p. 902) in list of Bureau of Mines publications (p. 248).

second stage. An excessive quantity of anhydrite will throw the system out of balance, but it should be possible to handle satisfactorily mixtures of syngenite and anhydrite in which the $\text{CaSO}_4 : \text{K}_2\text{SO}_4$ ratio is as high as 1.25, corresponding to a 60-percent excess over the calcium sulfate requirements of pure syngenite. Actual experiment has shown that an 18-gram concentration of K_2SO_4 in the top stage, with an indicated recovery of over 95 percent, is possible in the two-stage treatment when as much as 80-percent excess of calcium sulfate over syngenite is present.

Gypsum admixed with the syngenite as a result of incomplete conversion will affect the balance in the two-stage decomposition at 200°C . in the same manner as a corresponding amount of anhydrite.

In calculating a flow sheet for the process it has been assumed that concentrations of 25 and 10 grams of potassium sulfate per 100 grams of water may be attained respectively in the first and second stages with a loss of only 3 percent of the potassium sulfate in the anhydrite residue from the second stage (see p. 150).

If the ratio of CaSO_4 to K_2SO_4 in the material entering the process is increased above 1.25, the flow diagram must be modified to allow for the use of more water in the second stage. This will tend to reduce the concentration of the liquor leaving the first stage unless the amount of potassium sulfate transferred from the syngenite to the liquor in the first stage can be made to approach the theoretical value more closely.

It would also be possible to concentrate the liquor between the two stages by flash evaporation from 200°C . to the atmospheric boiling point. By employing this expedient, up to 17 or 18 percent of excess water above the quantity required to produce a concentration of 10 grams in the liquor leaving the bottom stage might be used in this stage.

These various factors have been considered, and what is believed to be a conservative scheme of operating such a two-stage treatment process has been developed and discussed in more detail on page 150 of this bulletin.

REMOVAL OF SODIUM CHLORIDE FROM CRUSHED POLYHALITE

Virtually all of the polyhalite deposits in the Permian Basin of Texas and New Mexico contain appreciable quantities of sodium chloride associated with the potassium minerals. The amount varies in the different samples of drill cores removed and examined during the extensive drilling operations. The work has been conducted over a period of years in that region, but even the most careful mining procedure would not permit complete avoidance of salt in the polyhalite. The percentage of sodium chloride in the carload of polyhalite ³⁶ obtained for experimental purposes from the mine of the U. S. Potash Co. was 12.8, and this figure has been accepted as possibly closely representative.

³⁶ See analysis on p. 30.

PURPOSE OF SALT WASHING

Several important reasons justify treatment of the crude polyhalite to eliminate the salt, chief of which is to make better recoveries of the potassium salts in the subsequent treatment. Unless salt is removed, the crystal crops of potassium sulfate and especially the mixtures of potassium and magnesium sulfates would be contaminated. In addition to sodium chloride per se, the contamination results from the formation of glaserite ($\text{Na}_2\text{SO}_4 \cdot 3\text{K}_2\text{SO}_4$), astrakanite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), and various other compounds which form by double decomposition, depending on the particular conditions of concentrations and temperatures obtaining. In spite of the added cost of this treatment its use is deemed desirable.

SPECIFIC EFFECTS OF SODIUM CHLORIDE

Obviously, the presence of 12 to 13 percent of sodium chloride in the crude polyhalite lowers the grade by that extent, but aside from this consideration other important specific effects are apparent. Excessive amounts of salt are objectionable, but moderate quantities are definitely beneficial under properly controlled conditions; and in process 7A (see p. 93), even large amounts can be tolerated. However, better efficiency is possible by extracting the salt, then returning it to the process at the most effective point to take advantage of the beneficial effects during the various extraction steps.

The presence of sodium chloride during hot extraction of the calcined polyhalite inhibits the formation of syngenite and polyhalite (both of which form at fairly rapid rates and thereby remove potassium sulfate from solution) and decreases the percentage extracted. Even higher concentrations of K_2SO_4 are attainable with large amounts (15 to 20 grams per 100 grams H_2O) of sodium chloride, and the production of good yields of schönite is made feasible by merely cooling the extract solutions. A saving in evaporation costs is possible when this procedure is adopted.

Some tendency toward adherence of the crushed polyhalite to the walls of the rotary kiln during calcination has been observed when the temperatures were locally excessive or if fine material were being calcined. Removal of the sodium chloride to about 1 percent obviates this difficulty.

The peculiar conditions necessary to obtain high extractions and recoveries of the potassium salts require that the sodium chloride be present not in excess of approximately 2.0 grams per 100 grams of H_2O in the extract solution and should be present in both the hot- and cold-extraction steps. This condition indicates the desirability for removing the salt from the polyhalite completely before calcination, then returning a limited amount under proper control. Complications prevent salt removal after calcination.

FACTORS CONTROLLING REMOVAL OF SALT

Obviously, the chief objects in removing salt are low costs and minimum losses of valuable salt constituents of the polyhalite.

The pertinent factors are those common to most dissolution processes—particle size; amount of salt to be dissolved; temperature, type, and amount of agitation; time of contact; and volume of water employed. Additional factors characteristic of this specific operation are composition of the solution and the components comprising the salt system. For example, whenever the magnesium sulfate concentration exceeds a certain concentration, double salts of Na_2SO_4 and MgSO_4 will form.

FUNDAMENTAL CHARACTERISTICS

The quantity of polyhalite dissolved, with resultant loss of potassium and magnesium sulfates, depends on the relative rate of solution and the time of solid-liquid contact. In turn, the rate of solution depends on the factors previously enumerated. Furthermore, the use of pure water or of solutions high in magnesium sulfate affects the results materially.

Storch,³⁷ in studies planned to delineate the feasibility of dissolving uncalcined polyhalite either by water or by concentrated salt solutions, to recover the potassium sulfate, showed that appreciable polyhalite could be dissolved in solutions saturated

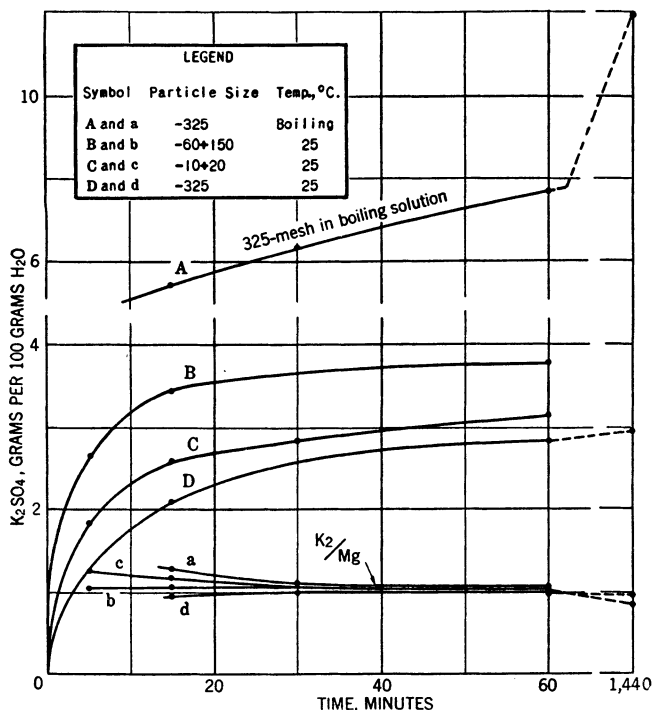


FIGURE 49.—Rate of dissolution of different particle-size fractions of raw polyhalite.

with sodium chloride when finely ground material was extracted near the boiling temperature; appreciably less polyhalite dissolved at temperatures approximating 25°C . Data on the relative amounts and rates of solution are illustrated by curves A and D in figure 49. Similar data for minus 10- plus 20- and minus 60- plus

³⁷ See references 23 and 24 in list of Bureau of Mines publications (p. 249).

150-mesh uncalcined polyhalite treated under slightly different conditions are given by curves *B* and *C* as obtained by Fraas and Davidson.³⁸

An insight into the limitations arising from the joint effects of temperatures and concentrations of the liquors obtained in salt washing is had by observing the $K_2:Mg$ ratios as indicated by curves *a-d* in this same figure. These considerations are independent from the other factors—particle size, rate of agitation, etc.—and actually determine the optimum procedure. Sodium chloride dissolves rapidly and approaches saturation with respect to astrakanite ($Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) in a very short time. This compound crystallizes out first; then, as the potassium sulfate concentration increases, syngenite begins to form also especially at the longer times of liquid-solid contact.

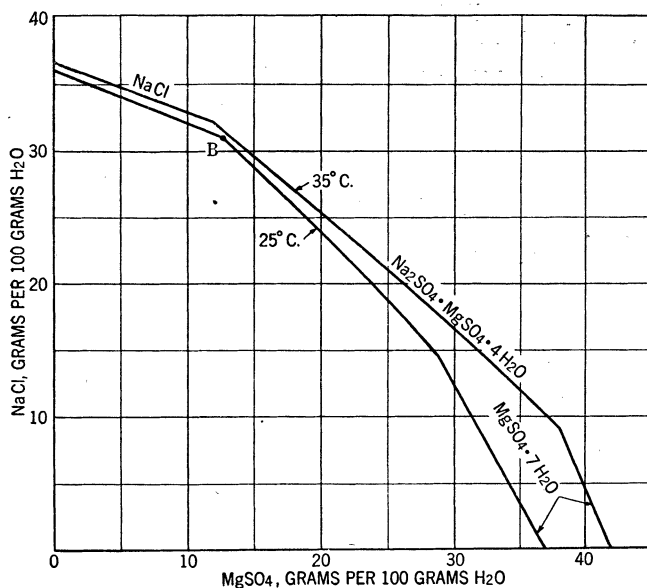


FIGURE 50.—Isotherms for system $NaCl-MgSO_4-H_2O$.

Figure 50 therefore illustrates probable limiting conditions, and point *B* represents the concentration of $MgSO_4$, roughly 13 grams per 100 grams of water, which must not be exceeded for best results. Obviously, at lower magnesium sulfate concentrations slightly higher amounts of sodium chloride may be carried in solution without effecting saturation with any solid phases other than $NaCl$. The small quantity of polyhalite dissolved in the short time required to extract the sodium chloride does not add enough magnesium sulfate to the solutions to reach these concentrations when water is used as extracting solution. However, if dilute waste liquors are utilized in the washing treatment the concentration of the magnesium sulfate must be controlled and maintained at values less than those corresponding to point *B*, or 13 grams $MgSO_4$ per 100 grams of water.

³⁸ See reference 11 in list of Bureau of Mines publications (p. 249)

From these latter experiments and from the data of Storch,³⁹ the optimum conditions for preventing excessive loss of potassium sulfate during the dissolution of the sodium chloride have been made known.

Best results are to be expected by extraction of material as coarse as possible, and due to the higher rate of solubility of the sodium chloride, material even up to three-eighths or five-eighths inch could be treated. Temperatures corresponding to those conveniently possible at the plant location are preferred to more elevated temperatures. A moderate amount of agitation, with use of the minimum volume of water or dilute solution necessary to approach, but not exceed, saturation with either NaCl or astrakanite, would be satisfactory. Furthermore, either dilute solutions purposely made by treating finely ground raw polyhalite with water or waste-process liquors containing small amounts of sodium chloride and relatively low in magnesium sulfate could be employed advantageously.

The losses of potassium sulfate arising from the salt-washing operations will depend on whether water is employed or if dilute solutions, normally destined to be discharged as waste, are available for the salt leaching step. Utilization of the waste liquors for byproduct recovery conceivably might preclude their use for salt washing.

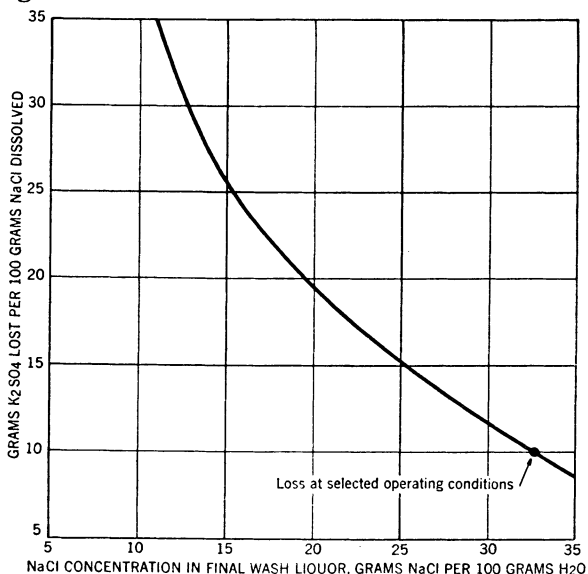


FIGURE 51.—Loss of K_2SO_4 in dissolving NaCl from crushed polyhalite as a function of wash-liquor concentration.

Figure 51 illustrates the probable losses of potassium sulfate when water is used for treating the crude polyhalite. Losses vary, depending on the concentration of sodium chloride attained, which in turn depends on the amount of water employed. The variation, however, is not strictly a linear function. On this curve, a point roughly corresponding to conservative estimated

³⁹ See reference 25 in list of Bureau of Mines publications (p. 249).

losses for this operation is indicated, and this loss has been conceded in the flow sheets and estimated recoveries of the salt-removal process as discussed in part I, page 28.

Unquestionably, losses could be decreased by diverting the waste liquors from the final crystallization steps of the various proposed processes. Table 42 summarizes the volumes and concentrations of these liquors that would be produced in the specific processes enumerated, and table 43 presents data on the conditions related to utilization of these waste liquors for removing the sodium chloride from the crude polyhalite.

TABLE 42.—*Compositions and waste liquors from various extraction processes for each ton of crude polyhalite treated*

Process	Composition, grams per 100 grams H ₂ O			H ₂ O per ton polyhalite, lb.
	K ₂ SO ₄	MgSO ₄	NaCl	
1.....	7.36	29.45	15.90	258
2.....	5.50	33.00	2.00	408
4.....	4.02	12.17	2.10	2,204
4B.....	4.11	26.08	4.82	1,002
5.....	4.25	30.00	10.30	870
7A.....	4.20	22.50	8.90	1,164
8.....	4.00	32.00	1.80	897

TABLE 43.—*Amount and composition of diluted waste liquors usable for salt washing of crude polyhalite*

Process	Diluted composition, grams per 100 grams H ₂ O			Total H ₂ O content, lb.	NaCl dissolution capacity, lb.	Percent usable
	K ₂ SO ₄	MgSO ₄	NaCl			
1.....	2.50	10.0	5.4	760	187	100
2.....	1.67	10.0	.6	1,236	363	71
4.....	3.30	10.0	1.7	1,810	512	50
4B.....	1.58	10.0	1.85	2,610	735	35
5.....	1.42	10.0	3.43	2,510	657	38
7A.....	1.87	10.0	3.96	2,620	684	37
8.....	1.25	10.0	.56	2,340	346	30

Experimental tests, as well as the equilibrium curves shown in figure 50, would suggest that if the waste liquors were diluted to 10 grams of MgSO₄ they could be safely used to extract sodium chloride to a concentration of 30 grams of NaCl without introducing any complications. Calculations based upon this assumption indicate that only in process 1 could all of the waste solution be consumed completely, approximately 30 percent of the discard solutions from process 8 being usable for this purpose. This is fortuitous in that other methods for byproduct utilization of these waste liquors would be possible.

The losses of potassium sulfate arising from unavoidable dissolution of the polyhalite during the leaching of the salt content would be appreciably lower. The loss of K₂SO₄ even though a concentration of 3 grams per 100 grams of H₂O is attained, which is well above the average usually occurring, would be decreased to 5 pounds or possibly lower for each 100 pounds of NaCl removed. Actually a 10-pound loss of K₂SO₄ was assumed as a conservative estimate in the flow sheets and processes discussed in part I.

EVAPORATION AND CRYSTALLIZATION OF POLYHALITE EXTRACT SOLUTIONS

The recovery of the potassium sulfate or of the potassium-magnesium sulfate from the solutions obtained by extracting calcined polyhalite with hot water entails the multiple-effect evaporation of these solutions, with subsequent cooling of the concentrated solutions to crystallize out the saturated phase. The system of special interest is that of K_2SO_4 - $MgSO_4$ - H_2O , although minor amounts of $CaSO_4$ and somewhat larger concentrations of $NaCl$ are usually present. The calcium sulfate invariably separates as syngenite or, in certain instances, as polyhalite but offers no difficulty from scale-forming tendencies and merely acts as a diluent of the primary crystal crop being recovered.

COMPOSITION OF EXTRACT SOLUTIONS

Aside from those processes concerned with the evaporation and crystallization of the K_2SO_4 - $MgSO_4$ liquors, certain processes involve only crystallization; and others present different salts to be recovered, notably processes 6 and 8, which produce potassium sulfide and/or potassium carbonate, and a mixed K_2SO_4 -(NH_4) $_2$ SO_4 product, respectively. It should be noted further that in processes 5 and 5A the bulk of the magnesium salts has been removed, so that the evaporation and crystallization are concerned chiefly with the recovery of the potassium sulfate. The extract liquors to be treated in the various proposed processes are listed in table 44. It should be noted that the processes enumerated involve only the sulfate systems of potassium and magnesium with added sodium chloride.

In addition to the processes listed in table 44, the special methods developed for processes 6 and 8 should be mentioned.

TABLE 44.—*Composition of extract liquors from polyhalite extraction processes*

Process	Concentration, grams per 100 grams H_2O			Products made	Remarks	
	K_2SO_4	$MgSO_4$	$NaCl$		Evaporation step	Crystallization step
1.....	11.0	7.6	1.82	K_2SO_4 , Schönite	Yes	Yes
2.....	12.9	14.0	.35	Yes	Yes
3.....	5.82	0	.24	Leonite,	Yes	Yes
4B.....	11.0	7.6	1.82	K_2SO_4	Yes	Yes
5.....	10.0	.74	.25	K_2SO_4	Yes	Yes
5A.....	25.2	.90	.10	K_2SO_4	Yes	Yes
7.....	12.4	30.0	19.35	Schönite	No	Yes
7A.....	12.4	30.0	19.40	Schönite	No	Yes
	30.4	17.5	1.1	K_2SO_4	No	Yes

Process 6 produces a concentrated solution of potassium sulfide containing also the bisulfide and carbonate as the three major constituents with the thiosulfate, sulfite, and sodium chloride in minor amounts. By treating with carbon dioxide a solution supersaturated with potassium carbonate results, containing an equivalent of 107.7 parts of K_2CO_3 , 1 part of $K_2S_2O_3$, and 1 part of $NaCl$ per 100 parts of H_2O . Evaporation in salt-trap evaporators or

with accessory vacuum coolers yields $\text{K}_2\text{CO}_3 \cdot 1\frac{1}{2} \text{H}_2\text{O}$, with small amounts of other salt impurities, as the final crystalline product.

Process 8 utilizes the sulfate of the calcium sulfate in the original polyhalite, via syngenite to react with ammonia to form ammonium carbonate, with subsequent addition of KCl to produce potassium sulfate-ammonium sulfate by double decomposition. Crystallization from supersaturated solutions is required, with no evaporation, for crystal-crop recovery. Ammonia recovery, by standard stripping methods, would be an essential step, however. Additional discussion of these processes was given in connection with the presentation of the proposed flow sheets in an earlier section of this report (see p. 96).

EQUILIBRIA IN THE SYSTEM K_2SO_4 — MgSO_4 — H_2O

The scope of this bulletin does not permit a detailed discussion of all of the pertinent points regarding the means devised for recovering the potassium sulfate and other mixed crystalline crops from the respective solutions treated in the various processes. However, figure 52 has been prepared to illustrate the

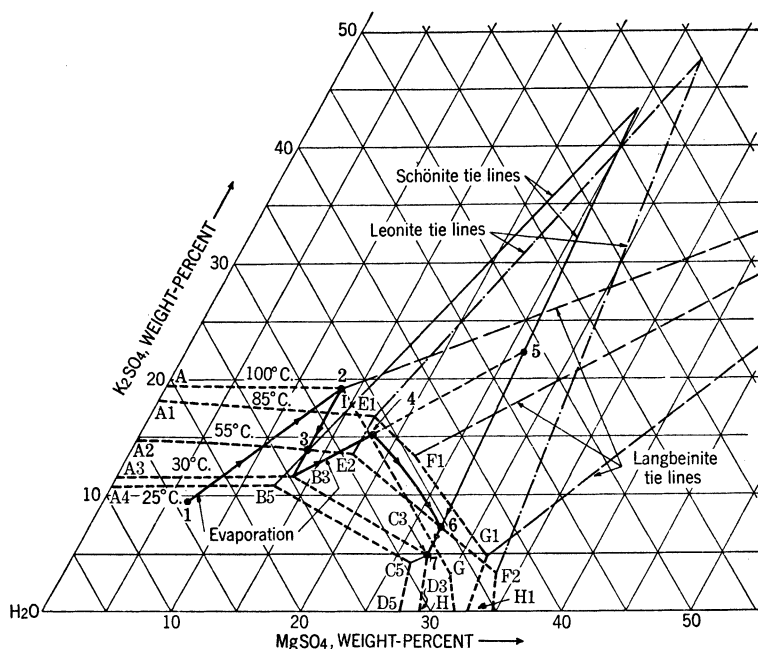


FIGURE 52.—Liquid-phase changes during evaporation and crystallization for recovery of solid phases in system K_2SO_4 — MgSO_4 — H_2O .

general development procedure. In this figure the 25°, 30°, 55°, 85°, and 100°C. isotherms have been plotted on a ternary diagram representing the equilibria upon a weight-percent basis and employing potassium sulfate, magnesium sulfate, and water as the principal components. The heavy dashed lines represent stable equilibria, and the regions of double-salt formation are delineated by the lines radiating from points corresponding to the three-component composition of the double salts and terminat-

ing at monovariant (isothermally invariant) points representing mixtures of two solid phases. Obviously, the tie lines represent the solution-composition changes or crystallization paths. The heavy lines illustrate solution-composition changes during evaporation and crystallization.

An idealized two-stage evaporation procedure has been drawn to show the operations involved in the recovery of a primary crop of K_2SO_4 and a second crop of the double salt, schönite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$). The original composition of an extract solution obtained by treating calcined polyhalite is given by point 1, corresponding to 9.28 percent K_2SO_4 and 6.40 percent $MgSO_4$. On evaporation the composition changes until at point 2 the solution becomes saturated with potassium sulfate at approximately $100^\circ C$. The solution may be cooled to point 3 without regard to cooling rates or amount of agitation, then in the interval 3- B_3 , requires slow controlled cooling to obviate crystallization of metastable compounds; point B_3 is the ultimate limit of attainable concentration and represents the maximum possible recovery. Up to point B_3 , potassium sulfate only crystallizes from solution and further elimination of water, at this temperature, results in coprecipitation of schönite. This behavior is typical of most of the solution compositions obtained in the hot extraction of polyhalite.

At point B_3 , further evaporation at more elevated temperatures causes a change in composition toward point 5, but at 4 attains saturation with leonite ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$), for which the line E_1-F_1 at $85^\circ C$. represents the limit. Temperatures approaching $85^\circ C$. could be utilized to effect the evaporation, but temperatures up to $100^\circ C$. must be avoided to prevent crystallization of langbeinite ($K_2SO_4 \cdot 2MgSO_4$), represented by line $I-G$. Any temperature between 55° and possibly 80° to $85^\circ C$. presumably would offer safe working conditions. Further evaporation from point 4 would therefore cause a solution composition change from 4 to 6, assuming 6 to fall on the $55^\circ C$. line, if this temperature were being used. On removal of the thick liquor from the evaporator and with cooling, leonite would separate along the line 6-7 down to $47.5^\circ C$., whereupon schönite would appear. Point C would then be the final end-liquor composition possible to limit the crystal crop to potassium salt mixtures. At C epsomite ($MgSO_4 \cdot 7H_2O$) would appear at $30^\circ C$., when equilibrium was attained, and if any additional water was removed.

FACTORS CONTROLLING CRYSTAL-CROP YIELDS

Unforeseen complications usually arise when uncontrolled attempts are made to utilize equilibria data as a basis for development of an efficient solute recovery from salt solutions. A knowledge of controlling factors is essential and indispensable. The most important of these are: (1) Rate of approach to equilibrium; (2) the effect of temperature, degree of supersaturation, and amount of agitation; (3) tendency toward metastable equilibria; (4) the effects of rate of heating or cooling; and (5) the effects of the presence of other components, or minor constituents. Conservative operations require an approach to, but safe margin from, final equilibrium and attainment of the compositions correspond-

ing to safe margins, in a relatively short time. Doubtless control of temperature, approach to equilibria, sodium chloride content, and rate of cooling, especially in the temperature interval 50° to 35° C. (122° to 95° F.), in the case of crystallization of potassium sulfate, will constitute the most important factors affecting the results. Figure 53 has been prepared to illustrate the manner in

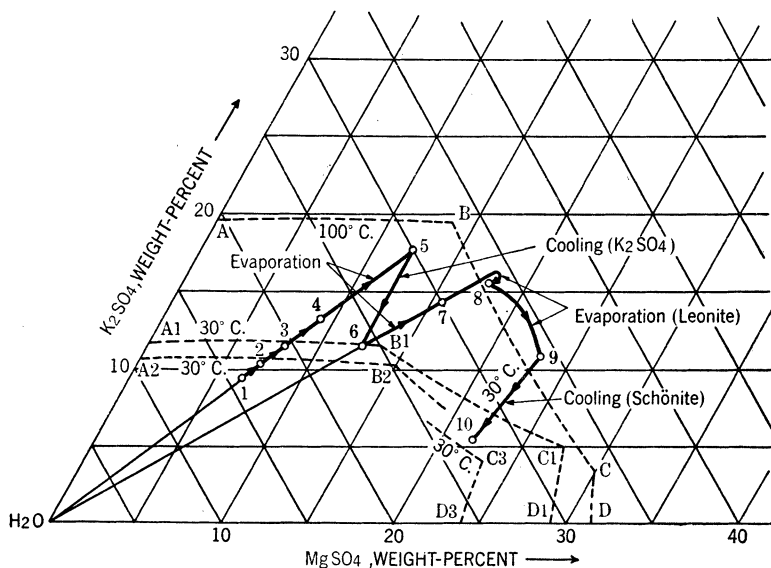


FIGURE 53.—Liquid-phase changes during evaporation and crystallization in system K_2SO_4 — MgSO_4 — H_2O , with added NaCl.

which the evaporation and crystallization procedures have been developed from equilibrium data in the literature, from data confirmed experimentally, and from new data obtained by laboratory tests. The heavy solid lines indicate the change in liquid-phase composition during the evaporation and cooling to produce potassium sulfate as a primary phase with a second evaporation of the potassium sulfate mother liquor to produce a leonite-schönite mixture according to proposed Bureau process 1 (see p. 48).

The starting solution is indicated by point 1 in the diagram and the end liquor discarded as waste is represented by point 10. By the multi-effect evaporation of solution 1 in four equal stages and at temperatures of 55° , 80° , 101.6° , and 120° C., compositions 2, 3, 4, and 5 are reached, respectively, without saturation and hence with no separation of K_2SO_4 during evaporation. The limitation of the amount of water which may be driven off is that corresponding to a magnesium sulfate concentration equivalent to point 6 in the figure. Cooling to 30° C. and crystallization to point 6 would yield a concentration slightly lower in MgSO_4 than B, which is the isothermally invariant point in the K_2SO_4 — MgSO_4 — H_2O system while point B_1 is the corresponding point when 5 grams of NaCl per 100 grams of water are present in the mother liquor, as would be the case in process 1 liquors.

Starrs⁴⁰ found that cooling rates of solutions comparable to point 5 were unimportant until 50° C. was reached, then slow cooling (2 hours) in the interval 50° to 35° C. was imperative to assure further crystallization of K_2SO_4 without contamination with schönite. This fact has been noted and provisions have been made to adopt this cooling procedure for best results in the K_2SO_4 recovery.

Countercurrent feeding of the potash solutions being concentrated would be employed in the first step to prevent separation of crystal in the evaporators, but parallel feeding of the mother liquor to produce the leonite crystal crop suggests itself as a means of maintaining the desirable temperature-concentration relations in the second step. Employing a three-effect evaporator set-up, point 7 would be reached in the first effect operating at atmospheric boiling temperature (101° to 102° C.) with no solid separation. The thick liquor (point 7) would pass to the second effect, operating at 80° C., and result in an appreciable flash evaporation with a simultaneous separation of crystalline leonite. The third and final effect, operating at 55° C. (131° F.), would remove enough water to produce an additional crystal crop and a final liquor composition of point 9. The 5-gram concentration of NaCl at point 6 now will have increased to 15.8 grams per 100 grams of water. This liquor, cooled to 30° C. (77° F.), will yield additional leonite and schönite to make the solution phase equal to point 10. This composition is well above the limiting concentration of point C_3 as located for the system when 16 grams of NaCl is present. The effect of the presence of sodium chloride will be apparent by observing the displacement of C_3 from point C_1 .

By this same scheme, the solution compositions, permissible ranges, necessary temperatures, and final end-liquor concentrations have been determined and incorporated in the various evaporation procedures presented as integral steps in the various processes proposed. Pilot-plant-scale checks on these operations would be desirable and recommended to assure the ultimate success, but a conservative policy has been adopted generally in the crystallizing and cooling procedures. Results even better than those indicated by the procedures incorporated in the processes would be expected; however, it is likely that other unforeseen difficulties would arise also.

⁴⁰ Unpublished data of potash studies at former New Brunswick (N. J.) Station of Bureau of Mines.

APPENDIX A. DETAILED COST ESTIMATES OF VARIOUS EXTRACTION PROCESSES

The details of the estimates of the equipment and direct operating costs for each separate step in the various processes must be considered in the evaluations of these items to arrive at process costs. However, the actual figures are of interest only to those readers who wish to check on the methods used in making such estimates. Therefore, the data covering the plant equipment and direct operating costs have been assembled and are recorded in this section of the report.

EQUIPMENT AND OPERATION COSTS OF PROCESS 1

The calcined polyhalite discharging from moisture-proof bins is conveyed to a small surge bin equipped with a rotating disk or automatic-weighing feed device which delivers the polyhalite to the agitators at the desired rate.

FEEDING CALCINED POLYHALITE

Feeders.—The estimated cost of the feed bin with automatic feed device and auxiliary conveyor with all controls to handle 1,301.6 tons per day is about \$1,925 complete. Power consumption should be about 90 kw.-hr. per day, and the services of a man for one-third of his time are required, equivalent to \$4.80 per day (8 hours at \$0.60). Maintenance, repairs, and supplies should be relatively small. The estimated summarized costs are as follows:

<i>Summarized costs of feeding calcined polyhalite to extraction agitators</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—90 kw.-hr. at \$0.003.....	\$0.27
Labor—8 man-hours at \$0.60.....	4.80
Maintenance and supplies.....	1.00
Total direct operating cost.....	6.07
Depreciation (15 years).....	.40
Combined direct operating and depreciation cost.....	6.47

HOT EXTRACTION OF CALCINED POLYHALITE

Agitators.—To assure the 15 to 20 minutes time necessary for dissolution of the calcined polyhalite and to prevent "short-circuiting" of solids, two 12- by 10-foot continuous agitators equipped with 15-hp. motor stirrers are employed. The 3,505.8 tons of make-up solution added to the agitators daily insure a pulp dilution facilitating the proper suspension and overflow of the extracted solids. The estimated cost of these agitators is \$3,960.

Power.—The two 15-hp. motor stirrers consume full-rated power equivalent to 720 kw.-hr. per day at a cost of \$2.16.

Steam and water.—The water added as make-up solution is charged against the hot extraction and amounts to 652.8 thousand

gallons daily at a cost of \$32.64. The steam consumption in heating the dilute make-up solution to 212° F. corresponds to that necessary for supplying the 100,630,000 B.t.u. required daily to heat the dilute make-up solution from 77° to 212° F. and amounts to 1,084 thousand pounds at a cost of \$433.60.

Labor.—One man per shift operates the agitators at a cost of \$18.00 per day. The other items of operating expense are of minor importance but are included in the summarized estimates.

Summary of operating costs for hot extraction of polyhalite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—720 kw.-hr. at \$0.003.....	\$ 2.16
Labor—24 man-hours	18.00
Steam—1,084 M pounds at \$0.40 per M.....	433.60
Water—652.8 M gallons at \$0.05 per M.....	32.64
Maintenance and supplies.....	2.50
Direct operating cost.....	488.90
Depreciation (10 years).....	1.32
Combined direct operating and depreciation cost.....	490.22

The dissolution of calcined polyhalite is exothermic; this phenomenon is an advantage in decreasing the steam requirements slightly.

FILTRATION OF EXTRACTED GYPSUM RESIDUE

After a 15-minute extraction treatment 90 percent or more of the potassium sulfate in the calcined polyhalite normally is dissolved; once the optimum concentration is attained, the 3,283.2 tons of extract solution should be separated from the 1,524.0 tons of wet filter cake without delay. Continuous rotary vacuum filters have been indicated for this filtration, but a study of the continuous horizontal centrifuge indicates that this machine would effect the separation with little loss in heat in the extract solution and with a satisfactorily low liquor retention in the extracted solids. Both types of machines are adapted to the discharge of the filter cake to facilitate the repulping and preparation of a dispersed thickener feed for the subsequent cold-water leaching treatment.

Equipment.—Estimates indicate that four 14-foot by 18-foot rotary filters are required costing about \$115,000 completely installed, which is slightly higher than the cost of continuous centrifuges.

Power.—The power consumption is estimated at 4,500 kw.-hr. per day at a cost of \$13.50.

Labor.—The services of possibly three operators per shift are necessary to operate the filters, or a total of 72 man-hours per day at an estimated cost of \$54.00.

Maintenance and supplies.—Assuming one set of filter cloths per year, the repairs and supplies for the filters are about \$6.50 per day; this does not include any charge for cooling water used in connection with condensers handling the flash evaporation from the hot liquors.

Depreciation is an important item in the operation of vacuum filters operating on hot solutions and has been included in the table, which summarizes the direct operating costs.

Costs of direct operating and depreciation of filtration equipment

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—4,500 kw.-hr. at \$0.003.....	\$ 13.50
Labor—72 man-hours at \$0.75.....	54.00
Maintenance and supplies.....	6.50
Direct operating cost.....	74.00
Depreciation (15 percent).....	57.50
Combined direct operating and depreciation cost.....	131.50

COLD EXTRACTION OF GYPSUM RESIDUE

The filter cake from the hot extraction, amounting to 1,524 tons every 24 hours, inclusive of retained solution, is repulped with the overflow liquor from No. 2 thickener, and the resulting slurry is charged to No. 1 thickener, from which 3,505.8 tons of solution carrying 169.8 tons of dissolved salts overflow daily. Four 100-foot reinforced-concrete thickeners 10 feet high are employed in countercurrent flow. The wash water, amounting to 4,684.0 tons each 24 hours and to which 37.2 tons of NaCl have been added, is charged to the last thickener.

Equipment.—The cost of the four concrete thickeners, with motors, raking mechanism, pumps, necessary piping, and launders, including repulpers, is estimated at \$74,000 complete. Two quadruplex pumps and the stirring motor on each thickener total 18 hp.

Power.—The total connected load on the thickeners should be about 75 hp. and consume 1,200 kw.-hr. at a daily cost of \$3.60.

Labor.—Labor costs to operate the thickeners should be very small, possibly not averaging more than 2 man-hours per day per thickener, equivalent to 1 man per shift.

Maintenance and supplies.—Repairs and supplies should not exceed 5 cents per day for each \$1,000 invested, or approximately \$4.00.

Water.—No charge is made for the salt used in the wash water, as this is supplied by diverting the necessary amount of the extract liquor from the salt-washing treatment step. Only the 471,000 gallons of water used to discharge the final gypsum residue (911.4 tons dry weight daily), at a pulp ratio of 2 : 1 are charged against the thickening operation. The summarized operating and depreciation costs are:

Costs of countercurrent washing of gypsum residue

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,200 kw.-hr. at \$0.003.....	\$ 3.60
Labor—24 man-hours at \$0.75.....	18.00
Water—471 M gallons at \$0.05 per M.....	23.57
Maintenance and supplies.....	4.00
Direct operating cost.....	49.17
Depreciation (15 years).....	16.50
Combined direct operating and depreciation cost.....	65.67

As the countercurrent-washing treatment can be done at atmospheric temperature and the size of the thickeners is large, the equipment should be placed outdoors and the final gypsum residue

pumped to a tailing pond, where a portion of the discharge water can be reclaimed. However, no deduction in cost of water has been considered in the calculations.

EVAPORATION AND CRYSTALLIZATION OF K_2SO_4 EXTRACT LIQUOR

The 3,283.2 tons of extract liquor from the rotary filters or centrifuges is pumped to quadruple-effect evaporators operating with countercurrent flow and containing about 6,850 square feet of heating surface to evaporate 1,540.7 tons of water. Forced-circulation evaporators installed with the necessary accessories cost \$137,000 and require 964,000 pounds of 30-pound-gage steam every 24 hours.

The cost of cooling water is an important item in a plant situated in New Mexico, where average daily temperatures are relatively high and where rainfall is low and natural water notoriously contaminated with soluble salts. Economy in cooling-water consumption would demand some provision for cooling condenser water by means of either spray ponds or cooling towers. Based upon the use of cooling towers, the cost of the cooling water is taken as \$0.02 per 1,000 gallons used, in comparison with an estimated cost of \$0.05 per thousand gallons for softened water. Details justifying these costs are given in a following section (see p. 171).

Upon the basis of 30 pounds of cooling water per pound of condensate, 2,307,600 gallons are circulated through the condensers and cooling towers daily and cost \$46.15.

Power.—The pumps required for feeding and for forced circulation consume 8,000 kw.-hr. per day.

Labor.—Three attendants consisting of one trained operator and two helpers are needed per shift.

Maintenance and supplies.—Repairs and supplies should amount to about 2½ percent of the total cost or the equivalent of \$11.40 per day.

The summarized costs, including an allowance for depreciation, will be as follows:

Evaporation costs for recovery of K_2SO_4

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—8,000 kw.-hr. at \$0.003.....	\$ 24.00
Labor—72 man-hours at \$0.75.....	54.00
Steam—964 M pounds at \$0.40 per M.....	385.00
Cooling water—2,307 M gallons at \$0.02 per M.....	46.15
Maintenance and supplies.....	11.40
Direct operating cost.....	521.15
Depreciation (15 years).....	30.45
Combined direct operating and depreciation cost.....	551.60

CRYSTALLIZATION OF K_2SO_4

No crystallization of K_2SO_4 occurs in the evaporators, and the 1,742.5 tons of thick liquor after passing through heat exchangers are charged at 190° F. to the vacuum coolers, where a total of 111 tons of K_2SO_4 separates from solution.

Equipment.—The vacuum crystallizers represent a major equipment investment of \$150,000 but serve the dual role of auxiliary

evaporators and continuous crystallizers with efficient operation and control.

Power.—Electric power equivalent to 1,800 kw.-hr. is consumed in the operation of the pumps handling the liquors and cooling water.

Steam.—High-pressure steam (150 pounds gage) is required to supply the necessary vacuum with 30,000 pounds consumed daily.

Cooling water.—It is estimated that 630,000 gallons of cooling water to cost \$12.60 are required also.

Labor.—One skilled operator per shift is necessary.

Maintenance and supplies.—The cost of repairs and supplies, principally for maintenance of the circulating pumps, is estimated at \$12.50 per day.

Depreciation has been included in table 12, giving summarized operating costs.

Costs of vacuum crystallization

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power, 1,800 kw.-hr. at \$0.003.....	\$ 5.40
Steam, 30 M pounds at \$0.40 per M.....	12.00
Cooling water, 630 M gallons at \$0.02 per M.....	12.60
Labor, 24 man-hours at \$0.75.....	18.00
Maintenance and supplies.....	12.50
	<hr/>
Direct operating cost.....	60.50
Depreciation (15 years).....	33.33
	<hr/>
Combined direct operating and depreciation cost.....	93.83
Credit for steam saved from water evaporated.....	53.04
	<hr/>
Net daily cost.....	39.79

During the vacuum cooling of the pregnant liquors, 212.25 tons of water are flash-evaporated so the load on the evaporators will be lightened and a corresponding saving in steam effected. Assuming a quadruple-effect performance of 3.2 pounds of water per pound of steam, the equivalent saving in steam is $\frac{212.25 \times 2,000}{3.2} = 132,500$ pounds per day, or a net equivalent of

\$53.04. This saving should be credited to the vacuum crystallizers, so that the net costs amount to only \$39.79 each 24 hours.

RECOVERY OF K_2SO_4

The potassium sulfate crystallized in the vacuum coolers, with the mother liquor discharged from the last vacuum cooler at 86° F., is pumped to conical settlers for thickening and then fed to top-feed vacuum filters, where 1,578.4 tons of filtrate are obtained for the thin liquor feed to the schönite evaporators and 164.1 tons of wet K_2SO_4 crystals are separated. The potassium sulfate, with retained liquor and including the syngenite which separated, is charged to a rotary dryer where 32.9 tons of water are driven off and a net weight of 131.2 tons of the crude K_2SO_4 product is recovered.

FILTRATION OF K_2SO_4

Equipment.—Vacuum filters to separate the K_2SO_4 from its mother liquor, including all necessary receivers, piping, etc., are estimated at \$7,500.

Power.—The cost of power for operating the filters is estimated at \$1.35, equivalent to a consumption of 450 kw.-hr. per day.

Labor.—The time of an attendant is required for half of each shift.

Maintenance and supplies.—These are estimated to be \$3.00 per day. Depreciation has been added to the direct operating costs, as in previous cost estimates.

Costs of filtering K_2SO_4

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—450 kw.-hr. at \$0.003.....	\$ 1.35
Labor—12 man-hours at \$0.75.....	9.00
Maintenance and supplies.....	3.00
	<hr/>
Direct operating cost.....	13.35
Depreciation (10 years).....	2.50
	<hr/>
Combined direct operating and depreciation cost.....	15.85

DRYING K_2SO_4

Equipment.—The 164.1 tons of wet crude K_2SO_4 are charged to a rotary dryer costing \$12,000 complete with all accessories and consuming 21 barrels of fuel oil daily to expel the 32.9 tons of retained water.

Power.—The power consumption of the rotary dryer is estimated at 630 kw.-hr. per day, costing \$1.90.

Labor.—One man per shift devoting half of his time to the filters and half to the dryer gives a labor cost of \$9.00 per day.

Fuel.—Fuel oil, which should be available in the New Mexico region at \$1.00 per barrel, supplies the necessary heat. At an estimated thermal efficiency of 63 percent, the cost of oil amounts to \$18 per day. The drying costs vary directly with the amount of fuel required, which, in turn, is proportional to the retained water. Low moisture content therefore is essential to low drying costs.

Maintenance and supplies.—Repairs and supplies are estimated to be \$2.62 per day.

Dryer costs for crude K_2SO_4

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—630 kw.-hr. at \$0.003.....	\$ 1.90
Labor—12 man-hours at \$0.75.....	9.00
Fuel—18 barrels oil at \$1.00.....	18.00
Maintenance and supplies.....	2.62
	<hr/>
Direct operating cost.....	31.52
Depreciation (15 years).....	2.67
	<hr/>
Combined direct operating and depreciation cost.....	34.19

EVAPORATION OF K_2SO_4 MOTHER LIQUORS FOR RECOVERY OF SCHÖNITE

Triple-effect forced-circulation evaporators are used to evaporate 776.1 tons of water from the 1,578.4 tons of K_2SO_4 mother liquor obtained at a temperature of 86° F. Parallel feeding with vapor at 212° F. from the last effect of the K_2SO_4 solution evaporators is employed. No crystallization occurs in the first effect, but 82.5 and 193.3 tons of leonite ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) separate in the second and third effects, respectively; and an

additional 69.3 tons of schönite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) separates in the subsequent cooling of the thick liquors. Either integral or auxiliary salt traps are necessary for the last two evaporator effects.

Equipment.—Evaporators having a total of 3,500 square feet of heating surface, complete with circulating pumps, salt traps and surge tanks, and all necessary piping are estimated to cost \$75,000.

Power.—The consumption of power in pumping the solutions and crystallized salts is estimated at 4,000 kw.-hr. per day.

Steam.—The cost of 30-pound-gage steam is the major item of expense and amounts to \$259.20 daily for a 648,000-pound consumption.

Cooling water.—The volume of cooling water required each day is estimated at 1,860,000 gallons, costing \$39.20.

Labor.—It is estimated that two men per shift or a total of 48 man-hours of skilled labor is required.

Maintenance and supplies.—This item is \$5.00 per day. Depreciation and the various other items listed above are summarized as follows:

Evaporation costs for production of schönite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—4,000 kw.-hr. at \$0.003.....	\$ 12.00
Steam—648 M pounds at \$0.40 per M.....	259.20
Cooling water—1,860 M gallons at \$0.02 per M.....	39.20
Labor—48 man-hours at \$0.75.....	36.00
Maintenance and supplies.....	5.00
Direct operating cost.....	351.40
Depreciation (15 years).....	16.67
Combined direct operating and depreciation cost.....	368.07

VACUUM CRYSTALLIZATION OF SCHÖNITE

The 526.5 tons of concentrated liquor at 131° F. are cooled to 86° F. in vacuum crystallizers to separate an additional 69.3 tons of schönite. Approximately, 45,368,000 B.t.u. must be removed during cooling to effect the crystallization.

Equipment.—Vacuum crystallizers of the necessary capacity are about \$15,200 completely installed and require both steam and cooling water to obtain the vacuum and condense the expelled water vapor.

Power.—The daily power consumption for the handling of solutions, crystal crops, and cooling water is estimated at 450 kw.-hr., costing \$1.35.

Cooling water.—The volume of cooling water required by the condensers of the vacuum coolers is 130,600 gallons per day at a cost of \$2.61.

Labor.—Only half the time of an experienced attendant or a total of 12 man-hours per day.

Maintenance and supplies.—The repairs and supplies at 2½ percent of the equipment costs amount to \$1.25 per day. Other items of costs are included in the following summary.

Costs of vacuum cooling for crystallizing schönite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—450 kw.-hr. at \$0.003.....	\$ 1.35
Steam—6 M pounds at \$0.40 per M.....	2.40
Cooling water—130.6 M gallons at \$0.02 per M.....	2.61
Labor—12 man-hours at \$0.75.....	9.00
Maintenance and supplies.....	1.25
Total direct operating cost.....	16.61
Depreciation (15 years).....	3.40
Combined direct operating and depreciation cost.....	20.01
Credit for 22 tons of water evaporated or 18.3 M pounds of steam saved at \$0.40 per M.....	7.32
Net cost of vacuum cooling.....	12.69

RECOVERY OF SCHÖNITE CRYSTAL CROP

The transition of schönite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$) to leonite ($K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$) varies with both the K_2SO_4 and $MgSO_4$ concentrations and ranges from approximately 117.5° to 105.8° F. as the $MgSO_4$ increases. Therefore, leonite is the double salt crystallizing in the evaporators, and schönite should appear only in the vacuum coolers when temperatures fall within the proper range.

Obviously, a saving in cost of dehydration will be obtained if the salt is recovered as leonite. However, since schönite is the form stable at low temperature, possible difficulties might result from the tendency of leonite to hydrate and "set up" during handling or storage in the wet state.

Leonite is recovered from the evaporators and schönite from the coolers by pumping the crystals and mother liquor to conical settlers, where the overflow is returned to the evaporators or discharged to waste as desired. The thickened solids are fed to continuous centrifuges, which discharge the 487.1 tons of wet salts containing the minimum possible amount of retained liquors. Washing of the dewatered crystals has been omitted in the interest of recovery, but at a sacrifice to quality. The chloride content of the dried salt, which can tolerate up to 2.5 percent of equivalent chlorine, is the limiting factor.

Equipment.—The centrifuges, including the conical settling tanks, will cost about \$19,500.

Power.—The power consumption of the centrifuges varies with the moisture content permitted in the crystal product, but greater economy is effected by the expenditure of low-cost electric power than by unnecessary fuel-oil consumption in the dryers. Power of 1,150 kw.-hr. per day is considered ample.

Labor.—With horizontal continuous centrifugal filters, one man per shift is required.

Maintenance and supplies.—The repairs and supplies are estimated at \$7.50 per day.

Summarized estimated costs are as follows:

Costs of filtering schönite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,150 kw.-hr. at \$0.003.....	\$ 3.45
Labor—24 man-hours at \$0.75.....	18.00
Maintenance and supplies.....	7.50
Direct operating cost.....	28.95
Depreciation (10 years).....	6.50
Combined direct operating and depreciation cost.....	35.45

DRYING SCHÖNITE

The 345.1 tons of double salt of potassium and magnesium sulfates, together with retained liquor, are charged to a rotary dryer fired with oil. Free and combined water are expelled to produce 323.2 tons of mixed anhydrous sulfates corresponding to the "kali-magnesia" or sulfate of potash-magnesia consumed by the fertilizer trade.

Equipment.—The two 7- by 55-foot rotary dryers, complete with automatic feeding devices, burners, and motor drives, are estimated to cost \$30,000 installed.

Power.—The power consumption of the rotary dryers is estimated at 1,600 kw.-hr. per day, costing \$4.80.

Labor.—One man per shift is required to handle the two dryers.

Fuel.—The major item of expense of drying the schönite is for fuel oil, and a considerable fraction of the oil consumed is required to evaporate the retained liquor. The heavy, viscous nature of the concentrated magnesium sulfate filtrate increases the water retained, but this moisture should be kept as low as possible.

Calculations show that a total net heat of 431,900,000 B.t.u. is necessary to dissociate and dehydrate the schönite and evaporate the retained water, approximately 44 percent being consumed for the latter purpose. This net heat requires the burning of 118 barrels of oil each day.

Maintenance and supplies.—These have been estimated at \$6.50. The summarized costs are as follows:

Costs of drying schönite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,600 kw.-hr. at \$0.003.....	\$ 4.80
Labor—24 man-hours at \$0.75.....	18.00
Fuel—118 barrels oil at \$1.....	118.00
Maintenance and supplies.....	6.50
Direct operating cost.....	147.30
Depreciation (15 years).....	6.67
Combined direct operating and depreciation cost.....	153.97

COOLING WATER FOR CONDENSERS

The relative scarcity of cooling water and especially the preparation of boiler feed water of the desired degree of purity necessitates the installation of both a water-treating plant and cooling towers of possibly the atmospheric type.

The cooling-water requirements of the condenser water for the evaporators and vacuum coolers are as follows:

Cooling water for process 1

	<i>Water, 1,000 gal.</i>
Evaporators for K_2SO_4	2,307
Vacuum coolers for K_2SO_4	630
Evaporators for schönite.....	1,860
Vacuum coolers for schönite.....	131
Total net cooling water, per day.....	4,928

The combined condensate from the evaporators and coolers producing both K_2SO_4 and schönite is 579.2 tons daily, equivalent to a liberation of 1,180,000 thousand B.t.u. Assuming a cooling range from 114° to 80° F.—that is, 34° F.—the net heat to be dissipated every 24 hours is approximately 1,200 million B.t.u. or the equivalent of the cooling required for 4,170 tons of refrigeration.

Equipment.—Cooling towers to handle this amount of water (3,420 gallons per minute), inclusive of the necessary pumps, are estimated to cost \$22.50 per equivalent ton of refrigeration or approximately \$95,000.

Power.—The principal costs are for depreciation and labor, as the power consumption is only about 1,350 kw.-hr. per day at a cost of \$4.05.

Labor.—One man per shift at \$0.60 per hour or a total of \$14.40 per day is required.

Maintenance and supplies.—This item should not exceed about \$3.50 per day. Other estimated costs are given in the following table.

Costs of cooling condenser water

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,350 kw.-hr. at \$0.003.....	\$ 4.05
Labor—24 man-hours at \$0.60.....	14.40
Maintenance and supplies.....	3.50
Evaporation loss (5 percent) or 246.4 M gallons at \$0.05 per M	12.32
Direct operating cost.....	34.27
Depreciation (15 years).....	21.11
Combined direct operating and depreciation cost.....	55.38

These costs should be increased by \$19.00 to allow for a 6-percent interest charge and by an additional \$5.00 for taxes, insurance, etc., or a total of \$79.38 per day.

Overhead, including supervision and general miscellaneous costs, adds another 12 percent or a final full cost of \$90.20 per day, corresponding to $\frac{9,020}{4,928}$ or \$0.018 per thousand gallons of water.

Thus, a charge of 2 cents per thousand gallons of cooling water used by the condensers is equitable.

EQUIPMENT AND OPERATING COSTS OF PROCESS 2**FEEDING CALCINED POLYHALITE TO HOT-EXTRACTION AGITATORS**

Equipment and operation.—Exactly the same equipment and operating costs are involved as in process 1; these are \$1,925 for machinery and a daily charge of \$6.47 for operation.

HOT EXTRACTION OF CALCINED POLYHALITE

Equipment.—The required agitator capacity is greater than in process 1, to handle the 1,301.6 tons of calcined polyhalite and the 3,699.2 tons of dilute make-up solution from the cold extraction-washing step. Two 14- by 10-foot turbo-mixers with 20-hp. motors are required to assure a 20-minute period of retention, the cost of which is estimated at \$4,500 complete with necessary motors, steel tanks, and steam heating coils.

Power.—Probably full-rated motor capacity equivalent to 720 kw.-hr. per day and costing \$2.16 is required.

Labor.—Cost of labor for one man per shift is \$18 per day.

Steam.—The cost of steam for heating the agitator charge to approximately 212° F. is one of the major items of expense, and doubtless the cold make-up solution should be passed through various heat exchangers to conserve the heat being dissipated in the subsequent steps, possibly in connection with the evaporators. Direct costs with no credit for recuperation are estimated at \$548.00 daily for 1,370,000 pounds of process steam.

Water.—Hard or raw untreated water might conceivably be usable for extraction make-up at a low cost, but to eliminate any chance of difficulty in such use, treated water at an estimated cost of \$0.05 per thousand gallons is suggested. Only the water recovered in the concentrated extract solution is charged to the agitators and amounts to 723.8 thousand gallons daily or \$36.19 every 24 hours.

Maintenance and supplies.—These are estimated to be \$2.50 per day.

The summarized operating costs, together with a depreciation charge, are as follows:

<i>Operating costs of hot extraction of calcined polyhalite</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—720 kw.-hr. at \$0.003.....	\$ 2.16
Labor—24 man-hours at \$0.75.....	18.00
Steam—1,370 M pounds at \$0.40 per M.....	548.00
Water—723,800 gallons at \$0.05 per M.....	36.19
Maintenance and supplies.....	2.50
Direct operating cost.....	606.85
Depreciation (10 years).....	1.50
Combined direct operating and depreciation cost.....	608.35

FILTRATION OF HOT-EXTRACTION MIXTURE AND COLD EXTRACTION OF FILTER CAKE

The filtration of the hot mixture after treatment of the calcined polyhalite and the subsequent countercurrent washing-extraction treatment in continuous thickeners is done by the same equipment as indicated in process 1. However, 464.3 gallons of water are required to hydrate the gypsum and discharge the settled solids from the last thickener and this additional item increases the total costs to \$65.31 or \$1.27 in excess of the costs in process 1.

DISSOLUTION OF SCHÖNITE CRYSTAL CROP

The dissolution of the 1,120.0 tons of wet schönite is accomplished by charging to agitators together with the 3,554.4 tons

of hot extract solution. About 96 million B.t.u. are required daily to dissolve the schönite and raise the temperature of the solution to 158° F., which is the temperature of saturation with K_2SO_4 . The hot extract liquor supplies approximately 6,000,000 B.t.u. per day for each degree (° F.) drop in temperature, so that a net heat absorption corresponding to 16° is involved. Additional heat to offset radiation and conduction losses is necessary, and at least a 20° drop should be allowed. Therefore, it is desirable to keep the extract liquor to a minimum working temperature of 178° F. and higher, if possible, and provide auxiliary heating with submerged steam coils.

Equipment.—To assure a retention of 30 minutes, the schönite dissolvers consist of three 14- by 10-foot turbo-mixers, each provided with a 20-hp. motor and with heating and cooling coils. They are estimated to cost \$10,000 installed complete.

Power.—At full rated load, the power consumption is estimated at 1,080 kw.-hr. per day at a cost of \$3.24.

Labor.—The labor required is estimated at one man per shift or a total cost of \$18.00 per day.

Steam and cooling water.—No charge is made for heating and cooling the solutions, as the use of heat exchangers that are included in the agitators costs provides a means of temperature control.

Maintenance and supplies.—Repairs and supplies are estimated to cost \$3.30 daily.

The summarized costs, including a charge for depreciation, are given in the following table.

<i>Costs of dissolution of schönite</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,080 kw.-hr. at \$0.003.....	\$ 3.24
Labor—24 man-hours at \$0.75.....	18.00
Maintenance and supplies.....	3.30
Direct operating cost.....	24.54
Depreciation (10 years).....	3.30
Combined direct operating and depreciation cost.....	27.84

CRYSTALLIZATION OF K_2SO_4

The pregnant solution resulting from dissolution of the schönite is cooled from 158° to 130° F. in not less than 2 hours to avoid coprecipitation of schönite by the use of the make-up solution from the thickeners en route to the hot extractors. Final cooling (130° to 59° F.) is effected by pumping the solution to vacuum crystallizers provided with vapor compression by means of steam jets or boosters on the final vacuum cooler. Thirty tons of K_2SO_4 , plus 19 tons of syngenite, separate between 158° and 130° F. and a balance of 205.6 tons on subsequent cooling to 59° F.

To cool the 4,625.4 tons of solution to 59° F., approximately 575,000,000 B.t.u. must be removed every 24 hours in the crystallization of the 205.6 tons of K_2SO_4 and the cooling of the solutions. This heat is dissipated by boiling and vapor expulsion, and 240 tons of water should be evaporated in this process. Obviously, this represents an appreciable saving in the steam requirements

for the schönite evaporators, and a credit for this steam should be considered to offset the high investment costs of the vacuum crystallizers.

Equipment.—Vacuum crystallizers, complete with all accessories—including the necessary circulating pumps, salt traps, and conical settling tanks—are estimated to cost \$185,000. This represents a major investment, but the results obtained and the cost of operation justify the expenditure.

Power.—The cost of power for handling the solutions and mixtures of crystallized salts is about 2,250 kw.-hr., a total of \$6.75 daily.

Labor.—The cost of labor (one man per shift or a total of 24 man-hours) is estimated at \$18.00 per day.

Steam.—High-pressure (150-pound-gage) steam is required to operate the boosters to effect the cooling of the final liquors to 59° F., which is approximately 21° F. below average cooling water temperature; 37,500 pounds is consumed daily.

Water.—The cooling water used by the condensers amounts to 1,560 thousand gallons every 24 hours at a cost of \$31.20.

Maintenance and supplies.—The cost of repairs and miscellaneous supplies—lubricants, packing, etc.—is estimated at \$15.65 per day.

The summarized costs for the operation and including a charge for depreciation are as follows:

Costs of crystallizing K_2SO_4 in vacuum coolers

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,250 kw.-hr. at \$0.003.....	\$ 6.75
Labor—24 man-hours at \$0.75.....	18.00
Steam—37.5 M pounds at \$0.40.....	15.00
Cooling water—1,560 M gallons at \$0.02 per M.....	31.20
Maintenance and supplies (2½ percent).....	15.42
Direct operating cost.....	86.37
Depreciation (15 years).....	41.10
Combined direct operating and depreciation cost.....	127.47
¹ Credit for steam saved, 200,000 pounds at \$0.40 per M.....	80.00
Net cost of vacuum crystallization.....	47.47

¹ Based upon triple-effect economy, 2.4 pounds of water per pound of steam.

EVAPORATION FOR RECOVERY OF SCHÖNITE

The evaporation requirements are such that triple-effect evaporators removing one-third of the total of 2,566.4 tons of water to be evaporated in each of three effects can be operated at 215°, 176°, and 131° F., with parallel liquor and vapor flow. This arrangement should result in the crystallization of 116.2 tons of leonite in the second effect and 663.0 tons in the third and places the work of the recovery of the remaining 90 tons of schönite on the vacuum coolers. Salt traps are required only on the last two evaporator effects, as no crystallization occurs in the first effect.

Equipment.—It is estimated that a battery of forced-circulation evaporators with a total of 11,400 square feet of heating surface and a steam (30-pound gage) consumption of 2,139,000 pounds

daily are necessary to evaporate the 2,566.4 tons of water. The cost of these evaporators, with all the latest-type accessories, is \$228,000. Since the vacuum crystallizers employed on the K_2SO_4 and in the final cooling of the thick liquor from the schönite evaporators vaporize about 280 tons of water each 24 hours, some reduction could be made in the size of the evaporators specified. However, to provide a liberal estimate for the necessary equipment, no decrease in capacity or a possible lower equipment cost is considered.

Power.—The daily power requirements are 12,000 kw.-hr. at a cost of \$36.00 per day.

Labor.—Possibly three skilled operators are required per shift, or a total of 72 man-hours per day at a cost of \$54.00.

Steam.—The cost of the 2,139,000 pounds of steam required daily is \$855.60, which represents one of the principal items of expense in the operation of this process.

Water.—The cooling water required for the condensers of the evaporators is estimated at 616,000 gallons daily, costing \$123.20.

Maintenance and supplies.—Maintenance and supplies are estimated to be about \$15.00 per day.

The total direct operating costs, with an estimated cost for depreciation, are as follows:

Operating and depreciation costs for schönite evaporators

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—12,000 kw.-hr. at \$0.003.....	\$ 36.00
Labor—72 man-hours at \$0.75.....	54.00
Steam—2,139,000 pounds at \$0.40 per M.....	855.60
Cooling water—616,000 gallons at \$0.02 per M.....	123.20
Maintenance and supplies.....	15.00
Direct operating cost.....	1,083.80
Depreciation (15 years).....	50.67
Combined direct operating and depreciation cost.....	1,134.47

FINAL CRYSTALLIZATION OF SCHÖNITE

Vacuum cooling is employed as a means for recovering the 90 tons of schönite which separate on the cooling of the 996.8 tons of thick liquor from the final effect of the evaporators from 131° to 59° F. The final vacuum cooler is equipped with the steam-jet vapor compressor or booster to compensate for the high-cooling-water temperature of 80° F.

Equipment.—Vacuum crystallizers of a capacity large enough to handle 996.8 tons of liquor feed and dissipate approximately 110,000,000 B.t.u. in the cooling of solution and crystal mixtures and absorption of the heat of crystallization will cost \$36,700 complete with all accessories, including the necessary conical settling tank to handle the combined crystal product from evaporators and vacuum coolers. Both steam (150-pound gage) and cooling water are required for the vacuum coolers.

Power.—The daily power consumption is 800 kw.-hr., costing \$2.40.

Labor.—One man per shift or a total of 24 man-hours, costing \$18, is required.

Steam.—The amount of high-pressure steam (150-pound gage) is about 12,000 pounds each day, costing \$4.80.

Cooling water.—An appreciable quantity of cooling water must be circulated through the condensers to carry off the heat evolved. This is estimated to require 488,000 gallons daily at a cost of \$9.76.

Maintenance and supplies.—The cost of this item is estimated to be \$3.15 every 24 hours.

The summarized costs of operation, including depreciation, are as follows:

<i>Costs of crystallizing final schönite liquors</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—800 kw.-hr. at \$0.003.....	\$ 2.40
Labor—24 man-hours at \$0.75.....	18.00
Steam—12,000 pounds at \$0.40 per M.....	4.80
Water—488,000 pounds at \$0.02 per M.....	9.76
Maintenance and supplies.....	3.15
Direct operating cost.....	38.01
Depreciation (15 years).....	8.15
Combined direct operating and depreciation cost.....	46.16
Credit for 42.5 tons of water evaporated equal to saving of 35,400 pounds steam at \$0.40 per M.....	14.16
Net cooling and crystallizing cost.....	32.00

FILTRATION OF SCHÖNITE CRYSTAL CROP

The combined crops of crystalline solids obtained from the evaporators and vacuum crystallizers are pumped to a settling tank, and the thickened crystal magma is discharged from the bottom to continuous centrifuges provided for a thorough washing treatment. The 944.8 tons of schönite, after washing in the centrifuge with 264.0 tons of water daily, amount to 896.0 tons carrying an additional 224 tons of retained water. This washed schönite is charged, without drying, to the dissolution step to which the hot concentrated polyhalite-extract solution is being added. Overflow from the conical settling tanks and filtrate and washings from the centrifuges, amounting to 918.8 tons daily, are pumped to waste.

Equipment.—The cost of the centrifuges with all necessary accessories is \$40,000.

Power.—The power consumed in the operation of the centrifuges and in handling the crystal product and waste solutions is 2,300 kw.-hr. per day, costing \$6.90.

Labor.—One man per shift, or a total of 24 man-hours, costing \$18.00 per day, is required.

Wash water.—Cold wash water, amounting to 264 tons every 24 hours and costing \$3.17 per day, is used in the thorough washing of the schönite crystal crop. Retained mother liquor must be eliminated as completely as possible at this point to prevent the build-up of MgSO_4 in the system.

Maintenance and supplies.—These costs are estimated to amount to \$15.00 daily.

Depreciation is a relatively important item in the cost of centrifuging and has been included in the following summarized costs:

Costs of filtering schönite crystal crop

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,300 kw.-hr. at \$0.003.....	\$ 6.90
Labor—24 man-hours at \$0.75.....	18.00
Water for washing—63,400 gallons at \$0.05 per M.....	3.17
Maintenance and supplies.....	15.00
Direct operating cost.....	43.07
Depreciation (10 years).....	13.33
Combined direct operating and depreciation cost.....	56.40

FILTRATION OF K_2SO_4 CRYSTAL CROP

The crystallized K_2SO_4 and mother liquor, totaling 4,674.4 tons daily, are discharged from the K_2SO_4 crystallizers and pumped to conical settling tanks to produce a crystal sludge for feeding to the centrifugal separators. The 244.8 tons of mixed K_2SO_4 and syngenite are separated from the mother liquor and charged directly to rotary dryers, where the retained liquor is driven off; the weight of final product is 263.4 tons of anhydrous salts.

Equipment.—Assuming centrifugal filtering machines, the cost for the necessary installed capacity is \$15,000.

Power.—The power to operate the centrifugal separators represents a 50-hp. load, or 900 kw.-hr. per day, and costs \$2.70.

Labor.—About two-thirds of the time of one operator, or a daily allotment of 16 man-hours per day at a cost of \$12.00, is necessary.

Maintenance and supplies.—Repairs and maintenance cost about \$6.00 per day.

No washing is provided for, as the retained magnesium sulfate is not objectionable to the fertilizer trade, but where K_2SO_4 is intended for chemical uses, a portion of the output is subjected to a wash.

The estimated costs of filtering the K_2SO_4 are given in the following table.

Costs of filtering K_2SO_4

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—900 kw.-hr at \$0.003.....	\$ 2.70
Labor—16 man-hours at \$0.75.....	12.00
Maintenance and supplies.....	6.00
Direct operating cost.....	20.70
Depreciation	5.00
Combined direct operating and depreciation cost.....	25.70

DRYING K_2SO_4

The wet K_2SO_4 crystal crop, carrying with it 19 tons of syngenite, is charged to rotary dryers heated by fuel oil. The drying treatment expels 69.6 tons of water, largely present as free moisture, to produce a final product of 263.4 tons of crude material containing 245.6 tons of K_2SO_4 equivalent to a 93-percent product.

Equipment.—A rotary 90- by 50-inch dryer costs \$19,500 delivered at Carlsbad, and probably about \$20,700 completely installed with all accessories—oil burners, motor drives, reducing gears, and dust-collecting chamber.

Power.—The electric power to operate the dryer is 1,160 kw.-hr. per day and costs \$3.48.

Labor.—Half the time of an attendant (a total of 12 hours per day) is required to operate the dryer. At \$0.75 per hour this amounts to \$9.00 per day.

Fuel oil.—To dry the wet potassium sulfate, 69.6 tons of water must be driven off and a small quantity of associated salts must be dehydrated. The net heat requirements have been calculated to be approximately 135,000,000 B.t.u. per day, which requires burning 37 barrels of fuel oil costing \$37.

Maintenance and supplies.—Repairs and maintenance have been estimated to cost \$6.67 per day.

Costs of drying K_2SO_4 product

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,160 kw.-hr. at \$0.003.....	\$ 3.48
Labor—12 man-hours at \$0.75.....	9.00
Fuel oil—37 barrels at \$1.00.....	37.00
Maintenance and supplies.....	6.67
	<hr/>
Direct operating cost.....	56.15
Depreciation (15 years).....	4.60
	<hr/>
Combined direct operating and depreciation cost.....	60.75

EQUIPMENT AND OPERATING COSTS OF PROCESS 3

The 1,301.6 tons of minus 10-mesh calcined polyhalite are added to the extraction agitators continuously by means of an automatic feeding device.

Equipment and operating costs for feeding.—The cost of the feeders is \$1,925 and the operating charge \$6.07 per day, as in processes 1 and 2.

HOT EXTRACTION OF CALCINED POLYHALITE

The 6,126.6 tons of dilute wash liquors used daily for make-up solution for the hot-extraction step are heated to temperatures near 212° F. by being passed through heat exchangers, possibly conserving some of the heat from the evaporator condensates. The heat evolved during dissolution of the calcined polyhalite maintains the agitators at the boiling temperature, but additional steam amounting to 1,890,000 pounds per day is required to supply the major portion of the heat.

Equipment.—To assure a 20-minute solid retention three 14- by 10-foot continuous agitators equipped with 20-hp. motor stirrers are required. This equipment, complete with tanks but not including heat exchangers, costs \$6,750 installed.

Power.—At full-rated power the daily consumption of electricity is 1,080 kw.-hr., costing \$3.24.

Labor.—One man per shift or a total of \$18.00 per day.

Steam.—With no allowance for waste-heat recovery, 1,890,000 pounds of 30-pound-gage steam are required to heat the agitators to 212° F. This costs \$756.00 per day.

Water.—Only the water recovered in the hot extract solution, amounting to 5,491.2 tons (1,318,000 gallons) each day, is charged against the agitators at a cost of \$65.89.

Maintenance and supplies.—This item is estimated at about \$3.75 per day.

Depreciation.—On this and all subsequent processes a general charge of 11.4 percent of the estimated installed equipment costs is made and included in the final summary of all production costs. This depreciation rate represents the average of the results obtained by applying a specific period of depreciation to each special type of equipment considered in connection with processes 1 and 2.

Costs of hot extraction of calcined polyhalite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,080 kw.-hr. at \$0.003.....	\$ 3.24
Labor—24 man-hours at \$0.75.....	18.00
Steam—1,890,000 pounds at \$0.40 per M.....	756.00
Water—1,318,000 gallons at \$0.05 per M.....	65.89
Maintenance and supplies.....	3.75
	<hr/>
Direct operating cost.....	846.88

FILTRATION OF GYPSUM

The hot mixture resulting from extraction of the calcined polyhalite is filtered with the minimum possible delay. This is accomplished by either continuous vacuum filters or by horizontal continuous centrifugal filters. Employing the former type requires a slightly higher capacity than in processes 1 and 2, in that nearly 50 percent more solids and liquids must be handled. However, the daily weight of filter cake is smaller. The weight of filtrate per day is 6,096.0 tons, and wet filter cake amounts to 1,332.2 tons every 24 hours. Assuming about the same filter area, a larger vacuum capacity as well as provision for handling an increased amount of vapor condensate is necessary.

Equipment.—The estimated cost of vacuum filters to handle this step of the process is \$145,000, or about 25 percent greater than on the previous two processes.

Power.—The daily power consumed in operating the vacuum filters is 6,750 kw.-hr., costing \$20.25.

Labor.—The labor requirements are three men per shift or a total of \$54.00 per day.

Maintenance and supplies.—These are estimated to be about \$9.75 per day, assuming one complete new set of filter cloths for each filter per year.

The direct operating costs for filtering the polyhalite residue are given in the following table:

Costs of filtering gypsum

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—6,750 kw.-hr at \$0.003.....	\$20.25
Labor—72 man-hours at \$0.75.....	54.00
Maintenance and supplies.....	9.75
	<hr/>
Direct operating cost.....	84.00

COLD COUNTERCURRENT WASHING OF GYPSUM RESIDUE

The 1,332.2 tons of unwashed filter cake are repulped and charged to four 100- by 10-foot thickeners, exactly the same as in process 1. If desired, wash water can be employed in any amount up to 6,441.7 tons daily, a treatment which assures the

complete dissolution of all of the K_2SO_4 and $MgSO_4$ as well as all of the secondary salts formed during the hot extraction. The final gypsum residue is discharged to waste as a thickened sludge consisting of 1,718.4 tons of free water and 859.2 tons of solids (dry weight), containing only 6.4 tons of K_2SO_4 or less than 2 percent of that originally charged in the calcined polyhalite.

Equipment.—The cost of a set of four 100-foot thickeners complete with reinforced-concrete tanks and all necessary accessories, pumps, motor drives, rakes, launders, etc., is \$74,000.

Operating costs.—The operating costs of the thickeners are the same as for processes 1 and 2, except for a slight correction for water used; this item corresponds only to the water used to discharge the final thickened sludge, and a portion of the water may be reclaimed. The estimated costs are as follows:

<i>Costs of countercurrent washing of gypsum residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,200 kw.-hr. at \$0.003.....	\$ 3.60
Labor—24 man-hours at \$0.75.....	18.00
Water—445,000 gallons at \$0.05 per M.....	22.25
Maintenance and supplies.....	4.00
Direct operating cost.....	47.85

LIME-SLURRY TREATMENT OF EXTRACT LIQUOR

The precipitation of the magnesium sulfate in the 6,096.0 tons of extract solution handled daily is accomplished by adding 335.2 tons of hot lime slurry containing an excess of lime to form $Mg(OH)_2$. Precipitation is accomplished by a 5-minute retention at 212° F. to prevent excessive formation of pentasalt ($K_2SO_4 \cdot 5CaSO_4 \cdot H_2O$) whose equilibrium concentration of K_2SO_4 with pentasalt and gypsum or hemihydrate as solid phases controls the attainable concentration.⁴¹ Dissolution of minor amounts of pentasalt can be accomplished during the cold-water countercurrent washing treatment. Filtration of the precipitated $Mg(OH)_2$ and calcium sulfate (anhydrite) is done without delay by continuous filters.

The reacting mixture is heated by conserving as much as possible of the heat in the polyhalite extract-liquor supplemented by additional heat from exchangers and steam coils placed in the slurry mixer. This auxiliary heating required corresponds to about a 17° F. temperature rise of the whole reacting mass of 6,421.2 tons.

Equipment.—One 14- by 10-foot turbo-mixing tank provided with a 20-hp. motor is large enough to allow a 5-minute precipitation time; complete with heating coils and all accessories, this costs \$2,250.

Power.—The power consumption closely approaches full connected load or about 360 kw.-hr. costing \$108 per day.

Labor.—Half of the time of one operator is necessary to slake the lime for the lime slurry and attend to the magnesia precipitation. The daily cost therefore is \$9.00.

Steam.—Assuming that the heat of reaction of the lime on slaking would permit the lime slurry and the extract liquors from

⁴¹ See figure 57, p.

the hot extraction of the polyhalite to be maintained at 185° F., then the additional heating to 212° F. would require approximately 186,000,000 B.t.u., equivalent to about 191,000 pounds of 30-pound-gage steam. The cost of this steam is \$76.40 per day.

Water.—Only the water retained in the filter cake, both free and combined and amounting to 448.0 tons or 107,520 gallons of water daily, is charged against the slurry mixers—that is, \$5.32 per day.

Cost of lime.—The 112.0 tons of CaO required daily correspond to approximately 120 tons of high-calcium commercial lime. This is produced in an auxiliary lime plant that entails an investment of about \$100,000. The cost of such quicklime is about \$5.50 per ton inclusive of all costs.

Maintenance and supplies.—This item probably does not exceed \$2.00 per day.

Costs of precipitation of magnesia by lime

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—360 kw.-hr. at \$0.003.....	\$ 1.08
Labor—12 man-hours at \$0.75.....	9.00
Steam—191,000 pounds at \$0.40 per M.....	76.40
Water—107,520 gallons at \$0.05 per M.....	5.32
Lime—120 tons at \$5.50.....	660.00
Maintenance and supplies.....	2.00
Direct operating cost.....	753.80

FILTRATION OF PRECIPITATED MAGNESIUM HYDROXIDE-GYPSUM

Rapid filtration with recovery of filtrate as hot as possible is desirable. Centrifugal filters are used for this purpose and the wet filter cake (amounting to 825.6 tons daily and containing 412 tons of retained water carrying 24.8 tons of soluble K_2SO_4) is discharged without washing to repulpers feeding the dispersed filter cake to countercurrent thickeners.

Equipment.—The three 14- by 18-foot vacuum filters, with 4,750 square feet of filtering to handle the filtration of the K_2SO_4 liquors, cost \$57,500 and consume 2,250 kw.-hr. daily.

Power.—The 2,250 kw.-hr. of electrical power consumed daily cost \$6.75.

Labor.—Two operators per shift or a total expenditure of \$36.00 per day is required for labor.

Maintenance and supplies.—Repairs and supplies are about \$4.75 per day. The filtration costs are as follows:

Costs of filtration of magnesium hydroxide-gypsum

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,250 kw.-hr. at \$0.003.....	\$ 6.75
Labor—48 man-hours at \$0.75.....	36.00
Maintenance and supplies.....	4.75
Direct operating cost.....	47.50

WASHING MAGNESIUM HYDROXIDE-GYPSUM FILTER CAKE

The 825.6 tons of wet magnesium hydroxide-gypsum are repulped to remove the retained liquor with its 24.8 tons of K_2SO_4 . The economics of using simply a displacement water wash on the filters or the installation of a series of thickeners to fully recover

the K_2SO_4 being retained in the precipitate will require some study to determine if the greater recovery, possibly an extra 12.4 tons of K_2SO_4 , justifies the added expense.

The gelatinous nature of the precipitated magnesium hydroxide-gypsum makes recovery of the retained liquor difficult, and re-pulping and thorough washing of the filter cake are necessary; a liberal settling area is essential to attain the desired degree of thickening.

Wide latitude in the distribution of the water entering the system is possible, and the relative amounts necessary to thoroughly remove the K_2SO_4 retained by the filter cake from the hot extraction of polyhalite and in the filter cake from the magnesia precipitation may be proportioned as needed. The quantity of water shown in the flow sheet is 1,466.3 tons daily to yield 930.3 tons of overflow containing 24.8 tons of K_2SO_4 and 1,361.6 tons consisting of 907.2 tons of free water in the gypsum-magnesium hydroxide sludge discharged to waste from the thickeners.

To provide liberal settling capacity to handle the 454.4 tons of solids occurring as the precipitate from the lime treatment, three 100- by 10-foot thickeners equivalent to 17 square feet of settling area per ton-day of solids are employed. This thickener capacity corresponds to three-fourths of that required in the washing of the residue from the hot extraction of the calcined polyhalite.

Equipment.—The cost of three 100-foot thickeners, completely installed with motor drives, rakes, sludge pumps, launders, etc., is \$55,500.

Powers.—The power consumed daily in driving the thickener rakes and pumping the overflow and the thickened solids is 900 kw.-hr., costing \$2.70.

Labor.—About two-thirds of the regular time of one attendant, equal to 16 hours per day or \$12.00, is expended on the thickeners and accessories.

Water.—The water to be charged against the washing operation is the amount in the discarded thickened sludge in excess of that present in the filter cake when charged to the thickener washing system. This is 338.4 tons, equivalent to 81,216 gallons or \$4.06 per day.

Maintenance and supplies.—These amount to possibly \$3.00 per day.

Operating costs of washing magnesium hydroxide-gypsum

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—900 kw.-hr. at \$0.003.....	\$ 2.70
Labor—16 man-hours at \$0.75.....	12.00
Water—81,216 gallons at \$0.05 per M.....	4.06
Maintenance and supplies.....	3.00
Direct operating cost.....	21.76

EVAPORATION OF K_2SO_4 LIQUORS

The economic feasibility of this process depends largely on the efficient evaporation of the large amount of 5,181.6 tons of water daily, corresponding to 16.4 times the weight of K_2SO_4 recovered. Efficient multiple-effect evaporation, therefore, is indispensable

and quadruple-effect evaporators operating with concurrent steam and liquor flow are used without auxiliary vacuum coolers.

Equipment.—The quadruple-effect forced-circulation evaporators with 23,000 square feet of evaporating surface and complete with all the necessary accessories, salt traps, and conical settling tanks and latest control devices are estimated to cost about \$450,000.

Power.—The daily power requirements are 28,500 kw.-hr., costing \$85.50 every 24 hours.

Labor.—Four men per shift are required to operate the evaporators or 12 per day at a cost of \$72.00.

Steam.—Assuming average efficient quadruple-effect evaporator performance—that is, an evaporation of 3.2 pounds of water per pound of steam—the amount of 30-pound-gage steam consumed per day is 3,240,000 pounds, costing \$1,296.

Cooling water.—The volume of cooling water circulated through the condensers of the evaporators is 9,326,880 gallons daily, costing \$186.54.

Maintenance and supplies.—These are estimated to amount to \$37.50 per day.

The summarized costs of evaporation then will be:

<i>Costs of evaporation of K_2SO_4 liquors</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—28,500 kw.-hr. at \$0.003.....	\$ 85.50
Labor—96 man-hours at \$0.75.....	72.00
Steam—3,240,000 pounds at \$0.40 per M.....	1,296.00
Cooling water—9,326,880 gallons at \$0.02 per M.....	186.50
Maintenance and supplies.....	37.50
Direct operating cost.....	1,677.50

FILTRATION AND RECOVERY OF K_2SO_4 CRYSTAL CROP

The crystallized K_2SO_4 resulting from the evaporation step and collected in the salt traps is pumped to open conical settling tanks. The excess mother liquor is returned to the evaporators, and the thickened crystal crop is fed to centrifugal separators for removal of as much of the retained liquor as is feasible. The 424 tons of wet K_2SO_4 crystals are then discharged to oil-fired rotary dryers, where 84.8 tons of water are expelled and 339.2 tons of crude potash containing 316.0 tons of K_2SO_4 obtained every 24 hours.

The continuous centrifuges are the same as those required for the schönite filtration in process 1. The cost of this equipment is \$19,500, and the operating expense exclusive of depreciation is \$28.95 per day.

DRYING K_2SO_4

The dryer requirements are different from those specified for the handling of the schönite in process 1, and the fuel consumption likewise is different.

Equipment.—Dryers to handle the drying of the 339.2 tons of crude potassium sulfate cost \$20,700 complete.

Power.—The amount of electric power required to operate the dryers is 1,160 kw.-hr. per day, costing \$3.48.

Labor.—Only half the time of one attendant (12 man-hours per day at \$9.00) is required for labor on the dryers.

Fuel.—Fuel-oil expense is a major item and corresponds to a consumption of 45 barrels at \$1.00 per barrel or \$45.00 per day.

Maintenance and supplies.—These are estimated to amount to \$6.65 per day. The direct operating costs for drying the crystallized K_2SO_4 are as follows:

<i>Costs of drying K_2SO_4</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,160 kw.-hr. at \$0.003.....	\$ 3.48
Labor—12 man-hours at \$0.75.....	9.00
Fuel oil—45 barrels at \$1.00 per barrel.....	45.00
Maintenance and supplies.....	6.65
Direct operating cost.....	64.13

EQUIPMENT AND OPERATING COSTS OF PROCESS 4

In general, the type of equipment required for process 4 is very similar to that recommended for the other processes discussed; the principal difference is the suggested use of a ball mill in closed circuit with a classifier to grind the calcined polyhalite being converted to syngenite. Another point that should be noted is the absence of any evaporation. Vacuum filters likewise are chosen as the means of separating the syngenite-gypsum and syngenite products from their solutions without the use of large thickener units.

FEEDING CALCINED POLYHALITE TO CONTINUOUS AGITATORS AND TO BALL MILLS

Two automatic feeders with separate surge bins and conveyors are required to charge the 812.1 tons to the agitators and the 489.3 tons of calcined polyhalite to the ball mills.

Equipment.—The estimated cost of the two separate feeders with necessary accessories is \$3,500.

Power.—The electric power consumed daily by the feeders will be 180 kw.-hr. at a cost of \$54.

Labor.—Possibly about two-thirds of the regular time of one attendant (a total of 16 hours per day) at a cost of \$9.60 is required to operate the feeders, conveyors, and various controls.

Maintenance and supplies.—This expense totals \$1.00 every 24 hours.

The total direct operating costs of feeding the calcined polyhalite are as follows:

<i>Costs of feeding calcined polyhalite</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—180 kw.-hr. at \$0.003.....	\$ 0.54
Labor—16 man-hours at \$0.60.....	9.60
Maintenance and supplies.....	1.00
Direct operating cost.....	11.14

HOT EXTRACTION IN CONTINUOUS AGITATORS

This extraction is made exactly the same as in process 1, except that the 812.1 tons of polyhalite and 2,185.5 tons of solution charged daily are 64.2 percent of the amount treated by that process. Heat is conserved by passing the hot filtrates through

heat exchangers to supply heat for the make-up solution, since concentrated K_2SO_4 is to be used in the syngenite conversion step at 122° F. rather than being pumped to evaporators at the highest practical temperature.

Two 12- by 10-foot continuous agitators equipped with auxiliary steam coils and stirred by means of 20-hp. motors are used.

Equipment.—These agitators, with motor drives, reducing gears complete with tanks, piping, etc., cost \$3,960 completely installed.

Power.—Based upon full rated horsepower connected, the daily electric power consumption is 720 kw.-hr., costing \$2.16.

Labor.—Operating labor consists of one man per shift, or a total of \$18.00 per day.

Water.—The amount of water required each day is charged upon the basis of recovery in the concentrated extract and amounts to 1,696.0 tons or 407,040 gallons at a cost of \$20.35.

Steam.—The daily steam consumption, with no allowance for heat recuperation, supplies about 693,000,000 B.t.u. and amounts to 715,000 pounds of 30-pound-gage steam at a cost of \$286.00. In practice, the judicious installation of heat exchangers for which an extra equipment allowance has been made in the final total plant cost estimates reduces this steam consumption appreciably.

Maintenance and supplies.—This item is estimated at \$2.50 per day.

Summarized costs of hot extraction of calcined polyhalite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—720 kw.-hr. at \$0.003.....	\$ 2.16
Labor—24 man-hours at \$0.75.....	18.00
Steam—715,000 pounds at \$0.40 per M.....	286.00
Water—407,040 gallons at \$0.05 per M.....	20.35
Maintenance and supplies.....	2.50
Direct operating cost.....	329.01

FILTRATION OF GYPSUM RESIDUE

The calcined polyhalite after a 15- to 20-minute extraction at 212° F. in the continuous agitators is fed directly to continuous vacuum or centrifugal filters, and the undissolved solids, largely calcium sulfate, are separated as quickly as possible and the 953.0 tons of wet filter cake repulped and washed in the countercurrent thickeners while the 2,044.8 tons of hot extract containing 186.4 tons of K_2SO_4 every 24 hours are first passed through heat exchangers and then pumped to the syngenite agitators.

Approximately 1,900 square feet of filtering area are required to handle the 953.0 tons of wet filter cake, and this needs three 14- by 8-foot vacuum filters costing \$86,500, completely installed with all necessary accessories, piping, vacuum tanks, filtrate storage receivers, etc.

Power.—The electric power consumption of the filters and vacuum and solution pumps is 3,400 kw.-hr. per day, costing \$10.20.

Labor.—Two men per shift receiving \$6.00 each or a total of \$36.00 per day represent the labor for operating the filters.

Maintenance and supplies.—The cost of lubricants, pump packing, filter-cloth replacement, and general repairs is estimated at \$5.00 per day.

Some additional expense will be incurred for cooling water for condensing the flash evaporation occurring during the vacuum filtration, but this cost will vary considerably with the operating temperatures. An allowance is made in the final estimates for this and other miscellaneous expense not exactly predictable. The known operating expenses are as follows:

<i>Costs of filtering gypsum residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—3,400 kw.-hr. at \$0.003.....	\$10.20
Labor—48 man-hours at \$0.75.....	36.00
Maintenance and supplies.....	5.00
Direct operating cost.....	51.20

WASHING GYPSUM RESIDUE

The filter cake from the hot extraction is repulped with overflow solution from No. 2 thickener and fed to No. 1 thickener to produce a clarified overflow of 2,185.5 tons of solution daily. Water amounting to 2,922.4 tons every 24 hours and containing 22.6 tons of NaCl, obtained by diverting the necessary amount of waste solution from the salt-washing operation, is added to the final thickener to supply the overflow solution and 1,141.6 tons additional to discharge the 1,712.4 tons of washed solids obtained as settled sludge.

Equipment.—The four 75- by 10-foot reinforced-concrete thickeners employed for the countercurrent washing treatment, complete with motors and raking equipment and the necessary sludge pumps, cost \$53,000 and require about 42 hp. to operate.

Power.—The power consumption of the thickeners is estimated 750 kw.-hr. per day at a cost of \$2.25.

Labor.—One man per shift should be more than able to keep the thickeners operating and take care of the auxiliary pumps. The cost of labor is therefore estimated at \$18.00 per day.

Water.—Only the water required to discharge the thickened sludge, and totaling 1,226.4 tons or 293,860 gallons, inclusive of the combined water, is charged to the thickeners; this amounts to \$14.70 every 24 hours.

Maintenance and supplies.—This expense is estimated at about \$2.70 per day.

<i>Costs of washing gypsum residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—750 kw.-hr. at \$0.003.....	\$ 2.25
Labor—24 man-hours at \$0.75.....	18.00
Water—294,000 gallons at \$0.05 per M.....	14.70
Maintenance and supplies.....	2.70
Direct operating cost.....	37.65

BALL MILLING FOR PRODUCTION OF SYNGENITE-GYPSUM

Experimental data have proved that the time required (even with minus 65-mesh polyhalite) to convert the calcium sulfate to syngenite by means of a solution of K_2SO_4 containing 10 or 11

grams of K_2SO_4 per 100 grams of water and to assure a reasonable approach to the equilibrium concentration of the K_2SO_4 (3.2 to 4.0 grams K_2SO_4 , varying with NaCl content) is 18 to 24 hours. However, by dividing the conversion into two stages, so as to provide a large excess of polyhalite and $CaSO_4$ in the first stage, the equilibrium concentration can be approached in 1 to 2 hours, and complete conversion to produce a high-grade syngenite can be effected in an equally short time by treating the syngenite-gypsum mixture from the first stage with the solution high in K_2SO_4 , thereby utilizing the effect of mass action.

Ball mills, operating in closed circuit with classifiers adjusted for minus 65-mesh separation, are used in the first stage to facilitate conversion of the calcined polyhalite. The grinding essential to reduce the fine fraction used in this step to the necessary particle size is accomplished by the treatment. After classifying, thickening, and filtering the syngenite-gypsum mixture is repulped and treated in continuous agitators while the filtrate is discharged to waste.

Equipment.—The ball mills, complete with motor drives and feeding and discharging devices for handling the 489.3 tons of new feed and the 2,395.2 tons of intermediate liquor in addition to the recirculated classifier sands, cost \$15,000.

Power.—The power consumption of the ball mills is 2,700 kw.-hr. daily at a cost of \$8.10.

Labor.—One man per shift can easily take care of the ball mill, classifier, and thickener, therefore one-half or a total of 12 man-hours at \$9.00 per day is charged against this operation.

Water.—No charge is made for water used in the first stage of syngenite-gypsum formation, except for the 400 tons consumed daily in washing the filter cake.

Maintenance and supplies.—Ball-mill liners and balls, with miscellaneous supplies and repairs, average \$5.00 per day.

The summarized costs of the wet-grinding in the ball mills are as follows:

<i>Costs of ball-milling syngenite-gypsum</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,700 kw.-hr. at \$0.003.....	\$ 8.10
Labor—12 man-hours at \$0.75.....	9.00
Maintenance and supplies.....	5.00
Direct operating cost.....	22.10

CLASSIFYING AND THICKENING SYNGENITE-GYPSUM

The 475.2 tons of syngenite-gypsum mixture resulting from the ball-milling operation are discharged to a continuous classifier delivering a minus 65-mesh product in the overflow. This overflow at a 4 or 5 : 1 liquid : solid ratio is collected in a thickener where the clarified overflow is partly returned to the classifier and partly discarded while the underflow is pumped at a 2 : 1 liquid : solid ratio to continuous vacuum filters.

Equipment.—The physical properties of the syngenite-gypsum and the heavy-density solution make liberal settling areas necessary. The classifier is 8- by 23-foot and costs \$6,500 installed with a 7½-hp. motor.

The thickener is 100- by 10-foot and if made of reinforced concrete, complete with motors, rakes, and accessory quadruplex electrical pump, costs about \$18,760. A single thickener serves principally as a surge tank, but washing is done on the vacuum filters, which are required whether or not a series of thickeners is employed for the washing operation.

Power.—The classifier requires a $7\frac{1}{2}$ -hp. motor, and the thickener requires a 3-hp. motor for driving the rake and a $7\frac{1}{2}$ -hp. motor for pumping the underflow sludge, that is, a total of 18 hp. or about 300 kw.-hr. per day at a cost of \$0.90.

Labor.—Half the time of one attendant is necessary to operate the classifier and thickener, or \$9.00 per day.

Maintenance and supplies.—Repairs and supplies amount to \$0.55 and \$0.51 for the classifier and thickener, respectively, a total of \$1.06 per day. No steam or water charges are made against these operations. The total direct costs for these two steps are as follows:

<i>Costs of classifying and thickening syngenite-gypsum mixture</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—300 kw.-hr. at \$0.003.....	\$ 0.90
Labor—12 man-hours at \$0.75.....	9.00
Maintenance and supplies.....	1.06
Direct operating cost.....	10.96

FILTRATION OF SYNGENITE-GYPSUM UNDERFLOW

Dewatering of the thickener sludge is necessary to discard the magnesium sulfate and produce high-grade syngenite. The 1,574.8 tons of thickened product are pumped to the filters and washed with 400 tons of water daily to yield 63.0 tons of washed solids and a wash liquor that is discarded with the filtrate and thickener overflow, which together total 2,386.4 tons of solution, containing 209.6 tons of $MgSO_4$ and 67.2 tons of K_2SO_4 .

Equipment.—The vacuum filters require about 3,200 square feet of net filtering area and with all accessories cost approximately \$65,000. This cost would be considerably less if the horizontal continuous centrifugal filter were found applicable.

Power.—The daily power consumption is 3,850 kw.-hr., costing \$11.55.

Labor.—Two attendants per shift or a total of six men costing \$36.00 daily are needed to operate the filters.

Water.—The 400 tons equivalent to 96,000 gallons of wash water cost \$0.80 per day.

Maintenance and supplies.—One new set of filter cloth per year, and the other miscellaneous supplies and repairs, average \$6.75 per day.

The direct operating costs for filtering the syngenite-gypsum are as follows:

<i>Costs of filtering syngenite-gypsum</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—3,850 kw.-hr. at \$0.003.....	\$11.55
Labor—48 man-hours at \$0.75.....	36.00
Water—96,000 gallons at \$0.05 per M.....	4.80
Maintenance and supplies.....	6.75
Direct operating cost.....	59.10

CONVERSION OF SYNGENITE-GYPSUM TO SYNGENITE

The second stage of the production of syngenite entails the conversion of the syngenite-gypsum mixture to syngenite by agitating with the 2,044.8 tons of K_2SO_4 extract liquor, to which the solution obtained from washing the syngenite filter cake with 400 tons of water has been added. A temperature of 122° F. (50° C.) is maintained to accelerate the reaction that results in a drop from 11.0 to 6.8 grams of K_2SO_4 per 100 grams of water or approximately 43.4 percent of the recoverable K_2SO_4 . Obviously, the large excess of K_2SO_4 available for reaction effects a rapid conversion and only about 90 minutes are required for this treatment.

Equipment.—Four 14- by 10-foot continuous agitators provided with 20-hp. motors cost about \$9,000 installed.

Power.—The power consumption at full rated load amounts to 1,440 kw.-hr. per day, costing \$4.32.

Labor.—One man per shift (24 man-hours) is required at a cost of \$18.00 per day.

Steam and water.—Steam costs to heat the charge from 70° to 122° F. are \$130.40 per day, corresponding to 326,000 pounds of 30-pound-gage steam; some steam economy may be possible if the heat in the hot extract solution is utilized efficiently. No water is charged to this conversion step, as it is supplied from two previous operations.

Maintenance and supplies.—These items amount to \$5.00 every 24 hours.

The operating expenses charged against the syngenite conversion step are as follows:

<i>Operating costs of conversion of syngenite-gypsum to syngenite</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,440 kw.-hr. at \$0.003.....	\$ 4.32
Labor—24 man-hours at \$0.75.....	18.00
Steam—326,000 pounds at \$0.40 per M.....	130.40
Maintenance and supplies.....	5.00
Direct operating cost.....	157.72

THICKENING AND FILTERING SYNGENITE

The thickening and filtering of the syngenite are accomplished exactly the same as for the syngenite-gypsum, and the equipment recommended for that purpose is duplicated for these operations. The 539.2 tons of syngenite are about 14 percent greater than the syngenite-gypsum, but settling and filtration are easier as the solution is less concentrated.

The combined thickener overflow and the filtrate, amounting to 2,395.2 tons containing 142.4 tons of K_2SO_4 and 128.8 tons of $MgSO_4$, are returned to the circuit by adding to the ball mills while the washed syngenite amounting to 524.8 tons after loss of 14.4 tons to the wash water is fed to the dryers to produce 522.9 tons of product inclusive of the retained salts. The 464.8 tons of wash liquor are returned to the syngenite agitators.

The cost of the 100-foot thickener complete with accessories is \$18,760 and entails the following operating expense:

Costs of thickening syngenite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—200 kw.-hr. at \$0.003.....	\$0.60
Labor—2 man-hours at \$0.60.....	1.20
Maintenance and supplies.....	.43
Direct operating cost.....	2.23

The cost of the vacuum filters is \$65,000, and the operating costs of \$59.10 per day are exactly the same as for the syngenite-gypsum filtration, in that the same quantity of wash water is used.

DRYING AND DEHYDRATION OF SYNGENITE

The dehydration or calcination of the syngenite product to produce 522.9 tons of anhydrous material with maximum K_2SO_4 content entails a major item of equipment and operating costs, as the syngenite retains a large amount of free water in addition to that combined in the molecular compound.

Two 8- by 160-foot rotary dryers with brick lining in the firing zone and operated at a maximum of 950° F. with oil fuel are required. The net thermal requirements per day are 851,200,000 B.t.u. Proper provision for the collection of any dust formed in the dryers must be made, also.

Equipment.—The two 8- by 160-foot rotary dryers, complete with burners, motor drives, reduction gears, feeding device, dust chambers, and collectors and brick stack, cost \$140,000.

Power.—The daily power consumption is 2,500 kw.-hr., costing \$7.50.

Labor.—One skilled kiln operator at \$0.75 and two helpers at \$0.60 per hour are required per shift, to operate the two kilns.

Fuel.—The fuel oil consumed daily amounts to 232 barrels and costs \$232.

Maintenance and supplies.—At 5 percent of installed cost the repairs and supplies on the dryers amount to \$23.33 every 24 hours.

The direct costs in connection with the calcination of the syngenite are as follows:

Costs of drying syngenite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,500 kw.-hr. at \$0.003.....	\$ 7.50
Labor—72 man-hours 24 at \$0.75—48 at \$0.60.....	46.80
Fuel oil—232 barrels at \$1.00.....	232.00
Maintenance and supplies.....	23.33
Direct operating cost.....	309.63

EQUIPMENT AND OPERATING COSTS OF PROCESS 4B

The decreased tonnages handled in the syngenite-production step in process 4B result in smaller equipment capacities and a saving in operating costs; but the increased capacity of the hot-extraction step together with the necessary investment and operating costs of the evaporators makes a larger over-all equipment investment than needed for process 4.

HOT EXTRACTION OF CALCINED POLYHALITE

The feeding devices for charging the polyhalite to the hot-extraction and syngenite-formation steps are essentially the same as in process 4; that is, two separate feeders costing \$3,500 and requiring a daily operating expenditure of \$11.14 are necessary.

Equipment.—The continuous agitators, comprising two 12- by 10-foot turbo-mixers with 20-hp. motors, cost \$3,960 installed. These extractors should be ample to provide a 15- to 20-minute solid-liquid contact for the 949.6 tons of calcined polyhalite and 2,552.1 tons of dilute make-up liquors charged daily.

Operating costs.—These are practically the same as for this step in process 4, with the exception of a slightly greater water and steam consumption. They are as follows:

Costs of hot extraction of calcined polyhalite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—720 kw.-hr. at \$0.003.....	\$ 2.16
Labor—24 man-hours at \$0.75.....	18.00
Steam—765,000 pounds at \$0.40 per M.....	306.00
Water—475,000 gallons at \$0.05 per M.....	23.75
Maintenance and supplies.....	2.50
Direct operating cost.....	352.41

FILTRATION OF GYPSUM RESIDUE

Gypsum residue can be filtered by continuous rotary vacuum filters or by continuous horizontal centrifugal-type filters. The quantity of calcined polyhalite treated in this step is 73 percent of that extracted in process 1, in which four 14- by 18-foot rotary drum filters were indicated. Therefore, three filters are large enough for this operation. The weight of wet filter cake is 1,114.1 tons, and the filtrate amounts to 2,387.6 tons daily. The temperature of the filtrate should be kept as high as possible to conserve heat and assure a hot liquor feed to the evaporators.

Equipment.—The completed filter-press installation costs \$86,500 and includes condensers to handle the flash evaporation and remove moisture from the air passing to the vacuum pumps.

Operating costs.—The costs of operating the vacuum filters are the same as in process 4, or a total of \$51.20 per day.

COUNTERCURRENT WASHING OF GYPSUM RESIDUE

The 1,114.1 tons of wet filter cake resulting from the hot extraction of the calcined polyhalite are repulped and thoroughly washed by 3,429.9 tons of water to discharge the 676.1 tons of gypsum residue and provide enough water to make 2,428.1 tons in the overflow carrying the 124.0 tons of dissolved salts.

Equipment.—Four 85- by 10-foot reinforced-concrete thickeners complete with sludge pumps, motor drives, rakes, launders, and piping will cost \$64,000 and represent a connected load of 52 hp.

Power.—At full-rated load the daily power consumption is 903 kw.-hr., costing \$2.71.

Labor.—One man per shift is allowed to operate the thickeners at a cost of \$18.00 per day, although part of his services is available for other work.

Water.—Only the water combined as gypsum and the free water used to discharge the solids from the final thickener (amounting

to 1,451.5 tons, or 348,400 gallons at \$17.42 per day) is charged against the thickeners.

Maintenance and supplies.—Repairs and supplies are estimated at \$3.20 per day.

The summarized operating costs are as follows:

<i>Costs of washing gypsum residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—903 kw.-hr. at \$0.003.....	\$ 2.71
Labor—24 man-hours at \$0.75.....	18.00
Water—348,400 gallons at \$0.05 per M.....	17.42
Maintenance and supplies.....	3.20
	<hr/>
Direct operating cost.....	41.33

EVAPORATION OF EXTRACT LIQUOR TO RECOVER K_2SO_4

The 2,387.6 tons of hot-extract solution are fed daily to multiple-effect forced-circulation evaporators and finally cooled in vacuum crystallizers to drop the K_2SO_4 crystal crop. Hot feed liquors suggest parallel steam and liquor flow, and by using quadruple-effect evaporators no crystallization of K_2SO_4 should occur in any but the final effect, except about 9 tons of syngenite ($K_2SO_4 \cdot CaSO_4 \cdot H_2O$), which separate at various stages during the evaporation; fortunately this compound is non-scale-forming.

If approximately one-fourth of the water is evaporated in each effect, K_2SO_4 separates only in the final effect, amounting to 53 tons daily; therefore, salt traps are required on this evaporator.

The thick liquor from the evaporators is discharged at 131° F. (55° C.) and pumped to the vacuum coolers for slow cooling in the critical range (130° to 95° F.), to prevent separation of schönite. Additional water is flash-evaporated in the vacuum coolers to decrease the load on the evaporators. This simultaneously displaces about 8 tons of the K_2SO_4 crystal crop from the evaporators to the coolers. The combined crop of K_2SO_4 and syngenite contains 81.9 tons of K_2SO_4 , which is pumped with its mother liquor to a conical settling tank and subsequently fed as a thickened sludge to centrifugal filters and discharged as a wet crystal product amounting to 94.0 tons of material after drying.

Equipment.—The forced-circulation quadruple evaporators contain approximately 5,000 square feet of heating surface and installed with all necessary accessories, pipes, valves, and controls cost \$100,000.

Power.—The electric power consumption is 6,000 kw.-hr. per day and costs \$18.00.

Labor.—Two men per shift are necessary to operate the evaporators at a daily cost of \$36.00.

Steam.—The steam required at average quadruple-effect performance is 708,000 pounds every 24 hours and costs \$283.20.

Cooling water.—The volume of cooling water necessary to condense the vapor from the last evaporator effect is 2,040,000 gallons per day; \$40.80 is the cost for water obtained from the cooling towers.

Maintenance and supplies.—This item is \$8.40 for each 24 hours of operation.

The various operating costs for the evaporation are summarized as follows:

Costs of evaporating water for recovering K_2SO_4

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—6,000 kw.-hr. at \$0.003.....	\$ 18.00
Labor—48 man-hours at \$0.75.....	36.00
Steam—708,000 pounds at \$0.40 per M.....	283.20
Water—2,040,000 gallons at \$0.02 per M.....	40.80
Maintenance and supplies.....	8.40
Direct operating cost.....	386.40

CRYSTALLIZATION OF K_2SO_4 IN VACUUM COOLERS

Vacuum crystallizers are used to cool the K_2SO_4 mother liquor to 86° F. (30° C.), and some additional evaporation is permitted during this treatment. The K_2SO_4 and syngenite, 53.7 tons of which have separated in the evaporators, are removed, and the remaining 1,242.6 tons of liquor are pumped to the coolers. Approximately 41.6 tons of water are driven off by flash evaporation and 24.2 tons more of K_2SO_4 crystallize from solution.

About 95,380,000 B.t.u. must be removed from the liquors to effect the crystallization. Steam ejectors are employed to create the vacuum, and cooling water is used to carry away the heat.

Equipment.—The vacuum coolers equipped with the necessary circulating pumps for solution and cooling water and suitable steam jets cost \$32,000 completely installed.

Power.—The electric power consumption is about 1,200 kw.-hr. and costs \$3.60 daily.

Labor.—Less than half the time of one attendant is allotted to vacuum crystallization at a cost per day of \$9.00.

Steam.—The consumption of high-pressure (150-pound-gage) steam is 21,500 pounds, equivalent to \$8.60 every 24 hours.

Cooling water.—About 266,000 gallons of cooling water are required daily, and by the use of spray ponds or cooling towers this should be available at \$0.02 per thousand gallons, or \$5.32 per day.

Maintenance and supplies.—This item amounts to \$2.70 each day.

The evaporation of 41.6 tons of water during the vacuum cooling decreases the steam necessary for the evaporators, and a credit of \$10.40 is allowed for this item.

The costs of the operation of the vacuum crystallizers are summarized as follows:

Operating costs of K_2SO_4 crystallization

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,200 kw.-hr. at \$0.003.....	\$ 3.60
Labor—12 man-hours at \$0.75.....	9.00
Steam—21,500 pounds at \$0.40 per M.....	8.60
Water—266,000 gallons at \$0.02 per M.....	5.32
Maintenance and supplies.....	2.70
Gross direct operating cost.....	29.22
Credit for steam saved (quadruple-effect economy) 26,000 pounds at \$0.40 per M.....	10.40
Net direct operating cost.....	18.82

FILTRATION OF K_2SO_4 CRYSTAL CROP

The combined crop of crystal product from the evaporators and coolers, totaling 81.9 tons per day, is pumped to conical settling tanks where the clarified overflow liquor and filtrate are pumped to the syngenite-gypsum step and the thickened crystal mass is fed to suitable centrifugal filters.

Equipment.—These centrifugal filters cost about \$5,750 and consume 350 kw.-hr. of power each day.

Power.—The 350 kw.-hr. required by the centrifuges costs \$1.05 daily.

Labor.—With continuous centrifuges, one man per shift can devote half time to the vacuum crystallizers and half to the operation of the centrifuges, as no washing of the recovered crystals is necessary; this labor cost is \$9.00 per day.

Maintenance and supplies.—This cost is estimated at \$2.50 per day.

Costs of filtering K_2SO_4 crystal crop

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—350 kw.-hr. at \$0.003.....	\$ 1.05
Labor—12 man-hours at \$0.75.....	9.00
Maintenance and supplies.....	2.50
Direct operating cost.....	12.55

DRYING K_2SO_4

The K_2SO_4 with retained mother liquor as discharged by the centrifugal filters amounts to 118 tons daily and after drying contains all of the dissolved salts in the adhering mother liquor, making a total of 94 tons of anhydrous product. Magnesium sulfate and sodium chloride introduced from the retained liquor amount to 3.9 and 1.2 tons, respectively.

Drying is done in oil-fired rotary dryers, and about 46,600,000 B.t.u. are necessary merely to evaporate the retained water and dehydrate the small amount of syngenite present.

Equipment.—The cost of the rotary dryers, with all necessary accessories, is \$10,000 completely installed.

Power.—The power consumed by the dryer is 450 kw.-hr. per day and costs \$1.35.

Labor.—Half the time of one attendant is required to operate the dryer at a cost of \$9.00 per day.

Fuel.—About 13 barrels of fuel oil are consumed in the dryer, at a daily cost of \$13.00.

Maintenance and supplies.—Repairs and supplies cost \$2.25 per day.

The costs of drying the K_2SO_4 are summarized as follows:

Operating costs of drying K_2SO_4 crystal crop

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—450 kw.-hr. at \$0.003.....	\$ 1.35
Labor—12 man-hours at \$0.75.....	9.00
Fuel oil—13 barrels at \$1.00.....	13.00
Maintenance and supplies.....	2.25
Direct operating cost.....	25.60

SYNGENITE-FORMATION STEP

The production of syngenite entails two steps: First, ball-milling of the calcined polyhalite in closed circuit with a classifier; and second, conversion of the syngenite-gypsum resulting from the first stage into syngenite by means of the K_2SO_4 mother liquor added to the mixture in continuous agitators. The estimated time of retention of solids is 90 minutes for each stage, with the temperature of the first stage not in excess of 86° F. and that of second stage preferably 122° F.

Particle-size reduction is accomplished in the ball-milling treatment to accelerate the reaction so as to lower the K_2SO_4 to a concentration that permits discard without appreciable loss of potassium salts.

Equipment.—Any one of several types of ball mills, either of cylindrical or conical construction, is suited to the wet-grinding operation. The cost of such a unit with motor drive and arranged for continuous feed and discharge is \$11,250 for an 8- by 6-foot mill or one of equivalent capacity.

Power.—The ball mill is equipped with a 120-hp. motor, which at full-rated load consumes 2,160 kw.-hr. daily at a cost of \$6.48.

Labor.—Half the time of one operator or a charge of \$9.00 every 24 hours is made against the ball mill for operating labor.

Maintenance and supplies.—The calcined polyhalite is relatively soft, and ball and liner consumption in the wet-grinding operation is small; the cost of repairs and supplies is estimated at \$3.75 per day.

No charge for water is made against the ball-milling step, as this charge has been placed against the step at which the water entered the system.

The cost of ball milling is summarized as follows:

Costs of wet-grinding syngenite-gypsum

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,160 kw.-hr. at \$0.003.....	\$ 6.48
Labor—12 man-hours at \$0.75.....	9.00
Maintenance and supplies.....	3.75
Direct operating cost.....	19.23

CLASSIFYING AND THICKENING SYNGENITE-GYPSUM

The estimated discharge from the ball mills (amounting to 2,914.3 tons of liquids and solids every 24 hours) is fed to the classifiers, with the necessary amount of clarified thickener overflow to remove the 313.6 tons of syngenite-gypsum in the classifier overflow. The classifier oversize (amounting to possibly 1,521.5 tons per day) is recycled through the ball mill and the overflow pulp discharged to an 85-foot thickener to produce underflow sludge suitable as feed for the vacuum filters.

Equipment.—The classifier, which may be of the reciprocating rake type or cylindrical shell with annular helical flights, costs about \$4,850.00. The 85- by 10-foot reinforced-concrete thickener, with driving motor, rakes, and the necessary pumps, costs an additional \$15,000 completely installed. The classifier requires a 5-hp. motor and the thickener drive a 3-hp. motor, while the sludge pump requires a 5-hp. motor.

Power.—The cost of electric power, assuming the full-rated load, is 234 kw.-hr. daily for the classifying and thickening steps.

Labor.—One attendant can operate the classifier and thickener in one-half of his time, and probably also watch the ball mill; this means a charge of \$9.00 per day against the classifying and thickening operations.

Maintenance and supplies.—The cost of these items is estimated at \$0.42 per day for the classifier and \$0.75 per day for the thickener, a total of \$1.17 every 24 hours.

The operating costs of the classifier and thickener are summarized as follows:

Costs of classifying and thickening syngenite-gypsum

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—234 kw.-hr. at \$0.003.....	\$ 0.70
Labor—12 man-hours at \$0.75.....	9.00
Maintenance and supplies.....	1.17
Direct operating cost.....	10.87

FILTRATION OF SYNGENITE-GYPSUM MIXTURE

The use of a thickener in conjunction with the classifier lightens the load on the filters, and the 313.6 tons of syngenite-gypsum are pumped as 1,155.6 tons of sludge comparable to a 2 : 1 solids : liquid ratio. The filtrate, with enough of the thickener-overflow solution to total 1,072.8 tons of solution, is discarded, while the balance of the clarified overflow is returned to the classifier to maintain the proper pulp ratio for effective classification.

Wash liquor (amounting to 348.0 tons and resulting from the washing of the finished syngenite filter cake) is employed as a wash for the syngenite-gypsum filter cake, and these washings are discarded.

Equipment.—The vacuum filter capacity is two-thirds of that required in process 4, and the complete installation costs \$45,000.

Power.—The power consumed by the filters and accessory vacuum and solution pumps is 2,900 kw.-hr. per day and costs \$8.70.

Labor.—An average of four men per day, or a labor expenditure of \$24.00, is required.

Maintenance and supplies.—The repairs and supplies, including lubricants, pump packing, filter cloths, etc., cost \$4.50 every 24 hours.

The filtration costs may be summarized as follows:

Costs of filtering syngenite-gypsum mixture

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,900 kw.-hr. at \$0.003.....	\$ 8.70
Labor—32 man-hours at \$0.75.....	24.00
Maintenance and supplies.....	4.50
Direct operating cost.....	37.20

AGITATION OF SYNGENITE-GYPSUM FOR CONVERSION TO SYNGENITE

The 313.6 tons of syngenite-gypsum, with the retained wash liquor and the 1,136.8 tons of K_2SO_4 motor liquor—making a total daily charge of 1,803.2 tons—are fed to a series of three continu-

ous agitators operating at 122° F. (50° C.). The capacity of these agitators is adjusted to permit a 90-minute retention; they are arranged to discharge continuously to a thickener.

The thickener clarified overflow and the filtrate from the vacuum filters, totaling 1,040.8 tons daily, are returned as intermediate liquor to the ball mills for precipitation of the K_2SO_4 in the form of syngenite-gypsum mixture. The final syngenite filter cake, after washing with water, is discharged and conveyed to rotary dryers, while the washings are reserved for use on the syngenite-gypsum filter cake.

Equipment.—The three 14- by 10-foot continuous agitators, complete with motor drives, piping, launders, etc., cost \$7,200, installed, and each agitator requires a 20-hp. motor.

Power.—The power consumed every 24 hours at full-rated load amounts to 1,080 kw.-hr. at a cost of \$3.24.

Labor.—One man per shift is allotted to operate the agitators at a cost of \$18.00 per day.

Steam.—Some auxiliary heating of the solutions is necessary, and by judicious provision for heat recuperation by exchangers a major portion of this requirement can be met. However, a full charge is made for 201,500 pounds of 30-pound-gage steam at a cost of \$80.60 in 24 hours. No fresh water is added to the agitators, hence no charge is made.

Maintenance and supplies.—This item has been estimated at \$4.00 per day.

The operating costs for syngenite conversion are summarized as follows:

<i>Costs of syngenite conversion</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,900 kw.-hr. at \$0.003.....	\$ 8.70
Labor—24 man-hours at \$0.75.....	18.00
Steam—201,500 pounds at \$0.40 per M.....	80.60
Maintenance and supplies.....	4.00
Direct operating cost.....	111.30

THICKENING SYNGENITE

The agitator discharge (1,803.2 tons) is thickened in an 85- by 10-foot reinforced-concrete thickener to produce a settled sludge of 1,422.9 tons and 380.3 tons of clarified overflow to return to the syngenite-gypsum production step. This thickener allows about 14 square feet of settling area for each ton of solids handled per day, which is ample for efficiently settling these slow-settling solids.

Equipment and operating costs.—The equipment cost is the same as for the first stage, that is, \$15,000, and the operating charge is \$0.43 for power, \$1.50 for labor, and \$0.75 for repairs and supplies, a total of \$2.68 per day.

FILTRATION OF SYNGENITE

The weight of syngenite to be filtered each day is 402.4 tons, which is about one-fourth greater than the syngenite-gypsum handled in the first stage, but the syngenite should filter more readily and the same-size filter area should suffice. Therefore, the

vacuum-filter installation costs \$45,000 and consumes about 2,900 kw.-hr. of electrical power per day. The operating cost also is the same as in the syngenite-gypsum filtration, that is, \$37.20 per day, plus the value of the water used in washing on the filters, amounting to 66,500 gallons costing \$3.53. The total daily operating expense is \$40.73.

DRYING SYNGENITE

The 396.0 tons of syngenite remaining after the washing of the filter cake, together with the retained water and soluble salts, amounts to 692.8 tons of wet material to be charged to the rotary dryers each day. Oil-fired dryers are employed, and the free and combined moisture (totaling 296 tons) is driven off to produce the 396.8 tons of dehydrated syngenite product.

Two 8- by 160-foot rotary kilns, with brick lining in the firing zone, are required to dry the syngenite, and heating may be applied up to 950° F. A net heat input of 583,700,000 B.t.u. is required to evaporate the water retained by the syngenite and to dehydrate the syngenite.

Equipment.—The rotary dryers cost \$115,000, complete with all accessories and with the necessary dust collectors and brick stack.

Power.—The electric power necessary to operate the dryers, oil burners, fans, feeders, etc., is 2,000 kw.-hr. and costs \$6.00.

Labor.—One skilled operator at \$0.75 per hour and two helpers at \$0.60 are required per shift to operate the dryers, giving a total daily labor charge of \$46.80.

Fuel.—About 159 barrels of fuel oil, costing \$159, are required to dry the syngenite.

Maintenance and supplies.—The repairs and supplies for the two dryers are estimated at \$20.00 per day.

The drying costs are summarized as follows:

<i>Costs of drying syngenite</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,000 kw.-hr. at \$0.003.....	\$ 6.00
Labor—72 man-hours: 24 at \$0.75—48 at \$0.60.....	46.80
Fuel—159 barrels at \$1.00.....	159.00
Maintenance and supplies.....	20.00
	<hr/>
Direct operating cost.....	231.80

EQUIPMENT AND OPERATING COSTS OF PROCESS 5

FEEDING CALCINED POLYHALITE AND SYNGENITE-GYPSUM TO EXTRACTION AGITATORS

Two separate automatic feeding devices with the necessary supply lines, elevators, and conveyors and with motor drives and controls are required, one to feed the calcined polyhalite to the syngenite-gypsum agitators and the other to charge the calcined mixture to the hot-extraction step.

Equipment.—The cost of the feeders, complete with all necessary accessories and controls, is \$3,950.

Power.—The power required to operate the auxiliary conveyors and elevators to the feed bins is 180 kw.-hr. per day, costing \$0.54.

Labor.—Two-thirds of the time of one attendant per shift is necessary to operate the feeders at a daily cost of \$9.60.

Maintenance and supplies.—These items are estimated at \$2.00 per day.

The operating costs for the feeders are summarized as follows:

<i>Costs of feeding calcined polyhalite and syngenite-gypsum mixture</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—180 kw.-hr. at \$0.003.....	\$ 0.54
Labor—16 man-hours at \$0.60.....	9.60
Maintenance and supplies.....	2.00
Direct operating cost.....	12.14

EXTRACTION OF CALCINED POLYHALITE FOR PRODUCTION OF SYNGENITE-GYPSUM MIXTURE

The 1,367.8 tons of calcined polyhalite, together with the make-up and recycled solutions totaling 6,952.7 tons of charge per day, require five 16- by 10-foot agitators, each equipped with a 20-hp. motor, to allow a 90-minute contact time. The cost of these five steel tanks with motor drives, beam supports, stirrers, and all accessories installed is \$13,500.

Power.—The daily power consumed by the agitator motors is 1,800 kw.-hr., costing \$5.40.

Labor.—One man per shift is required to operate the agitators at a cost of \$18.00 per day.

Maintenance and supplies.—These items are estimated at \$5.00 per day.

No charge is made for water, as this has been used to wash the filter cake and is charged against that operation.

The cost of agitating the syngenite-gypsum mixture is summarized as follows:

<i>Costs of agitating syngenite-gypsum mixture</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,800 kw.-hr. at \$0.003.....	\$ 5.40
Labor—24 man-hours at \$0.75.....	18.00
Maintenance and supplies.....	5.00
Direct operating cost.....	28.40

THICKENING SYNGENITE-GYPSUM

The overflow from the agitators is discharged to a 110- by 10-foot reinforced-concrete thickener to lighten the load on vacuum filters handling the syngenite-gypsum mixture and permit additional time for completion of the formation of syngenite. The 4,545 tons of thickened sludge are collected by the rakes and removed by the sludge pumps servicing the filter supply; the balance of the agitator discharge (amounting to 2,437.7 tons) is obtained as clarified overflow and recycled to maintain the proper pulp density in the agitators.

Equipment.—The 110-foot reinforced-concrete thickener with motor drives and the two necessary quadruplex sludge pumps and all accessories costs \$21,300.

Power.—The connected load for the thickener drive and sludge pumps is 18 hp., and the power consumption is 324 kw.-hr., costing \$0.97 per day.

Labor.—Only about 2 hours per day, equal to \$1.20, is expended for labor.

Maintenance and supplies.—Repairs and maintenance are estimated at \$1.05 per day.

The cost of thickening the syngenite-gypsum mixture is summarized as follows:

Costs of thickening syngenite-gypsum mixture

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—324 kw.-hr. at \$0.003.....	\$0.97
Labor—2 man-hours at \$0.60.....	1.20
Maintenance and supplies.....	1.05
Direct operating cost.....	3.22

FILTRATION OF SYNGENITE-GYPSUM

The thickened sludge, consisting of 1,162.4 tons of syngenite-gypsum mixture with possibly as much as 3,382.6 tons of associated magnesium-sulfate liquor, is pumped to the vacuum filters every 24 hours where the bulky filter cake amounts to 2,007.4 tons daily, even after displacement of the major portion of the retained MgSO_4 liquor by means of the wash solution from the washing thickeners treating the residue from the hot extraction of the calcined syngenite-gypsum.

The cost of the vacuum filters, vacuum pumps, filtrate receivers, and solution pumps installed is \$130,000.

Power.—The electric power consumption is 7,700 kw.-hr. per day, and the cost will be \$23.10.

Labor.—Possibly two men per shift are necessary to operate the filters, at a total cost of \$36.00 per day.

Water.—The 1,596.8 tons of water in the portion of the overflow from the countercurrent-decantation washing of the gypsum residue from the hot-extraction step, amounting to 383,200 gallons, cost \$19.16 per day.

Maintenance and supplies.—This expense, in which filter-cloth replacement is a major item, amounts to \$13.50 per day.

The cost of filtering is summarized as follows:

Costs of filtering syngenite-gypsum

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—7,700 kw.-hr. at \$0.003.....	\$23.10
Labor—48 man-hours at \$0.75.....	36.00
Water—383,200 gallons at \$0.05 per M.....	19.16
Maintenance and supplies.....	13.50
Direct operating cost.....	91.76

CALCINING SYNGENITE-GYPSUM

The 2,007.4 tons of wet syngenite-gypsum mixture must be dried and dehydrated at 950° F. to convert the gypsum in the mixture to inactive calcium sulfate. Heating for 16 minutes gives optimum results, and a temperature in excess of 995° F. must be avoided. This is essential to attain a concentration of 10 grams of K_2SO_4 per 100 grams of water in the subsequent extraction at 212° F. by decreasing the tendency for formation of the pentasalt ($\text{K}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot \text{H}_2\text{O}$).

Equipment.—The calcination is accomplished in three 8- by 160-foot, brick-lined, oil-fired rotary kilns, each kiln equipped with

an 8- by 80-foot cooler. These kilns, complete with all accessories and auxiliary equipment inclusive of dust collectors and brick stack, cost \$225,000, which is more than the kilns required for calcining the polyhalite.

Power.—It is estimated that 3,000 kw.-hr. are required to operate the calciners, at a cost of \$9.00 per day.

Labor.—Four men per shift, comprising one skilled kiln operator and three helpers, are required to operate the kilns at a cost of \$61.20 per day.

Fuel.—The expulsion of the large amount of water unavoidably retained by the syngenite-gypsum filter cake, as well as the water combined in the gypsum and in the syngenite, requires an enormous amount of heat, equivalent to a net absorption of 1,813,900,000 B.t.u. per day. This heat necessitates burning 494 barrels of oil, at a cost of \$494.00.

Maintenance and supplies.—Assuming a new lining every year for the combustion zone of each kiln, maintenance and supplies are estimated at \$37.50 per day.

The operating costs for calcining the 1,107.4 tons of syngenite-gypsum mixture (dry product) are summarized as follows:

Costs of calcining syngenite-gypsum mixture

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—3,000 kw.-hr. at \$0.003.....	\$ 9.00
Labor—man-hours: 24 at \$0.75—72 at \$0.60.....	61.20
Fuel—494 barrels of oil at \$1.00.....	494.00
Maintenance and supplies.....	37.50
	<hr/>
Direct operating cost.....	601.70

HOT EXTRACTION OF CALCINED SYNGENITE-GYPSUM

The automatic feeders charge the 1,107.4 tons of calcined syngenite-gypsum to a series of continuous agitators operating at 212° F. and of the necessary capacity to retain the charge for a 2½-hour extraction treatment. Either steam coils within the agitators or heat exchangers outside are employed for heating the daily make-up solution of 4,164.0 tons to approximately 212° F. A lower exothermic effect occurs when calcined syngenite-gypsum is dissolved than when calcined polyhalite is used.

Equipment.—A relatively large retention capacity is required to assure the time necessary to effect a net decomposition of approximately 81 percent of the syngenite in the charge. Five 18- by 20-foot reinforced-concrete tanks, each provided with 25-hp. motors and with impellers of a type that provide vigorous agitation, are required. The five concrete agitators, with motor drives and supports and with turbo-mixer impellers, completely installed, cost \$22,500.

Power.—The power consumption is 2,250 kw.-hr. at full-rated load, costing \$6.75 per day.

Labor.—One attendant per shift, with occasional assistance from the man operating the feeders, can take care of the agitators except in emergency. However, two men per shift are allotted to service the agitators at a daily cost of \$36.00.

Water.—Only the water recovered in the concentrated extract liquors, amounting to 2,824 tons or 677,760 gallons, is charged against the agitators. This amounts to \$33.88 per day.

Steam.—The cost of steam represents a major item. To heat the 4,164 tons of solution obtained at 77° F. (25° C.) as overflow from the washing thickeners to 212° F. as well as the 1,107.4 tons of calcined syngenite-gypsum mixture, 1,283,000 pounds of 30-pound-gage steam are required every 24 hours at a cost of \$493.20 per day. A saving can be effected by charging the calcined material to the agitators with some residual heat from the calcining operation.

Maintenance and supplies.—The cost of these items should not exceed \$5.00 per day.

The costs for extraction of the syngenite-gypsum are summarized as follows:

<i>Costs of hot extraction of calcined syngenite-gypsum</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,250 kw.-hr. at \$0.003.....	\$ 6.75
Labor—48 man-hours at \$0.75.....	36.00
Steam—1,283,000 pounds at \$0.40 per M.....	493.20
Water—677,760 gallons at \$0.05 per M.....	33.88
Maintenance and supplies.....	5.00
Direct operating cost.....	574.83

FILTRATION OF GYPSUM RESIDUE

The hot mixture of extracted syngenite and solution containing 10 grams of K_2SO_4 per 100 grams of water, totaling 5,270.4 tons per day, is pumped either to rotary vacuum filters or to continuous horizontal centrifugal filters where 3,140 tons of filtrate and 2,130.4 tons of the bulky wet gypsum filter cake containing 174.4 tons of K_2SO_4 as unextracted syngenite or as secondary pentasalt are separated.

Equipment.—To allow for the bulky nature of this filter cake and its tendency to retain large amounts of liquor and to handle the vapor from the flash evaporation, large-capacity vacuum pumps are necessary. Provision also must be made to condense the water vapor. Equipment capable of meeting these requirements and consisting of six 14- by 18-foot rotary-drum filters costs \$175,000 completely installed.

If the continuous horizontal-centrifugal filter can be employed to effect this filtration instead of rotary-vacuum filters, a substantial saving in equipment costs can be accomplished. Obviously, a vacuum filter is not the ideal type of machine to apply on mixtures approaching the boiling point of water.

The estimated installed cost of three large continuous centrifugal filters is \$60,000, but power costs are larger and maintenance and supply costs lower than for the rotary vacuum filter.

The fine particle size of the residue obtained from hot extraction of the calcined syngenite might prevent satisfactory handling on the centrifugal filters. This point needs checking in pilot-plant tests to determine the applicability. In view of this uncertainty, the equipment and operating costs covering the rotary vacuum filters are retained.

Power.—The daily electric power consumption is 6,750 kw.-hr., costing \$20.25 per day.

Labor.—Two men per shift at a total cost of \$36.00 per day are able to operate these six vacuum filters.

Maintenance and supplies.—These items amount to \$15.00 per day, chiefly for filter-cloth replacement.

Only a small amount of cooling water is required to condense the flash evaporation and this charge may be neglected, as the filter cake is now washed on the filters at this point.

The costs of the gypsum filtration are summarized as follows:

<i>Costs of filtration of gypsum residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—6,750 kw.-hr. at \$0.003.....	\$20.25
Labor—48 man-hours at \$0.75.....	36.00
Maintenance and supplies.....	15.00
	<hr/>
Direct operating cost.....	71.25

WASHING GYPSUM RESIDUE

To recover all of the K_2SO_4 solution retained by the filter cake, it is repulped and washed in a series of countercurrent thickeners in which the remainder of the unextracted syngenite, as well as a considerable portion of the pentasalt, is decomposed.

Wash water, amounting to 5,876.6 tons daily, is added to the final thickener to supply the water necessary to discharge the gypsum residue and to provide the 5,636 tons of water required for the 5,811 tons of overflow solution.

Equipment.—The four 110- by 10-foot reinforced-concrete thickeners, with motors, drives, supports, bearings, rakes, sludge pumps, launders and piping, etc., cost about \$21,300 each or \$85,200 for the complete installation, including the repulper.

Power.—About 18 hp. is connected for each thickener; thus, four units consume 1,296 kw.-hr. per day at a cost of \$3.90.

Labor.—One man per shift or \$18.00 per day is required to operate the thickeners.

Water.—Water totaling 5,876.6 tons (1,410,384 gallons) is added to the thickeners, but only the 1,340 tons necessary to complete the hydration of the gypsum and discharge the thickened sludge are charged against the washing operation. This amounts to 321,600 gallons at a cost of \$16.08 per day.

Maintenance and supplies.—These costs are estimated at \$4.30 per day.

The costs of the countercurrent-decantation washing of the gypsum residue are summarized as follows:

<i>Costs of washing gypsum residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,296 kw.-hr. at \$0.003.....	\$ 3.90
Labor—24 man-hours at \$0.75.....	18.00
Water—321,600 gallons at \$0.05 per M.....	16.08
Maintenance and supplies.....	4.30
	<hr/>
Direct operating cost.....	42.28

EVAPORATION OF K_2SO_4 EXTRACT LIQUOR

All of the water (amounting to 2,824 tons) in the K_2SO_4 extract solution must be expelled to recover the dissolved salts; to accom-

plish this objective approximately 2,745 tons of water are evaporated in the forced-circulation multiple-effect evaporators. Solution unavoidably retained by the wet-crystal crops as well as that combined as hydrated double salts is removed by the dryers.

Quadruple-effect evaporators operated with parallel steam and liquor flow are suggested, and vacuum coolers are unnecessary, as cooling need not be applied. Build-up of magnesium salts, especially MgCl_2 , occurs in the final effect as evaporation proceeds, and bleeding with return of the liquors withdrawn to the syngenite formation step is employed.

The cost of the evaporators, complete with circulating pumps and all accessories installed, is \$240,000, and the handling of liquors and crystallized salts requires a connected load of possibly 700 hp.

Power.—The power consumption of the evaporator accessories is 12,000 kw.-hr. per day and costs \$36.00.

Labor.—Four men per shift, or a total of 96 man-hours, at a cost of \$72.00 per day, are required to operate the evaporators.

Steam.—Assuming average quadruple-effect economy, 1,715,000 pounds of 30-pound-gage steam are required at a cost of \$686.00 per day.

Water.—The amount of cooling water (including make-up) to condense the vapor effluent from the evaporators is 4,950,000 gallons every 24 hours. The cost of cooling water by cooling towers (see p. 77) is estimated at \$99.00 per day.

Maintenance and supplies.—Repairs and supplies for the evaporators and accessories will cost \$20.00 daily.

The costs of evaporating the K_2SO_4 solution are summarized as follows:

Costs of evaporating extract liquors for recovery of K_2SO_4

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—12,000 kw.-hr. at \$0.003.....	\$ 36.00
Labor—96 man-hours at \$0.75.....	72.00
Steam—1,715,000 pounds at \$0.40 per M.....	686.00
Water—4,950,000 gallons at \$0.02 per M.....	99.00
Maintenance and supplies.....	20.00
Direct operating cost.....	913.00

FILTRATION OF K_2SO_4 CRYSTAL CROP

The K_2SO_4 , with associated minor quantities of other crystalline salts, is recovered by salt traps on the evaporators and by pumping the trapped solids to conical settling tanks, where the crystals form a thickened sludge suitable for feeding to the centrifuges for removal of the mother liquor. The mother liquor from the settling tanks and from the centrifugals is returned to the evaporators, while the 395.0 tons of wet crystals are conveyed to the dryers.

Equipment.—The centrifugal filters cost about \$18,750 and represent a connected load of 60 hp.

Power.—The cost of power is \$3.24 per day, corresponding to 1,080 kw.-hr. and equivalent to full-rated load.

Labor.—No washing of the crystal product is done, so that a continuous-type automatic centrifugal filter is used and two such

machines can be operated by one man per shift at a daily cost of \$18.00.

Maintenance and supplies.—Repairs and supplies are estimated at \$3.25 per day.

The costs of separating the K_2SO_4 from its mother liquor are summarized as follows:

<i>Costs of filtering K_2SO_4 crystal crop</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,080 kw.-hr. at \$0.003.....	\$ 3.24
Labor—24 man-hours at \$0.75.....	18.00
Maintenance and supplies.....	3.25
	<hr/>
Direct operating cost.....	24.49

DRYING K_2SO_4 CRYSTAL CROP

The drying of the crystal crop involves expulsion of 79 tons of water daily, including a portion combined in approximately 52 tons of schönite. The net heat requirements are 190,000,000 B.t.u. per day, supplied by oil fuel burned in rotary dryers.

Equipment.—These dryers cost about \$26,000 complete with the necessary accessories and consume 42 barrels of oil per day.

Power.—The electric power consumed by the dryers is estimated at 1,450 kw.-hr., costing \$4.35 per day.

Labor.—One man per shift, or a total expense of \$18.00 per day, should be sufficient to operate the dryers.

Fuel.—Assuming fuel oil as a source of heat, approximately 42 barrels are required, at a cost of \$42.00 per day.

Maintenance and supplies.—The costs of these items are estimated at \$5.85 per day.

The various costs of drying are summarized as follows:

<i>Costs of drying and dehydrating K_2SO_4 crystal product</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,080 kw.-hr. at \$0.003.....	\$ 3.24
Labor—24 man-hours at \$0.75.....	18.00
Fuel—42 barrels oil at \$1.00.....	42.00
Maintenance and supplies.....	5.85
	<hr/>
Direct drying cost.....	69.09

EQUIPMENT AND OPERATING COSTS OF PROCESS 5A

FEEDING CALCINED POLYHALITE AND CALCINED SYNGENITE TO EXTRACTORS

Equipment.—Two separate feeding set-ups, including the conveyors, elevators, and surge bins, are required, in addition to the automatic feeding devices charging the 1,301.6 tons of calcined polyhalite to the ball mills producing syngenite and the 1,364 tons of calcined polyhalite to the pressure autoclaves. These two complete installations cost \$3,950.

Operating costs.—These are the same as for process 5; power costs \$0.54, labor \$9.60, and maintenance and supplies about \$2.00, or a total of \$12.14 per day.

BALL-MILLING SYNGENITE-GYPSUM MIXTURE

Three 8- by 6-foot ball mills are required to grind the 1,301.6 tons of calcined polyhalite to which the 2,200.3 tons of intermedi-

ate liquor and the oversize from the classifier are added daily. The connected horsepower required is about 450.

Equipment.—The ball mills, each with a 150-hp. motor, reducing gears, feed and discharge devices, and accessories to operate in closed circuit with the classifiers, cost about \$15,000 installed or a total of \$45,000.

Power.—The daily power consumption is 8,100 kw.-hr. and costs \$24.30.

Labor.—One man per shift can operate the ball mills at a total cost of \$18.00 per day.

Maintenance and supplies.—Repairs and supplies are estimated at \$15.00 per day. No charge is made for water used in this operation.

The costs of ball milling are summarized as follows:

<i>Costs of ball-milling syngenite-gypsum mixture</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—8,100 kw.-hr. at \$0.003.....	\$24.30
Labor—24 man-hours at \$0.75.....	18.00
Maintenance and supplies.....	15.00
Direct operating cost.....	57.30

CLASSIFYING SYNGENITE-GYPSUM MIXTURE

The discharge from the ball mills is diverted to four 6- by 25-foot type-6F rake classifiers, where classified solids (amounting to 1,132.2 tons every 24 hours) are discharged at minus 65-mesh to the thickener and the "sands" are returned to the mills for additional grinding. A portion of the thickener overflow and of the filtrate from the vacuum filters also is recirculated before being discarded, to maintain the proper pulp density in the classifiers.

Equipment.—The four classifiers, with necessary launders and piping, cost about \$19,400 and require about 40 connected horsepower.

Power.—The electric power consumption is estimated at 720 kw.-hr., costing \$2.16 per day.

Labor.—One man per shift can easily operate the classifiers and also spend possibly 2 hours per day in checking and adjusting the thickeners; this gives a labor cost of \$16.50 per day.

Maintenance and supplies.—The cost of these items is estimated at \$1.67 per day.

The classifying costs are summarized as follows:

<i>Costs of classifying syngenite-gypsum mixture</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—720 kw.-hr. at \$0.003.....	\$ 2.16
Labor—22 man-hours at \$0.75.....	16.50
Maintenance and supplies.....	1.68
Direct operating cost.....	20.34

THICKENING SYNGENITE-GYPSUM MIXTURE

A thickener is used to act as a surge tank and to lighten the solution load on the filters. The 1,132.2 tons of syngenite-gypsum (dry weight), if thickened to a 2 : 1 liquid : solid ratio, make 4,257.7 tons of sludge, which is collected and pumped to the filters

every 24 hours. Two 100- by 10-foot thickeners in parallel, equipped with a large quadruple pump, are required for this purpose.

Equipment.—The cost of the two reinforced-concrete thickeners 100 feet in diameter by 10 feet in height and equipped with a large quadruplex suction pump is \$18,750 each, or \$37,500 complete.

Power.—The estimated connected horsepower at full rating consumes 378 kw.-hr. of electric power, costing \$1.13 per day.

Labor.—Two hours daily of the time of the classifier operators is devoted to the thickeners, and this means a charge of \$1.50 per day.

Maintenance and supplies.—Repairs and supplies are estimated at \$1.88 per day.

The daily costs for thickening are summarized as follows:

<i>Costs of thickening syngenite-gypsum mixture</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—378 kw.-hr. at \$0.003.....	\$1.13
Labor—2 man-hours at \$0.75.....	1.50
Maintenance and supplies.....	1.88
	<hr/>
Direct operating cost.....	4.51

FILTRATION OF SYNGENITE-GYPSUM MIXTURE

The solids from the thickener underflow, amounting to 1,132.2 tons daily, are pumped to rotary-vacuum filters, where a filter cake carrying 1,380 tons of retained liquor and equal to a total of 2,512.2 tons of wet cake is recovered. No washing is done at this stage, and the syngenite-gypsum filter cake is conveyed to the continuous agitators for conversion to syngenite.

Equipment.—The cost of the vacuum filter, with pumps, receivers, and necessary piping, completely installed, is \$160,000.

Power.—The electric power required is 9,500 kw.-hr., costing \$28.50.

Labor.—Two men per shift, at a cost of \$36.00 per day, can operate the filters.

Maintenance and supplies.—The costs of repairs and supplies are estimated at \$16.20 per day, including the major expense of filter-cloth replacement.

The costs of filtering are summarized as follows:

<i>Costs of filtration of syngenite-gypsum mixture</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—9,500 kw.-hr. at \$0.003.....	\$28.50
Labor—48 man-hours at \$0.75.....	36.00
Maintenance and supplies.....	16.20
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Direct operating cost.....	80.70

AGITATION OF SYNGENITE

The syngenite-gypsum filter cake from the first stage is charged to two 18- by 20-foot continuous agitators to which 2,795.1 tons of liquor previously used as a displacement wash on the vacuum filters recovering the finished syngenite are added every 24 hours. This wash liquor is passed through heat exchangers to absorb

enough heat to maintain the agitator charge at a minimum of 122° F. during the 90-minute period of retention. In raising the temperature of the charge from 77° to 122° F., approximately 387,000,000 B.t.u. (net) must be supplied by the exchangers.

Equipment.—The estimated cost of the two 18- by 20-foot turbo-mixer-type agitators with 25-hp. motors and with launders and piping is \$17,500.

Power.—The power consumed by the agitators at full-rated load is 900 kw.-hr. per day, costing \$2.70.

Labor.—One man per shift at a total cost of \$18.00 per day should operate the two agitators and also devote the necessary 2 hours per day to the thickeners.

Steam.—To operate the heat exchangers and supply the 387,000,000 B.t.u. of heat for the agitator charge 443,500 pounds of 30-pound-gage steam are required at a cost of \$177.40 per day.

Maintenance and supplies.—The cost of these items is estimated at \$10.00 per day. No charge is made for water used.

The costs of operating the agitators used to convert the syngenite-gypsum are summarized as follows:

<i>Costs of agitating syngenite to effect conversion</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—900 kw.-hr. at \$0.003.....	\$ 2.70
Labor—22 man-hours at \$0.75.....	16.50
Steam—443,500 pounds at \$0.40 per M.....	177.40
Maintenance and supplies.....	10.00
Direct operating cost.....	206.60

THICKENING SYNGENITE

The 5,307.3 tons of agitator discharge carry 1,344.8 tons of syngenite and 3,962.5 tons of solution; this discharge is separated into an overflow of 567.2 tons and an underflow of 4,740.1 tons, to be pumped to the syngenite-vacuum filters. Two 110- by 10-foot reinforced-concrete thickeners in parallel serve as surge tanks and bypass as much of the solution as possible.

The thickeners, complete with quadruplex sludge pumps and with the motors, raking mechanism, and all piping, valves, etc., cost \$43,000. Operating costs include: 378 kw.-hr. of power at \$1.13, 2 man-hours of labor at a total cost of \$1.50, and about \$2.15 for repairs and supplies, a total of \$4.78 per day for the thickening operation.

FILTRATION OF SYNGENITE

The syngenite obtained as a sludge from the thickeners amounts to 1,344.8 tons per day and requires thorough washing on the filters to remove the magnesium sulfate in the retained liquor. About 20 percent more filtering area is required than in the syngenite-gypsum filtration.

Equipment.—The complete vacuum-filter installation costs about \$190,000 and represents a connected load of 600 hp.

Power.—The power consumption to operate the syngenite vacuum filters is 10,800 kw.-hr., costing \$32.40 per day.

Labor.—Two operators per shift can handle the vacuum filters at a cost of \$36.00 per day.

Water.—The solution used for washing the syngenite has been charged against a previous step.

Maintenance and supplies.—The cost of repairs and miscellaneous supplies, including the major item of filter cloth, is estimated at \$19.40 per day.

The various operating costs are summarized as follows:

<i>Costs of filtering syngenite</i>		
<i>Item:</i>		<i>Cost per day (24 hours)</i>
Power—10,800 kw.-hr. at \$0.003.....		\$32.40
Labor—48 man-hours at \$0.75.....		36.00
Maintenance and supplies.....		19.40
Direct operating cost.....		87.80

DRYING SYNGENITE

The syngenite obtained after filtering and washing amounts to 2,273.2 tons daily and requires drying to expel the retained moisture. Lower-temperature drying should be satisfactory, as the water combined in the syngenite need not be driven off. Water amounting to 909.6 tons must be evaporated during the drying of each day's production of syngenite, and especial care is desirable to keep the filter cake as low in retained liquor as possible. However, even under the most favorable conditions, the syngenite retains unusually large volumes of water.

Equipment.—Rotary oil-fired dryers are used to remove the water; for this purpose, four 8- by 160-foot brick-lined kilns are necessary. This equipment, complete with all accessories including an efficient dust-collecting system and brick stack, costs \$275,000 and represents about 205 connected horsepower.

Power.—The electric-power consumption is estimated at 3,700 kw.-hr., costing \$11.10 each day.

Labor.—One skilled kiln operator and two helpers operate two kilns so that 6 operators and 12 helpers are needed, at a daily cost of \$93.60.

Fuel.—The quantity of fuel oil to supply the 1,765,000,000 B.t.u. required in evaporating the retained water is estimated at 481 barrels, costing \$481.

Maintenance and supplies.—The calcining temperature is relatively low so that a long life of the brick lining, even in the firing zone, is assured; and in the feed end of the kilns no special lining is employed, as drying can be accomplished in an unlined shell. The cost of repairs and supplies for the four kilns and coolers is estimated at \$45.00 per day.

The calcining costs are summarized as follows:

<i>Costs of drying and calcining syngenite</i>		
<i>Item:</i>		<i>Cost per day (24 hours)</i>
Power—3,700 kw.-hr. at \$0.003.....		\$ 11.10
Labor—man-hours: 48 at \$0.75—96 at \$0.60.....		93.60
Fuel—481 barrels fuel oil at \$1.00.....		481.00
Maintenance and supplies.....		45.00
Direct operating cost.....		630.70

AUTOCLAVING CALCINED SYNGENITE

The 1,364 tons of calcined syngenite are fed to slurry mixers, to which the 2,562.4 tons of heated dilute K_2SO_4 liquors are

charged every 24 hours and then pumped into the pressure autoclaves, where the charge is heated to approximately 392° F. for 60 minutes. A 61-percent decomposition of the syngenite is essential to successful operation of the process, and after this extraction has been obtained the pressure in the autoclaves is utilized to force the mixture into Kelly-type pressure-leaf filters designed to withstand these high pressures.

Assuming a 60-minute pressure treatment and an additional 30 minutes for charging and discharging, 12 steam-jacketed autoclaves 8 feet in diameter by 12 feet in height and provided with dished bottom and bottom outlets are required, each equipped with a 25-hp. motor drive.

Equipment.—An 8- by 12-foot autoclave with motor, reducing gears, stirrer, necessary valves, and an accessory pump and heat exchanger costs \$12,000, completely installed. This means a total investment of \$144,000 for a battery of 12 pressure vessels to extract the syngenite.

Power.—The 375 connected horsepower consume 6,000 kw.-hr. every 24 hours, because continuous operation is necessary during filling and discharging, as well as for the reaction period.

Labor.—One man can operate 2 of the pressure autoclaves including the charging and discharging, which means 6 men are required per shift or 18 per day, at a cost of \$86.40.

Steam.—A large quantity of steam is required to heat the daily 4,926.4 tons charged to the autoclaves. With no allowance for heat recovery from other steps, 1,716,000,000 B.t.u. must be supplied to raise the temperature to 392° F., and this requires 2,575,000 pounds of steam at 250 pounds pressure, costing \$1,030 per day. However, this estimated cost should be reduced, because the 2,575,000 pounds of condensate at 392° F. (210-pound-gage) contains recoverable heat for preheating the charge. A credit for this makes the net steam consumption 1,775,000 pounds, equivalent to \$710 per day.

Water.—Only the water recovered in the hot concentrated K_2SO_4 -extract liquor, which totals 2,062.4 tons, is charged to the autoclaves; this corresponds to 494,976 gallons of water at a daily cost of \$24.75.

Maintenance and supplies.—At 5 percent of the total investment, this cost is \$24.00 per day.

The pressure-extraction treatment costs are summarized as follows:

<i>Costs of autoclave pressure extraction of calcined syngenite</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—6,000 kw.-hr. at \$0.003.....	\$ 18.00
Labor—144 man-hours at \$0.60.....	86.40
Steam—1,775,000 pounds at \$0.40 per M.....	710.00
Water—495,000 gallons at \$0.05 per M.....	24.75
Maintenance and supplies.....	24.00
Direct operating cost.....	863.15

FILTRATION OF PENTASALT-ANHYDRITE RESIDUE

Twin pressure-leaf filters with a combined filter area of 2,200 square feet are suggested as suitable equipment for filtering the

autoclave discharge. The two units are mounted on a common frame and operated alternately to permit discharge of the filter cake. The temperature drop to 356° F. corresponds to about 130-pound-gage pressure, and this allows a pressure differential large enough to effect the filtration. The surplus liquid and suspended solids remaining in the shell at the end of each filtration operation are pumped to the second member of the twin unit without appreciable release of pressure to prevent excessive flash evaporation. Moreover, the filter shells are insulated to obviate cooling.

Equipment.—One filter unit is used for each autoclave, and this means that six of the twin units (having a combined filtering area of 13,200 square feet) are needed. The cost of these filters, with all necessary accessories, is \$145,000.

Power.—The power consumption is confined to the motors operating the accessory equipment, possibly for compressing air and for pumps to transfer and maintain the pressures, and should not exceed 10-hp. connected load per twin unit. This would mean an electric-power consumption of about 1,000 kw.-hr. per day at a cost of \$3.00.

Labor.—One man can operate two autoclaves and the twin filter unit provided the proper automatic controls are made available. However, one man must be allotted to each double-filter unit to be conservative, and this means the same labor cost as on the autoclaves—that is, \$86.40 per day.

Maintenance and supplies.—The cost of repairs and supplies, including filter-cloth replacement, is estimated at \$30.00 per day.

The costs of filtering the autoclave discharge are summarized as follows:

<i>Costs of filtering pentasalt-anhydrite residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,000 kw.-hr. at \$0.003.....	\$ 3.00
Labor—144 man-hours at \$0.60.....	86.40
Maintenance and supplies.....	30.00
Direct operating cost.....	119.40

AUTOClave EXTRACTION OF PENTASALT-ANHYDRITE

The second pressure treatment for extracting the pentasalt-anhydrite mixture containing the residual syngenite not decomposed in the first stage and the subsequent filtration are identical with the operations in the previous step. However, washing is applied to displace the liquors retained by the anhydrite filter cake, and maintenance of pressure on the filtrate is optional, as it could be allowed to flash and cool to atmospheric temperatures. Nevertheless, the flow sheet has been based upon the release of pressure on the wash solutions only.

The daily charge for the second autoclave extraction is about 6 percent greater in volume than in the first stage, although 3,572.2 tons are treated in comparison with 4,026.4 tons in the former step. The same autoclave capacity therefore is employed, and the equipment and operating costs, exclusive of water and steam charges, are identical.

The steam employed to heat the daily charge to 392° F. actually must supply slightly more than 1,667,000,000 B.t.u., but the 2,562.4 tons of filtrate, if recovered at 356° F., carry approximately 1,000,000,000 B.t.u., or a net requirement of only 667,000,000, equal to about 702,360 pounds of 250-pound steam, costing \$280.94 per day. Only the water used in the autoclaves and not charged against the first pressure treatment, that is, 1,872.8 plus 354.4 minus 2,062.4 or 164.8 tons, equivalent to 39,652 gallons, is charged, amounting to \$1.98 per day.

The costs of the second autoclave treatment are summarized below:

Costs of autoclave extraction of pentasalt-anhydrite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—6,000 kw.-hr. at \$0.003.....	\$ 18.00
Labor—144 man-hours at \$0.60.....	86.40
Steam—702,360 pounds at \$0.40 per M.....	280.94
Water—39,652 gallons at \$0.05 per M.....	1.98
Maintenance and supplies.....	24.00
Direct operating cost.....	411.32

FILTRATION OF FINAL ANHYDRITE RESIDUE

The final filter cake of anhydrite is similar to the pentasalt-anhydrite filter cake obtained in the first stage, except that 986.4 tons (wet weight) are obtained instead of 1,321.6 tons, and this reduced quantity requires about three-fourths of the filtering area. Therefore, pressure filters with about 900 square feet of filtering surface in each half of the twin units are used to supply a separate filter for each autoclave discharged. Insulated filter shells are employed and twin types of filters installed.

Equipment.—The 12 pressure-leaf filters, arranged as 6 twin units, cost about \$119,000, with all accessories.

Operation.—These costs are slightly less than 90 percent of those of the first stage, except labor expense, which is assumed to be the same. These costs are summarized as follows:

Costs of filtering final anhydrite residue

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—820 kw.-hr. at \$0.003.....	\$ 2.46
Labor—144 man-hours at \$0.60.....	86.40
Maintenance and supplies.....	24.54
Direct operating cost.....	113.40

EVAPORATION OF CONCENTRATED K₂SO₄ LIQUORS

The 2,604.8 tons of filtrate issuing from the pressure filters at 356° F. are fed to evaporators provided with the usual calandria to supplement the flash evaporation and to drive off the 354.4 tons of water that must be expelled every 24 hours. Salt traps are required, and final cooling to 86° F. is accomplished in vacuum crystallizers.

If a temperature drop to 131° F. in the evaporators and a subsequent drop to 86° F. in the crystallizers are employed, the evaporator investment would be less than the cost of the crystallizers. Evaporation can be done in a double-effect evaporator

equipped with salt traps and with an equal distribution of evaporation. With parallel steam and liquor flow, 12.9 tons of crystals separate in the first effect and 208.2 tons in the last.

Equipment.—The double-effect evaporators completely installed cost \$32,000 and represent about 350 hp. of connected load.

Power.—Power consumption, largely for circulation and handling of liquors, amounts to 6,000 kw.-hr. daily at a cost of \$18.00.

Labor.—One skilled operator per shift or a total of 24 man-hours costs \$18.00 per day.

Steam and cooling water.—No charge is made for steam, although occasionally some might be needed. Cooling water amounts to about 1,275,000 gallons per day and costs \$25.50.

Maintenance and supplies.—The cost of these items is estimated at \$2.70 per day.

Evaporation costs are summarized as follows:

<i>Costs of flash evaporation of K_2SO_4 liquors</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—6,000 kw.-hr. at \$0.003.....	\$18.00
Labor—24 man-hours at \$0.75.....	18.00
Steam	nil
Cooling water—1,275,000 gallons at \$0.02 per M.....	25.50
Maintenance and supplies.....	2.70
	<hr/>
Direct operating cost.....	64.20

VACUUM CRYSTALLIZING OF K_2SO_4 LIQUORS

The 2,029.3 tons of thick liquor from the evaporators pass to the vacuum crystallizers at 131° F. and contain approximately 148,000,000 B.t.u., which must be dissipated to effect separation of 66.6 tons of K_2SO_4 plus 1.6 tons of $CaSO_4$ as syngenite on cooling to 86° F.

Equipment.—Vacuum coolers to cool the 1,961.1 tons of solution necessitate an investment of \$55,500 to remove 149,480,000 B.t.u., a part of which can be utilized in evaporating a portion of the water.

Power.—About 2,000 kw.-hr. of electric power at a cost of \$6.00 per day are expended in handling liquors and cooling water and in removing crystallized solids.

Labor.—One man per shift (three per day) at a cost of \$18.00 per day can operate the vacuum coolers.

Steam.—The vacuum is maintained by means of steam jets, and the steam consumption is 10,000 pounds every 24 hours at a cost of \$4.00.

Cooling water.—The volume of water required to condense the vapor effluent is 417,000 gallons every 24 hours at a cost of \$8.34.

Maintenance and supplies.—The cost of these items is estimated at \$4.60 daily.

During the cooling, approximately 77.5 tons of water are evaporated and normally a credit of \$32.60 upon the basis of double-effect evaporator steam equivalent would be justified; however, no charge for steam consumed in the evaporators has been made and no credit is justified.

The vacuum-crystallizing costs are summarized as follows:

Costs of vacuum crystallizing K_2SO_4 liquors

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,000 kw.-hr. at \$0.003.....	\$ 6.00
Labor—24 man-hours at \$0.75.....	18.00
Cooling water—417,000 gallons at \$0.02 per M.....	8.34
Maintenance and supplies.....	4.60
Direct operating cost.....	36.94

FILTRATION OF K_2SO_4 CRYSTAL CROP

The K_2SO_4 crystallizing in the evaporators and crystallizers is collected from the traps and pumped to conical settlers, where the major portion of the 1,961.6 tons of mother liquor overflows while the thickened crystal sludge is discharged to continuous centrifuges for dewatering and washing.

Equipment.—The centrifugal filters to recover the 320.8 tons of moist washed crystals cost \$42,500 and represent about 150 connected horsepower.

Power.—The electric-power consumption is 2,500 kw.-hr., or \$7.50 per day.

Labor.—One man per shift or three per day at a cost of \$18.00 are necessary.

Water.—Thirty-two tons of wash water equivalent to 7,680 gallons and \$0.15 per day are consumed.

Maintenance and supplies.—These total \$16.50 per day.

The costs of recovering the K_2SO_4 product are summarized as follows:

Costs of filtering K_2SO_4 crystal crop

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,500 kw.-hr. at \$0.003.....	\$ 7.50
Labor—24 man-hours at \$0.75.....	18.00
Water—7,680 gallons at \$0.02 per M.....	.15
Maintenance and supplies.....	16.50
Direct operating cost.....	42.15

DRYING K_2SO_4 CRYSTAL CROP

The 320.8 tons of wet crystals obtained every 24 hours from the filters or centrifuges are dried in oil-fired rotary dryers to drive off 32 tons of water and yield 288.8 tons of product containing 287.2 tons of K_2SO_4 .

Equipment.—The dryer costs \$26,000 and corresponds to that specified for process 5.

Power.—The electric power consumed daily is estimated at 1,450 kw.-hr., at a cost of \$4.35.

Labor.—The labor named consists of one man per shift (three per day) at a cost of \$18.00 per day.

Fuel.—Approximately 62,000,000 B.t.u. are required to evaporate the retained water, and this requires about 17 barrels of fuel oil costing \$17.00.

Maintenance and supplies.—Repairs and supplies average \$5.85 per day.

The drying costs are summarized as follows:

<i>Costs of drying final K_2SO_4 product</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,450 kw.-hr. at \$0.003.....	\$ 4.35
Labor—24 man-hours at \$0.75.....	18.00
Fuel—17 barrels fuel oil at \$1.00.....	17.00
Maintenance and supplies.....	5.85
Direct drying cost.....	45.20

EQUIPMENT AND OPERATING COSTS OF PROCESS 6

The large volume of natural gas (methane) that must be converted to a mixture of carbon monoxide and hydrogen necessitates the use of equipment representing the major items of the proposed treatment plant. The estimated costs of the converters and the rotary furnaces in which the converted gas is utilized to reduce the polyhalite are relatively high.

The steps involved in extraction of the reduced solids and recovery of the potassium salts are common chemical-engineering operations. No serious difficulties are anticipated in their successful application. One possibility to which no special attention has been given is the necessity for eliminating the large volumes of hydrogen sulfide gas liberated. Further treatment of this gas for recovery of the fuel value and of the sulfur content would be desirable also.

Equipment.—The estimate of the cost of the equipment is at best only a rough guess, but tentatively it is suggested that 12 special multitube rotary furnaces, each composed of six 12-inch by 30-foot tubes mounted in headers or end supports and rotating about a common axis, are required to effect reduction of the 1,424.8 tons of wet polyhalite daily. The kilns are indirectly fired, and only the converted gas in 50-percent excess is passed countercurrently over the charge. Each kiln has its own converter and gas preheater, and aluminum oxide impregnated with nickel oxide serves as catalyst to convert the mixture of gas and water vapor (steam).

The estimated cost of such kilns is \$25,000 each, completely installed, and the gas preheater and converter cost \$10,000 and \$15,000 each, respectively, a total of \$50,000. The extra suction fans, blowers, and automatic controls cost about \$2,000, and gas scrubbing equipment to cool and remove dust from the exit gases entails an expenditure of another \$35,000.

Operating costs.—With full automatic feed and discharge and with modern recording and controlling instrumentation one man can operate at least two complete units. Natural gas as fuel for heating the converters and rotary kilns would be cheaper than fuel oil, but to make production costs on all the processes comparable, natural gas is used only in the reduction step. The water vapor is introduced as steam at the same unit costs charged in the other processes.

The equipment costs are summarized as follows:

Estimated costs for rotary kilns, preheaters, and converters

<i>Item:</i>	<i>Cost</i>
12 rotary kilns at \$25,000.....	\$300,000
12 gas preheaters at \$10,000.....	120,000
12 gas converters at \$15,000.....	180,000
12 accessory and control apparatus at \$2,000.....	24,000
1 flue-gas scrubbing system.....	35,000
Total cost of equipment.....	659,000

FUEL REQUIREMENTS FOR REDUCING POLYHALITE

The fuel consumed in the calcining, converting the natural gas, and effecting the reduction of the polyhalite to potassium and calcium sulfide and to magnesium oxide represents the major direct cost of the process. Certain thermochemical and thermodynamic data necessary for exact calculation of the heats of reaction are not available. Likewise, specific data on the thermal efficiencies in the calcining and preheating steps and in the converter furnace and reducing kiln are unknown.

The authors,⁴² who investigated the process, have calculated the fuel requirements as closely as is warranted from the available thermal data. Based upon the conservative use of an over-all heat efficiency of 50 percent in the converters supplying the hydrogen monoxide mixture and in the reduction step, 15,800 cubic feet of 900-B.t.u. natural gas would be required per ton of 100-percent polyhalite treated.

In processing the 1,324.8 tons of polyhalite that result from washing of 1,600 tons as mined, approximately 21 million cubic feet of gas are consumed daily. If this quantity of gas is not available, fuel oil or crude oil can be substituted for all except the 9,089,000 cubic feet required for conversion to CO-H₂ for reducing purposes. Therefore, 12,000,000 cubic feet of gas required can be supplied by burning oil.

The 12,000,000 cubic feet of gas would be equivalent to approximately 10.8 times 10⁹ B.t.u., if the thermal efficiency suggested by the authors is used. The actual calculation for the efficiency of calcining polyhalite (see p. 39), was 63 percent. Therefore, the assumption of 50-percent efficiency for the heating operations would appear to be conservative. Upon this latter basis, the net thermal requirements are 40 percent of 10.8 times 10⁹ or 4.32 times 10⁹ B.t.u., equivalent to 745 barrels of oil (138,000 B.t.u. per gallon).

The direct operating costs for reducing polyhalite are summarized below:

Direct operating costs for reduction of polyhalite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—10,800 kw.-hr. at \$0.003.....	\$ 32.40
Labor—144 man-hours at \$0.75.....	108.00
Steam—229 tons at \$0.80 per ton.....	183.20
Gas—203.6 tons (9,089 M cu. ft. at \$0.06 per M).....	545.30
Fuel oil—745 barrels at \$1.00.....	745.00
Maintenance and supplies at 5 percent.....	109.80
Direct operating cost.....	1,722.70

⁴² Fraas, F., and Partridge, Everett P., Potash from Polyhalite by a Reduction Process—Continuous Reduction by Converted Gas: Ind. Eng. Chem., vol. 28, 1936, p. 230.

EXTRACTION OF REDUCED POLYHALITE

Either a hot or cold treatment can be employed for the extraction of the mixed sulfate product obtained by the reduction of polyhalite. However, the extract-liquor composition varies with the temperature used; and increasing proportions of potassium hydrosulfide with decreasing amounts of carbonate are obtained with increasing temperatures. Likewise, a considerable hydrolysis of the calcium sulfide occurs. Subsequent cooling of the solutions is necessary before the carbonation treatment, therefore the cold extract (30° C.) is the logical procedure. The reduced polyhalite is charged to continuous agitators that are provided with a means of cooling the reacting charge.

FEEDING OF REDUCED POLYHALITE

The reduced and cooled product from the rotary kilns is conveyed to a small surge bin provided with an automatic discharge and mechanical feeder of a capacity to handle the 711.6 tons daily.

Equipment.—This equipment is estimated to cost about \$1,750 and requires about 5 hp.

Power.—The 5 hp. operates at nearly full capacity and consumes 90 kw.-hr. at a cost of \$0.27 per day.

Labor.—The man operating the agitators can watch the feeders also, and 3 hours per day or \$2.25 is allowed for this work.

Maintenance and supplies.—This item amounts to about \$1.00 daily.

The costs of feeding are summarized as follows:

Costs of feeding reduced polyhalite to agitators

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—90 kw.-hr. at \$0.003.....	\$0.27
Labor—3 man-hours at \$0.75.....	2.25
Maintenance and supplies.....	1.00
Direct operating cost.....	3.52

DISSOLUTION OF REDUCED POLYHALITE

In extraction of the reduced polyhalite, approximately 104,000 B.t.u. per ton of solids are evolved from the heat of solution, principally from the K_2S present. This is equivalent to slightly more than 74,000,000 B.t.u. daily and for dissipation requires nearly 260 tons of refrigeration. Obviously, the equipment costs for this refrigeration cost more than the extraction agitators. The logical arrangement for this extraction and cooling is to feed the reduced polyhalite directly to the agitators and to circulate a portion of the reacting mixture, together with all of the make-up solution, through the cooling tubes of the refrigerating units. Cooling is effected by vaporization of the refrigerant on the outside of the tubes of the cooling units.

Equipment.—Two 7- by 8-foot turbo-mixers with 10-hp. motors and enclosed steel tanks assure a 15-minute retention and prevent short-circuiting of the solids. These mixers cost about \$1,310 each, or a total of \$2,620.

Power.—The daily electric-power consumption is 360 kw.-hr., costing \$1.08.

Labor.—Twenty-one hours each day of the total time of one man per shift operating both the agitators and feeders, or \$15.75, are charged against extraction.

Water.—Only the water in the clarified overflow from the No. 1 thickener but including the combined water and totaling 74,544 gallons (310.6 tons) or \$3.72 is charged to the extraction.

Maintenance and supplies.—The daily cost for repairs and supplies is \$1.50.

The costs of extraction, not including the cooling, are summarized as follows:

Costs of agitator treatment of reduced polyhalite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—360 kw.-hr. at \$0.003.....	\$ 1.08
Labor—21 man-hours at \$0.75.....	15.75
Water—74,544 gallons at \$0.05 per M.....	3.72
Maintenance and supplies.....	1.50
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Direct operating cost.....	22.05

COOLING AGITATOR CHARGE

The agitator charge is cooled by pumping the 1,985.8 tons of the countercurrent-decantation washing system with a proportioned quantity of the agitator pulp to maintain the temperature below 86° F. with a minimum cooling to 35° F. A circulating pump is required, in addition to the refrigeration unit, which might be of the centrifugal type and operate with direct cooling.

Equipment.—The installed cost of the refrigeration unit, including the pumps for circulating the agitator charge and make-up solution and for the condenser water with all necessary piping and valves, is \$26,000. The connected horsepower is about 350, including the circulating pumps.

Power.—The electric-power consumption is 5,850 kw.-hr. and costs \$17.55 per day.

Labor.—Two hours per day or \$1.50 covers labor charges.

Cooling water.—The cooling-water requirements for the refrigeration condenser will be approximately 3 gallons per minute per ton of refrigeration if available at 85° F.; this corresponds to a circulation of 274,000 gallons, costing \$5.28 per day.

The total expense of cooling the agitator charge is summarized as follows:

Costs of refrigerating agitator charge

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—5,860 kw.-hr. at \$0.003.....	\$17.55
Labor—2 man-hours at \$0.75.....	1.50
Water—274,000 gallons at \$0.02.....	5.28
Maintenance and supplies.....	2.25
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Direct operating cost.....	26.58

THICKENING EXTRACTED SOLIDS

The agitator discharge, amounting to 2,697.4 tons every 24 hours and carrying 473.6 tons of solid residue, empties into thickeners arranged for countercurrent-decantation washing. The clarified overflow from No. 1 thickener (amounting to 548.2 tons containing 244.6 tons of dissolved salts chiefly as K₂S, KHS, and

K_2CO_3) is pumped to the carbonating towers, while the washed residue is discharged as a sludge from the final thickener. The water for washing and sludge discharge is added to the final thickener only, and the overflow from No. 2 thickener is used in the agitators.

Equipment.—The settling characteristics of the extracted residue are unknown, so that the liberal allowance of 10 square feet per ton-day of solids means that thickeners 80 feet in diameter are required. Four 80- by 10-foot thickeners of reinforced concrete with enclosures and fans to remove evolved hydrogen sulfide vapors and complete with the motor drives, rakes, sludge pumps, and launders cost about \$60,000. The connected load is 60-hp.

Power.—The electric-power consumption at full-rated load is 1,080 kw.-hr., costing \$3.24 per day.

Labor.—Two man-hours or \$1.50 cover operating labor.

Water.—The water used to discharge the final thickened sludge, amounting to 1,184 tons or 284,160 gallons, costing \$14.20 per day, is charged against the thickeners.

Maintenance and repairs.—This expense is about \$3.00 per day.

The costs of thickening are summarized as follows:

<i>Costs of thickening extracted sulfide residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,080 kw.-hr. at \$0.003.....	\$ 3.24
Labor—2 man-hours at \$0.75.....	1.50
Water—284,000 gallons at \$0.05 per M.....	14.20
Maintenance and supplies.....	3.00
Direct operating cost.....	21.94

CARBONATING EXTRACT SOLUTION

The 548.2 tons of clarified overflow from the thickeners are pumped to coke-filled absorption towers through which 872.9 tons or 22,497,000 cubic feet of flue gas containing 134.5 tons of carbon dioxide are passed each day. The K_2S and KHS contents of the solution are converted to carbonate with the liberation of hydrogen sulfide, which is evolved as 76.8 tons (1,690,000 cubic feet) of H_2S in the exit gases.

Equipment.—It is estimated that twelve 10- by 100-foot steel absorption towers filled with coke and operated with two towers in series are required. These towers, complete with tower packing, solution pumps, and blowers, and with solution-pump tanks, cost about \$8,000 each or a total of \$96,000. Including miscellaneous controls, valves, piping, etc., a cost of \$100,000 is assumed for total tower installation.

Power.—Each pump on the towers must handle one-sixth of the feed liquor, and the 12 pumps represent about 45 hp. connected load; the blower motor on each pair of towers is 10 hp., and this means an additional 60 hp. connected. The 105 hp. requires 1,800 kw.-hr. of electrical power, costing \$5.40 per day.

Labor.—One operator and a helper are allotted to absorption towers per shift at a cost of \$32.40 per day.

Maintenance and supplies.—With a 20-percent annual coke replacement in the towers and 5-percent upkeep on the machinery used in connection with the towers, the repairs and supplies average about \$20 daily.

The absorption-tower operating costs are summarized as follows:

<i>Costs of carbonating extract liquors</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,800 kw.-hr. at \$0.003.....	\$ 5.40
Labor—{ 24 man-hours at \$0.75—\$18.00 }	32.40
{ 24 man-hours at \$0.60—\$14.40 }	
Maintenance and supplies.....	20.00
Direct operating cost.....	57.80

EVAPORATION OF CARBONATE LIQUORS

The 562.6 tons of carbonated liquor containing 255.2 tons of K_2CO_3 are passed through heat exchangers to raise the temperature to approximately 248° F. and then fed to quadruple-effect forced-circulation evaporators arranged for parallel liquor and steam flow. Approximately 48.7 tons of water are evaporated in each effect (a total of 194.8 tons), and with the temperatures of 248°, 223°, 185°, and 131° F. crystal crops separate only in the last two evaporators. Salt traps are necessary on these evaporators to collect the 111.1 tons crystallizing in the third effect and the 187.7 tons of $K_3CO_3 \cdot 3/2H_2O$ obtained in the last effect.

These crystal crops are combined and pumped to conical settlers where the crystals settle into a thickened magma suitable for centrifuging while the overflow is returned to the evaporators.

A gradual build-up of sodium chloride and potassium thiosulfate occurs in the last evaporator effect, but eventually saturation with these compounds results in the separation of Na_2CO_3 , $Na_2S_2O_3$, and finally KCl; the over-all average composition of total crystalline product is as indicated in the flow sheet. No complications arising from excessive increase of highly soluble salts are anticipated.

Equipment.—Evaporators of the capacity necessary to evaporate the 194.4 tons of water daily require about 875 square feet of evaporating surface, and the cost, complete with circulating pumps, salt traps, and all necessary accessories and controls, is \$17,500. The connected load is about 100 hp.

Power.—The power consumption is 1,800 kw.-hr., costing \$5.40 per day.

Labor.—One operator per shift, or a total labor cost of \$18.00 per day, is required to tend the evaporators.

Steam.—The amount of 30-pound-gage steam consumed every 24 hours is 121,750 pounds, costing \$48.70 per day.

Cooling water.—The cooling water required amounts to 350,000 gallons, costing \$7.00 per day.

Maintenance and supplies.—This item is \$1.50 per day.

The costs of evaporation are summarized as follows:

<i>Costs of evaporating K_2CO_3 liquors</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,800 kw.-hr. at \$0.003.....	\$ 5.40
Labor—24 man-hours at \$0.75.....	18.00
Steam—121,750 pounds at \$0.40 per M.....	48.70
Cooling Water—350,000 gallons at \$0.02 per M.....	7.00
Maintenance and supplies.....	1.50
Direct operating cost.....	80.60

FILTRATION OF $K_2CO_3 \cdot 3/2H_2O$ CRYSTAL CROP

The 298.8 tons of solids obtained from the evaporators and thickened in the settlers are fed to centrifugal filters or continuous centrifuges, and the excess mother liquor is removed. The wet crystal mass, amounting to 368.1 tons, is conveyed to the dryers.

Equipment.—The centrifugal filters cost about \$15,000 and require about 50 hp. connected load.

Power.—The electric-power consumption is 900 kw.-hr. per day at a cost of \$2.70.

Labor.—One man per shift can operate the centrifuges, as no washing is employed; this will mean an expenditure of \$18.00 per day.

Maintenance and supplies.—The repairs and supplies required are estimated at \$5.00 per day.

The filtering costs are summarized as follows:

<i>Costs of filtering K_2CO_3 crystal crop</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—900 kw.-hr. at \$0.003.....	\$ 2.70
Labor—24 man-hours at \$0.75.....	18.00
Maintenance and supplies.....	5.00
	<hr/>
Direct operating cost.....	25.70

DRYING $K_2CO_3 \cdot 3/2H_2O$ PRODUCT

The 368.1 tons of wet crystals from the centrifugal filters are conveyed to oil-fired rotary dryers, where the 79.3 tons of combined water and the 28.8 tons of free water are driven off by the net absorption of 204,000,000 and 64,000,000 B.t.u., respectively, every 24 hours.

Equipment.—Two 72-inch by 45-foot rotary dryers, each costing \$15,000 completely installed with dust collectors and representing a total connected load of 90 hp., are required.

Power.—The electric power consumed is 1,600 kw.-hr., costing \$4.80 per day.

Labor.—One man can operate the two dryers, and this means an expenditure of \$18.00 per day.

Fuel.—The dryers consume about 73 barrels of fuel oil to supply the net thermal requirements of approximately 268,000,000 B.t.u. The cost of this oil is \$73.00 per day.

Maintenance and supplies.—These items are estimated at \$6.50 per day.

The drying costs are summarized as follows:

<i>Costs of dehydrating and drying $K_2CO_3 \cdot 3/2H_2O$ product</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,600 kw.-hr. at \$0.003.....	\$ 4.80
Labor—24 man-hours at \$0.75.....	18.00
Fuel oil—73 barrels at \$1.00.....	73.00
Maintenance and supplies.....	6.50
	<hr/>
Direct operating cost.....	102.30

EQUIPMENT AND OPERATING COSTS OF PROCESS 7A

HOT EXTRACTION OF CALCINED POLYHALITE

The calcined polyhalite that must be extracted for production of the schönite contains approximately 68.4 percent of the potassium sulfate in the total amount treated daily, and the remainder is contained in the material used to make the syngenite. This arrangement is necessary to maintain a balanced process and assure maximum recoveries; and if variable quantities of schönite, syngenite, or finished potassium sulfate are to be removed, the calcines fed to each step of the process must be adjusted by a corresponding amount.

FEEDING CALCINED POLYHALITE

The calcined polyhalite is fed to the hot-extraction agitators and to the cold-extraction ball-milling step for production of syngenite. The coarse material has been assigned to the schönite step to maintain as large a particle size as possible to facilitate the thickening operation, but actually it may be necessary to feed the finer fraction to this step and rely upon the ball mills to grind the coarser fraction of the minus 10-mesh calcines to a size satisfactory for making syngenite. In either event, the feed bins and automatic feeding machinery are very similar to that specified for processes 4 and 4B (see pp. 185 and 191). The equipment costs about \$3,500, and the operating costs are as follows:

*Costs of feeding calcined polyhalite to schönite and syngenite
production steps*

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—180 kw.-hr. at \$0.003.....	\$0.54
Labor—6 man-hours at \$0.75.....	4.50
Maintenance and supplies.....	1.00
	<hr/>
Direct operating cost.....	6.04

EXTRACTION IN CONTINUOUS AGITATORS

The polyhalite composition indicated in the flow sheet requires 902.4 tons to be treated daily and to be charged to the agitators, 7,571.6 tons of solutions resulting from the combined hot overflow of the countercurrent-decantation thickeners being employed in washing the extracted polyhalite residue, and the 6,076.0 tons of schönite mother liquors being recycled. To assure a 15-minute time of solid retention, two 14- by 10-foot turbo-mixers with 20-hp. motors are required.

Equipment.—The two 14- by 10-foot continuous agitators are operated in series and can be made from heavy-gage steel plate. The installed cost, complete with the motor drives, gear reducers, stirrers, and piping, is estimated at \$4,500.

Power.—The agitators are operated 24 hours daily and consume 720 kw.-hr. of electric power, costing \$2.16.

Labor.—The time of one man is allotted for operating the two agitators and the care of the feeder, but obviously this man is available for other duties at times. This charge for labor is \$15.75 per day.

Steam.—Tests show that excellent extraction can be accomplished at 194° F. (90° C.) so that the charge of calcined poly-

halite and the 1,495.6 tons of thickener overflow at 176° F. and the 6,076 tons of schönite mother liquors at 86° F. must be heated by passing the solutions through heat exchangers. The 1,150,000 B.t.u. required are furnished by 1,188,000 pounds of 30-pound-gage steam at a cost of \$475.20 per day.

Water.—Only the water actually consumed and lost in the schönite- and K_2SO_4 -production steps should be charged against these operations. Examination of the flow sheet will disclose that these losses occur in the thickener-sludge discharge and during the drying of the K_2SO_4 final product. This, of course, arises from the cyclic nature of the process, and only unavoidable losses of solutions from spillage that cannot be closely estimated will occur. No charge for water is made, except against the thickeners and washing of the K_2SO_4 crystals.

Maintenance and supplies.—This item is \$2.50 per day.

The agitator charges are summarized as follows:

Costs of hot extraction of calcined polyhalite

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—720 kw.-hr. at \$0.003.....	\$ 2.16
Labor—21 man-hours at \$0.75.....	15.75
Steam—1,188,000 pounds at \$0.40 per M.....	475.20
Water00
Maintenance and supplies.....	2.50
	<hr/>
Direct operating cost.....	495.61

FILTRATION OF GYPSUM RESIDUE

The filtration of the extract solution containing about 38.3 per cent of dissolved salts or approximately 62 parts per 100 parts of water must be accomplished without appreciable cooling; therefore, pressure-leaf or continuous-centrifugal filters are necessary. Data obtained from a responsible manufacturer of centrifugal filters indicate that this type of machine is applicable, and a separation can be effected without excessive temperature drop to obtain a filter cake relatively low in retained liquor.

Three 54- by 70-inch centrifugal filters with 150-hp. motors have been recommended as having the necessary capacity.

Equipment.—The cost of the 54- by 70-inch continuous centrifugals is \$20,000 each, installed in New Mexico; to assure ample capacity four filters at a cost of \$80,000 are used in the estimates.

Power.—A power consumption corresponding to possibly two-thirds of the connected load or 7,200 kw.-hr. is allotted at a cost of \$21.60 per day.

Labor.—One operator with a helper can operate the four centrifugals; this corresponds to a labor charge of \$32.40 per day.

Maintenance and supplies.—At 5 percent of equipment cost, these items amount to \$13.33 per day.

The filtration costs are summarized as follows:

Costs of filtering gypsum residue

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—7,200 kw.-hr. at \$0.003.....	\$21.60
Labor—man hours: 24 at \$0.70—24 at \$0.60.....	32.40
Maintenance and supplies.....	13.33
	<hr/>
Direct operating cost.....	67.33

THICKENING GYPSUM RESIDUE

The 1,859.4 tons of filter cake obtained from the centrifugal filters every 24 hours are repulped and fed to a series of four thickeners for countercurrent-washing treatment. Unless the retained-liquor content of the filter cake can be kept very low, the high concentrations of this solution require elevated temperatures during the washing treatment to prevent crystallization. With the composition of filter cake indicated in the flow sheet, the temperatures must be maintained at a minimum of: 176° F. (80° C.) in the first thickener; 140° F. (60° C.) in the second; and possibly 100° F. in the third. Heat input by exchangers operating on the clarified overflow is necessary, in addition to well-insulated thickeners.

Equipment.—These four reinforced-concrete thickeners are 85- by 10-foot; with covers, insulation, necessary motors, rakes, launders, and piping their cost is estimated at \$67,500.

Power.—The power consumption is estimated at 936 kw.-hr., costing \$2.71 per day.

Labor.—One man per shift is necessary to operate the thickeners and maintain the necessary temperatures by heat-exchanger control; this gives a labor charge of \$18.00 per day.

Steam.—Approximately 400,000,000 B.t.u. must be supplied to heat the solutions; this requires at least 424,000 pounds of steam costing \$169.60 per day. However, all of the heat stored in the clarified overflow from No. 1 thickener is utilized in the hot extraction in the agitators.

Water.—Only the water actually used to discharge the washed residue from the final thickener, amounting to 1,290.2 tons or 333,600 gallons and costing \$16.68, is charged against the thickeners.

Maintenance and supplies.—These items are estimated at \$3.50 per day.

The thickening or washing costs are summarized as follows:

<i>Costs of countercurrent-decantation thickening of gypsum residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—936 kw.-hr. at \$0.003.....	\$ 2.71
Labor—24 man-hours at \$0.75.....	18.00
Steam—424,000 pounds at \$0.40 per M.....	169.60
Water—333,600 gallons at \$0.05 per M.....	16.68
Maintenance and supplies.....	3.50
Direct operating cost.....	210.49

COOLING POLYHALITE EXTRACT LIQUORS

The 6,624.2 tons of hot extract liquors obtained daily from the filters at possibly 165° F. can be cooled about 45° F. for heat exchange without any crystallization occurring. The liquors are then pumped into continuous vacuum crystallizers, where nearly 430,000,000 additional B.t.u. must be dissipated to cool the solutions and crystal crop to a final temperature of 86° F. Some of this heat can be recovered after being utilized in evaporating a portion of the solution to effect higher recoveries, but this procedure entails careful adjustment of the NaCl concentration to

prevent crystallization of sodium salts from double decomposition. This potential evaporative capacity is probably as much as 370,000 pounds of water, or an equivalent of 100,000 pounds of steam saved. However, no allowance is made for this possible saving.

The vacuum coolers operating between 120° and 86° F. produce a crop of 472 tons of schönite ($K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$), and this yields 640.2 tons of wet crystals after filtering and washings.

Equipment.—These vacuum coolers or crystallizers, completely installed with all necessary accessories, cost about \$140,000 and represent a connected load of 250 hp.

Power.—The electric-power consumption is 4,500 kw.-hr., costing \$13.50 per day.

Labor.—Two men per shift are employed to operate the crystallizers at a cost of \$36.00 per day.

Steam.—Steam ejectors are necessary to maintain the vacuum in the crystallizers, and 30,000 pounds are consumed at a cost of \$12.00 per day.

Cooling water.—A portion of the estimated 2,060,000 gallons of cooling water used in the condensers of the vacuum coolers can be diverted to the thickeners to recover the heat, but the major portion must be circulated to the cooling towers. The cost of the cooling water with no credits for heat recovered is estimated at \$41.10 per day.

Maintenance and supplies.—Repairs and supplies at 2½ percent of equipment cost are estimated at \$11.67 per day.

The cooling costs are summarized as follows:

<i>Costs of cooling extract liquors to crystallize schönite</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—4,500 kw.-hr. at \$0.003.....	\$ 13.50
Labor—48 man-hours at \$0.75.....	36.00
Steam—30,000 pounds at \$0.40 per M.....	12.00
Cooling water—2,055,000 gallons at \$0.02 per M.....	41.10
Maintenance and supplies.....	11.67
Direct operating cost.....	114.27

DISSOLUTION OF SCHÖNITE CRYSTAL CROP

The wet crop of 640.2 tons of schönite produced in the vacuum crystallizers by cooling the polyhalite-extract liquor is conveyed to slurry-mixing tanks or agitators and dissolved with the 689.6 tons of K_2SO_4 solution obtained from hot extraction of the syn-genite. The mixture is heated to 176° F. to effect dissolution and two 8- by 8-foot agitators with 10-hp. motors are employed to assure a 30-minute retention. Batch operation might be necessary to handle the K_2SO_4 separating during decomposition of the schönite. After removal of the crystallized salts, the mother liquor is fed to a second battery of vacuum crystallizers to recover additional K_2SO_4 .

Equipment.—The 8- by 8-foot agitators, with heating coils and motor drives, cost \$1,500 each installed, or \$3,000 for the two units.

Power.—The power consumption is estimated at 360 kw.-hr., costing \$1.08 per day.

Labor.—One man per shift is required at a cost of \$18 per day.

Steam.—Assuming the syngenite-extract solution at 120° F. and the schönite crystal crop at 86° F. and allowing for the negative heat of solution of the schönite, approximately 167,700,000 B.t.u. must be added to the agitator charge to effect dissolution and raise the temperature to 176° F. (80° C.), which is slightly above the saturation temperature of the K_2SO_4 . Much if not all of this heat can be supplied by recovery of heat from other plant liquors; nevertheless, \$76.80, equivalent to 192,000 pounds of steam, is charged to this operation.

Maintenance and supplies.—No extra water is required for the dissolution step, and the repairs and supplies for the agitators and accessories are nominal, possibly \$0.25 per day.

The costs of dissolving the schönite are summarized as follows:

<i>Costs of dissolving schönite crystal crop</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—360 kw.-hr. at \$0.003.....	\$ 1.08
Labor—24 man-hours at \$0.75.....	18.00
Steam—192,000 pounds at \$0.40 per M.....	76.80
Maintenance and supplies.....	.25
Direct operating cost.....	96.13

COOLING SCHÖNITE-EXTRACT LIQUORS

The discharge from the schönite-dissolution agitators, amounting to 1,329.8 tons every 24 hours, is caught in conical settlers to trap the crystallized K_2SO_4 , and the liquor is separated and further cooled to 86° F. in the vacuum crystallizer. In cooling from 120° F. approximately 92,500,000 B.t.u. must be dissipated from the liquors and crystal product.

Equipment.—Vacuum coolers to effect this cooling and with the necessary and auxiliary equipment cost about \$31,000 installed.

Power.—The power consumption is 1,200 kw.-hr. at a cost of \$3.60 per day.

Labor.—One man can operate the vacuum coolers and handle filtration of the crystallized K_2SO_4 , so that half the labor is charged against each operation. This amounts to \$9.00 per day.

Steam.—The steam required to maintain the necessary vacuum in the various cooler units is estimated at 21,500 pounds, costing \$8.60 per day.

Cooling water.—The water required to cool the condensers is 445,000 gallons every 24 hours, and the cost of the water from the cooling towers at \$0.02 per thousand gallons amounts to \$9.10.

Maintenance and supplies.—The cost of these items is estimated at \$2.60 per day.

The cooling costs are summarized as follows:

<i>Costs of cooling schönite-extract liquors to obtain K_2SO_4</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,200 kw.-hr. at \$0.003.....	\$ 3.60
Labor—12 man-hours at \$0.75.....	9.00
Steam—21,500 pounds at \$0.40 per M.....	8.60
Cooling water—445,000 gallons at \$0.02 per M.....	9.10
Maintenance and supplies.....	2.60
Direct operating cost.....	32.90

FILTRATION OF SCHÖNITE AND POTASSIUM SULFATE CRYSTAL CROPS

The schönite resulting from the cooling of polyhalite-extract liquors and the K_2SO_4 from the schönite-extract solutions are recovered by transferring the mixtures of crystals and mother liquor to conical settlers where the thickened solids are removed to the filters and the liquor overflow pumped to other process steps. Essentially the same type of centrifuges or centrifugal filters is used in each instance to dewater the crystals, but the quantities of wet products are 640.2 tons of schönite and 181 tons of K_2SO_4 ; washing of crystals is necessary with both products.

Equipment.—The equipment costs for these operations are estimated at \$19,500 for the schönite and \$7,500 for the K_2SO_4 .

Power.—Power consumed is 1,150 and 450 kw.-hr., respectively, costing \$3.45 and \$1.35 per day.

Labor.—Possibly one man per shift is required to operate the schönite filtration, but one man's time can be divided between the coolers and filters for the K_2SO_4 . This arrangement gives a labor charge of \$18.00 and \$9.00 per day, respectively.

Water.—Water for washing the crystal crops amounts to 92 and 33.6 tons, equal to \$1.10 and \$0.40.

Maintenance and supplies.—The costs of repairs and miscellaneous supplies are estimated about \$4.35 and \$2.00 per day.

The filtering costs of schönite and K_2SO_4 are summarized as follows:

Filtration of schönite and K_2SO_4 crystal crops

Item	Cost per day (24 hours)			
	Schönite		Potassium sulfate	
	Amount	Cost	Amount	Cost
Power—kw.-hr. at \$0.003.....	1,150	\$3.45	450	\$1.35
Labor—man-hours at \$0.75.....	24	18.00	12	9.00
Water—M gallons at \$0.05 per M.....	22	1.10	8	.40
Maintenance and supplies.....	4.35	2.00
Direct operating costs.....	26.90	12.75

DRYING K_2SO_4 CRYSTAL CROP

The 181 wet tons of K_2SO_4 are dried in oil-fired rotary dryers, and only the expulsion of free water as retained liquor, estimated to require about 65,200,000 B.t.u. (net), is necessary. Temperatures ranging from 250° to 1,090° F. can be used. Evaporating 33.6 tons of water produces 147.4 tons of anhydrous product containing 132 tons of K_2SO_4 .

Equipment.—The dryer costs \$12,000, complete with burners, drives, etc. It is equipped with a 35-hp. motor.

Power.—At full-rated load the electric-power consumption is 630 kw.-hr., costing \$1.89 per day.

Labor.—The labor represents one-half of one operator's time, or \$9.00 per day.

Fuel.—The fuel required is estimated at 18 barrels of oil, costing \$18.00 per day.

Maintenance and supplies.—The cost of these items is estimated at \$2.67 per day.

Drying costs for the potassium sulfate are summarized as follows:

<i>Costs of drying K₂SO₄ product</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—630 kw.-hr. at \$0.003.....	\$ 1.89
Labor—12 man-hours at \$0.75.....	9.00
Fuel—18 barrels of oil at \$1.00.....	18.00
Maintenance and supplies.....	2.67
Direct operating cost.....	31.56

PRODUCTION OF SYNGENITE

The remaining major steps of process 7A that require estimates on equipment and direct operating costs are (a) the production of syngenite and (b) the hot extraction of approximately 31.8 percent of the syngenite to yield a solution containing 10 parts of K₂SO₄ per 100 parts of water for use in dissolving the schönite. Of these two steps only (b) need be considered in detail, since the production of syngenite has been discussed elsewhere (see pp. 66 to 71), and in process 4B (p. 71) estimates have been made on essentially the same daily capacity. Detailed operations have been given before, and only the summarized costs of the various steps involved are incorporated in table 24, covering the estimated costs for process 7A. However the hot extraction of the syngenite is discussed more completely.

HOT EXTRACTION OF WET SYNGENITE

The 240 tons of undried syngenite containing 62.4 tons of K₂SO₄ are extracted for 2½ hours in continuous agitators at approximately 212° F. to produce a solution containing 10 parts of K₂SO₄ in 100 parts of water. The extract liquor is separated from the insoluble residue by means of centrifugal filters to conserve the sensible heat, and the 689.6 tons of warm, clarified solution are pumped to the schönite dissolution agitators. The filter-cake residue is repulped and washed in countercurrent-decantation thickeners to recover the retained soluble salts as a thickener overflow totaling 580.9 tons of dilute liquors subsequently used for make-up solution for the hot extraction. The insoluble residue, now essentially gypsum, is discharged to waste. Virtually complete extraction of the K₂SO₄ is effected, in that the small amount of syngenite or pentasalt remaining undissolved in the residues from the agitators is decomposed completely during the prolonged washing treatment in the thickeners.

AGITATION OF SYNGENITE

The daily charge of 820.9 tons to the agitators, consisting of 140.8 tons of solids and 680.1 tons of liquids, is handled in two 14- by 10-foot turbo-mixers, provided with steam coils and equipped with 20-hp. motors.

Equipment.—The two turbo-mixers, complete with drives, steam coils, and impellers, all installed cost \$4,500.

Power.—Full-rated power consumption amounts to 720 kw.-hr., costing \$2.16 per day.

Labor.—One man per shift is required, giving a cost of \$18.00 per day.

Steam.—The steam consumption to supply the necessary 168,600,000 B.t.u. (net) and with no allowance for heat recovery is 193,000 pounds and costs \$72.20 per day.

Water.—The solution recovered as K_2SO_4 -extract liquor contains 624 tons of water, but 96 tons of this is supplied by the wet syngenite, leaving 528 tons or 126,720 gallons to be charged against the agitators. The cost of this water is \$6.34 per day.

Maintenance and supplies.—The cost of these items is estimated at \$2.50 per day.

The costs for treatment of the syngenite are summarized as follows:

<i>Costs of hot extraction of wet syngenite</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—720 kw.-hr. at \$0.003.....	\$ 2.16
Labor—24 man-hours at \$0.75.....	18.00
Steam—193,000 pounds at \$0.40 per M.....	77.20
Water—126,700 gallons at \$0.05 per M.....	6.34
Maintenance and supplies.....	2.50
	<hr/>
Direct operating cost.....	106.20

FILTRATION OF EXTRACTED SYNGENITE RESIDUE

The discharge from the continuous agitators, consisting of 84 tons of solids suspended in 736.9 tons of solution, is pumped to the centrifugal filters, which separate 689.6 tons of filtrate and produce 131.3 tons of filter cake.

Equipment.—The installed cost of these filters, equipped with motors totaling 50 connected horsepower, is estimated at \$10,000.

Power.—The daily power consumption is approximately 600 kw.-hr., costing \$1.80.

Labor.—Only half the time of one operator—a daily charge of \$9.00—covers the labor expense.

Maintenance and supplies.—The cost of repairs and supplies required in the filter operation is estimated at \$1.67 per day.

The costs of filtration of the extracted syngenite are summarized as follows:

<i>Costs of filtering extracted syngenite</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—600 kw.-hr. at \$0.003.....	\$ 1.80
Labor—12 man-hours at \$0.75.....	9.00
Maintenance and supplies.....	1.67
	<hr/>
Direct operating cost.....	12.47

THICKENING EXTRACTED SYNGENITE RESIDUE

The filter cake from the hot extraction is repulped and washed in a series of three 30-foot thickeners arranged for countercurrent washing. The wash water, amounting to 700.8 tons, is added to the final thickener, and the daily overflow of 580.9 tons of solution is passed through heat exchangers, then used as make-up for the hot extraction, while the insoluble residue (now essentially gypsum) is discharged as 250.4 tons of waste sludge.

Equipment.—The three 30- by 10-foot thickeners can be constructed of steel or wood and with the necessary motor drives,

rakes, and solution pumps cost approximately \$5,000 each—a total of \$15,000 for the complete installation.

Power.—Each thickener is equipped with a 1.5-hp. motor drive and a 2-hp. pump, which totals 10.5 hp. for the three thickeners; this means about 180 kw.-hr. of power consumed at a cost of \$0.54 per day.

Labor.—Two hours of operating labor should be ample, costing \$1.50 per day.

Water.—The 166.4 tons of free water and the 13.6 tons of combined water, equal to 43,200 gallons, cost only \$2.15 per day.

Maintenance and supplies.—The cost of these items is estimated at \$0.75 per day.

The thickening costs are summarized as follows:

<i>Costs of thickening gypsum residue</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—180 kw.-hr. at \$0.003.....	\$0.54
Labor—2 man-hours at \$0.75.....	1.50
Water—43,200 gallons at \$0.05 per M.....	2.10
Maintenance and supplies.....	.75
Direct operating cost.....	4.89

DRYING SYNGENITE

The 297.6 tons of calcined syngenite produced represent a daily feed of 516.8 tons of wet material in comparison with 397 tons of dehydrated product and 692.8 tons of wet feed handled in the dryers, as specified for process 4B (see p. 199). However, same-size dryers, comprising two 8- by 160-foot brick-lined rotary kilns, each with coolers, are recommended for handling the syngenite from process 7A. The estimated cost of these kilns is \$115,000.

Likewise, the operating costs, exclusive of fuel requirements, are nearly the same as for process 4B. The fuel-oil consumption necessary to supply the 410,900,000 B.t.u. (net) required daily is 112 barrels instead of 159, as consumed in the kilns for process 4B.

With these modifications, the dryer costs are summarized as follows:

<i>Costs of calcining syngenite for process 7A</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—2,000 kw.-hr. at \$0.003.....	\$ 6.00
Labor—man-hours: 24 at \$0.75—48 at \$0.60.....	46.80
Fuel—112 barrels oil at \$1.00.....	112.00
Maintenance and supplies.....	20.00
Direct operating cost.....	184.80

EQUIPMENT AND OPERATING COSTS OF PROCESS 8

PRODUCTION OF SYNGENITE-GYPSUM

The 390.5 tons of calcined polyhalite treated daily yield 340.3 tons of syngenite-gypsum in comparison with 314.4 tons of this mixture produced from 352 tons of calcined polyhalite extracted in the syngenite-formation step of process 4B. However, the ample equipment allowance for that process is large enough to handle the materials in this process. The equipment and direct operating costs, therefore, are as follows:

Equipment.—The cost of equipment for feeding the calcined polyhalite is \$1,750; for ball-mill grinding, it is \$11,250; for classifying, it is \$4,850; and for the four 85- by 10-foot reinforced-concrete thickeners all completely installed at \$15,000 each, the total cost is \$60,000.

Power.—The power consumption of the feeder is 90 kw.-hr. per day or \$0.27; the ball-mill grinding consumes 2,700 kw.-hr., amounting to \$8.10 daily; the classifier requires 180 kw.-hr. every 24 hours at a cost of \$0.54; and the thickeners consume 576 kw.-hr. at a cost of \$1.73 each day.

Labor.—One man per shift can operate the feeders, ball mills, classifier, and thickeners by allotting half time to the feeder and ball mills and half time to the classifier and thickeners; this corresponds to a \$9.00 charge each day for feeding and ball-milling and \$9.00 for classifying and thickening.

Water.—The 927.5 tons (222,600 gallons) of water added to the thickeners to remove the washed syngenite and to provide overflow solution for use in extracting the magnesium sulfate during the ball-milling and classifying steps are charged to the thickeners at a cost of \$11.13 daily. In processes 4 and 4B the water is supplied as filter washings and as recycled K_2SO_4 solutions instead of as fresh water.

Maintenance and supplies.—The costs of these items are estimated at \$1.00, \$3.75, \$0.42, and \$3.00, respectively, for the feeders, ball mills, classifier, and thickeners.

The costs involved in the production of the wet syngenite-gypsum correspond closely to those given previously for process 4B (see table 20, p. 74) and are summarized in table 30 (p. 100) without being itemized separately in this section.

EXTRACTION OF SYNGENITE-GYPSUM BY AMMONIUM CARBONATE SOLUTION

The volume of carbon dioxide necessary to react with all of the calcium sulfate other than anhydrite in the syngenite-gypsum mixture is so large that it would be preferable to absorb this gas in ammonia liquors, presumably by use of coke-filled absorption towers, to produce an ammonium carbonate solution for the carbonation treatment.

Wide latitude in choice of concentrations of ammonium carbonate solution are possible, in that all or any desired portion of the 505.3 tons of overflow solution from No. 2 thickener employed in the countercurrent-decantation washing of the carbonated residue plus the 225.9 tons of ammoniacal washings from K_2SO_4 filters can be carbonated in the towers. This provides any concentration of $(NH_4)_2CO_3$ in the range 91.4 to 14.3 parts per 100 parts of water. Saturation concentration at room temperature corresponds to about 65 parts of $(NH_4)_2CO_3$ per 100 parts of water, so that the amount of solution employed is chosen to prevent attainment of saturation and to limit the handling of unnecessarily large quantities of liquors.

The ammonium carbonate solution must absorb 66.5 tons of CO_2 daily and the total of 797.7 tons of resulting liquor is added to continuous reaction agitators to which the 1,020.9 tons of wet syngenite mixture are fed every 24 hours. Thickening is effected

by discharging the agitators to a series of four reinforced-concrete thickeners operating for countercurrent washing. The carbonated residue, essentially consisting of CaCO_3 , is discharged as 504.6 tons of sludge from the final thickener while the 1,207.7 tons of clarified overflow is obtained from No. 1 thickener for subsequent treatment with sylvite and ammonia to produce potassium sulfate.

EQUIPMENT AND DIRECT OPERATING COSTS FOR CARBONATION OF SYNGENITE-GYPSUM

To assure a 60-minute retention of the charge, two 11- by 9-foot continuous agitators of the turbo-mixer or similar type are employed, each driven by a 10-hp. motor.

Equipment.—The two 11- by 9-foot turbo-mixers with covered wooden tanks and stirrers and with motor drives all installed will cost \$4,500.

Power.—Operating continuously at full-rated load requires 360 kw.-hr., costing \$1.08 per day.

Labor.—One man per shift can operate the agitators and devote the necessary time, possibly an average of 1 hour per shift, to care of the washing thickeners. This means a charge of \$15.75 for labor on the agitators.

Water.—Most of the water utilized in the agitators is supplied by the wet syngenite-gypsum mixture and as washings, but 62.7 tons (15,048 gallons) must be obtained every 24 hours from the thickener feed at a cost of \$0.75 per day.

Maintenance and supplies.—The cost of repairs and supplies for the agitators is estimated at \$2.00 per day.

The costs of carbonating are summarized as follows:

<i>Costs of carbonating syngenite-gypsum</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—360 kw.-hr. at \$0.003.....	\$ 1.08
Labor—21 man-hours at \$0.75.....	15.75
Water—15,000 gallons at \$0.05 per M.....	.75
Maintenance and supplies.....	2.00
Direct operating cost.....	19.58

THICKENING OF CARBONATED RESIDUE

The clarified overflow from No. 1 thickener amounts to 1,207.7 tons daily and serves as feed liquor to the agitators for the ammonia and KCl treatment while the washed residue of calcium carbonate is discarded as a thickened sludge. Overflow from No. 2 thickener is partly added to the ammoniacal washings from the final K_2SO_4 product, and the combined liquors after use in the towers are returned and added with the balance of the overflow to the carbonating agitators.

An allowance of 8 square feet per ton-day of settled solids requires 45-foot thickeners to effect satisfactory sedimentation.

Equipment.—Four 45- by 10-foot reinforced-concrete thickeners with sludge pumps, motor drives, rakes, and supporting structure and with 2-hp. motors cost \$25,500 installed and represent a total connected load of 20 hp.

Power.—The electric-power consumption is 360 kw.-hr., costing \$1.08 per day.

Labor.—An average of 3 hours per day represents an outlay of \$2.25 for labor.

Water.—Only the water required to discharge the calcium carbonate sludge and amounting to 336.4 tons (80,736 gallons every 24 hours) is charged against the thickeners. The cost of this water is \$4.04 per day.

Maintenance and supplies.—The cost of these items is estimated at \$1.28 per day.

The thickening costs are summarized as follows:

<i>Costs of countercurrent washing of carbonate sludge</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—360 kw.-hr. at \$0.003.....	\$1.08
Labor—3 man-hours at \$0.75.....	2.25
Water—80,700 gallons at \$0.05 per M.....	4.04
Maintenance and supplies.....	1.28
	<hr/>
Direct operating cost.....	8.65

CRYSTALLIZATION OF POTASSIUM SULFATE BY TREATMENT OF AMMONIUM SULFATE LIQUOR WITH POTASSIUM CHLORIDE AND AMMONIA

The 1,207.7 tons of solution obtained as overflow from the thickeners contain 181.4 tons of $(\text{NH}_4)_2\text{SO}_4$ and 91.0 tons of K_2SO_4 , as well as minor amounts of NH_4Cl , KCl , and $(\text{NH}_4)_2\text{CO}_3$, dissolved in 909.6 tons of water. This liquor is cooled by refrigerating and then pumped to enclosed reaction agitators and 208.5 tons of 98 percent sylvite added, whereupon a small amount of K_2SO_4 crystallizes from solution.

Liquid ammonia, amounting to 287.2 tons every 24 hours, and an additional 14.9 tons of water are forced into the closed agitators to effect saturation with ammonia, which decreases the solubility of the K_2SO_4 . The crystal crop resulting from this treatment contains 290.6 tons of K_2SO_4 and 30.2 tons of $(\text{NH}_4)_2\text{SO}_4$ and is pumped to settlers and finally discharged as a thickened sludge to continuous vacuum or centrifugal filters.

The double decomposition of the ammonium sulfate and potassium chloride and the dissolution of the potassium chloride, including the crystallization of the K_2SO_4 , results in an over-all evolution of heat of approximately 6,640,000 B.t.u. every 24 hours. The heat of solution of the liquid ammonia evolves additional heat amounting to 115,000,000 B.t.u., so that refrigeration is required to control the temperatures and attain efficient recovery of salt.

CRYSTALLIZATION OF K_2SO_4 IN CLOSED AGITATORS

Two 14- by 10-foot closed agitators equipped with auxiliary cooling coils and efficient stirrers of the turbo-mixer or a similar type are operated by a batch process on 90-minute cycles.

Equipment.—The cost of the two 14- by 10-foot agitators constructed of heavy steel and equipped with 20-hp. motors is estimated at \$3,000 each or a total of \$6,000.

Power.—With electric power consumed assumed at full-rated load, 720 kw.-hr. are required, at a cost of \$2.16 per day.

Labor.—One man per shift, at a cost of \$18.00 per day, is allotted for operating labor.

Sylvite.—The 208.5 tons of 98-percent KCl consumed daily represent a major item of operating expense, and an equitable and accurate estimate of the probable cost of this material is extremely difficult to make. However, it has been assumed that both polyhalite and sylvinite are mined and treated to supply the grades of calcined polyhalite and refined sylvite required in the proposed flow sheet of the process.

If \$10.00 per ton of 98-percent KCl is used as the probable cost of producing this material, exclusive of all supervision, administration, and selling costs, the 208.5 tons consumed daily amount to \$2,085.

Ammonia.—Although 287.2 tons of pure ammonia are needed every 24 hours to saturate the volume of $(\text{NH}_4)_2\text{SO}_4\text{--K}_2\text{SO}_4$ liquors handled, no charge is made against this operation because an ammonia-recovery plant is employed to regenerate the ammonia. An estimate of the costs of such a recovery plant has been made in a previous section (see p. 100). Actually, the only fresh ammonia added to the process to offset the losses in the waste liquors and in the finished product enters the process as a wash for the finished K_2SO_4 and is converted into ammonium carbonate in a subsequent step.

Maintenance and supplies.—The cost of these items is estimated at \$2.00 per day.

The costs of crystallization of the K_2SO_4 , exclusive of the necessary refrigeration of the solutions, are summarized as follows:

<i>Costs of crystallizing K_2SO_4 from $(\text{NH}_4)_2\text{SO}_4$ liquors by addition of KCl and NH_3</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—720 kw.-hr. at \$0.003.....	\$ 2.16
Labor—24 man-hours at \$0.75.....	18.00
KCl (98 percent), 208.5 tons at \$10.00.....	2,085.00
Maintenance and supplies.....	2.00
Direct operating cost.....	2,107.16

COOLING OF AMMONIATED $\text{K}_2\text{SO}_4\text{--}(\text{NH}_4)_2\text{SO}_4$ SOLUTION

The addition of ammonia to the $(\text{NH}_4)_2\text{SO}_4$ solution to which the sylvite has been added results in the evolution of approximately 115,000,000 B.t.u. every 24 hours. This heat, together with the 6,640,000 B.t.u. evolved from the over-all chemical reactions in the agitators, totals 121,640,000 B.t.u., which must be dissipated to prevent excessive temperature and pressure increases.

A self-contained refrigeration unit is installed adjacent to the agitators, and the solutions are circulated through the cooling coils of the refrigerator to effect the necessary cooling. The heat to be absorbed daily requires a machine of 422.5 tons of refrigeration capacity, so that possibly a 500-ton machine should be installed.

Equipment.—The installed cost of a rotary-compressor type of refrigeration machine, operating with the refrigerant outside of the central tubes of the heat exchanger and within the outer shell and effecting the cooling of the solution being circulated through the tubes by the direct vaporization, is \$50,000; the power represents a connected load of 675 hp.

Power.—The electric-power consumption is 1,000 kw.-hr., costing \$3.00 per day.

Labor.—Half the time of one attendant is required to operate the refrigeration machine at a cost of \$9.00 per day.

Cooling water.—Condenser water for effecting the necessary cooling of the refrigerant is obtained from cooling towers and approximately 1,825,000 gallons must be circulated every 24 hours at a cost of \$36.50.

Maintenance and supplies.—The cost of repairs and supplies is estimated at \$4.25 per day.

The costs of dissipating the heat of reaction are summarized as follows:

Cooling costs for ammoniated $(\text{NH}_4)_2\text{SO}_4$ - K_2SO_4 liquors

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,000 kw.-hr. at \$0.003.....	\$ 3.00
Labor—12 man-hours at \$0.75.....	9.00
Water—1,825,000 gallons at \$0.02 per M.....	36.50
Maintenance and supplies.....	4.25
	<hr/>
Direct operating cost.....	52.75

RECOVERY OF K_2SO_4 CRYSTAL CROP

The crop of K_2SO_4 crystals containing 9 to 10 percent $(\text{NH}_4)_2\text{SO}_4$, after being collected in the conical settling tanks, is fed to centrifuges or centrifugal filters and given a thorough spray wash with 210.5 tons of aqua ammonia containing 51.6 tons of NH_3 to remove the retained liquor. The 433.9 tons of wet washed crystals are then conveyed to rotary dryers, and the 225.9 tons of ammonical liquor resulting from the washing operation are diverted to the carbonating towers for preparation of ammonium carbonate solution.

Equipment.—The centrifugal filters of the same capacity and at the costs indicated for handling the schönite in processes 1 and 7A and the K_2SO_4 in process 3 are required. These filters, completely installed, cost \$19,500.

Operating costs.—The power, labor, and maintenance costs are \$3.45, \$18.00, and \$7.50, respectively. In addition, the 13.7 tons of ammonia added daily to the system to replace losses are charged against this operation, together with the 74.2 tons of water; the total cost amounts to approximately \$1,235 per day.

The K_2SO_4 recovery costs are summarized as follows:

Costs of filtering K_2SO_4 -(NH_4) $_2\text{SO}_4$ crystal crop

<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,150 kw.-hr. at \$0.003.....	\$ 3.45
Labor—24 man-hours at \$0.75.....	18.00
Maintenance and supplies.....	7.50
Ammonia wash: 27,400 pounds at \$0.045 per pound.....	1,235.00
	<hr/>
Direct operating cost.....	1,263.95

DRYING K_2SO_4 -(NH_4) $_2\text{SO}_4$ CRYSTAL CROP

Rotary dryers, provided with special equipment for recovery of the ammonia from the liquors and salts retained by the filtered crystalline product, are required. The cost of these dryers is

slightly greater than the dryers employed on processes 1, 7A, and 3, amounting to possibly \$32,500; the operating costs are the same as for those processes.

Operating costs.—The direct operating costs, exclusive of fuel oil, are the same as for drying the schönite in process 1, namely: Power, 1,600 kw.-hr. or \$4.80; labor, \$9.00; and maintenance and supplies, \$6.50. To supply the necessary 190,400,000 B.t.u. (net) to evaporate the retained water and expel the free ammonia, 52 barrels of oil at \$1.00 per barrel or \$52.00 daily are needed. The total operating cost, therefore, is \$72.30 per day.

PRODUCTION OF AMMONIUM CARBONATE SOLUTION

The conversion of the syngenite-gypsum mixture to calcium carbonate and ammonium and potassium sulfates requires 66.5 tons of carbon dioxide daily to provide a slight excess of precipitant. This gas can be recovered either from waste flue gases or from the kilns burning lime for use in the ammonia-recovery plant.

To avoid difficulties from saturation, the 225.9 tons of ammoniacal filter washings are diluted with 166.8 tons of the clarified-overflow liquor from the No. 2 thickener employed in washing the carbonate sludge. These combined liquors are pumped daily to coke-filled absorption towers to be converted to $(\text{NH}_4)_2\text{CO}_3$ solutions similar to the method for producing potassium-carbonate solution for process 6 (see p. 89).

Equipment.—The costs of the 10- by 100-foot steel absorption towers filled with coke and equipped with solution pumps, blower fans, sprays, attachments, piping, and the necessary control devices are estimated at \$8,400 each. Assuming that each tower absorbs 500 pounds of CO_2 per hour, equivalent to 6 tons per day, 11 of these towers are required. The complete battery of towers costs \$92,400.

Operating costs.—These costs are essentially the same as for the towers specified in process 6 and are summarized as follows:

<i>Operating costs of production of ammonium carbonate by means of absorption towers</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—1,400 kw.-hr. at \$0.003.....	\$ 4.20
Labor—48 man-hours at \$0.75.....	36.00
Maintenance and supplies.....	15.00
Direct operating cost.....	55.20

RECOVERY OF AMMONIA

The 1,278.1 tons of liquor obtained as the mother liquor from the K_2SO_4 crystallization and saturated with 272.6 tons of ammonia and also containing 121.4 tons of ammonium chloride must be treated every 24 hours to recover the ammonia for reuse. The usual method of stripping by treating with quicklime and distilling the free ammonia is employed. High recoveries (98 percent) of ammonia are possible from solutions of this type, and complete ammonia-recovery plants may be purchased for this purpose.

Equipment.—An estimate from a responsible engineering firm indicates that the probable cost of the equipment of an ammonia-recovery plant of the necessary capacity is \$195,000, f.o.b. Boston, with an additional charge of \$55,000 for transportation and installation at Carlsbad, N. Mex. This gives a total cost of \$250,000 for the ammonia-recovery unit.

Power.—Electric-power requirements are estimated at 960 kw.-hr. and would cost \$2.88 per day.

Labor.—Only two men per shift are required to operate the plant, representing a labor cost of \$36.00 per day.

Steam.—The steam consumption is estimated at 3,600,000 pounds at a cost of \$1,440 per day.

Cooling water.—Fifty-six thousand gallons of water are required for cooling the condensers and exchangers at a cost of \$26.88 per day.

Lime.—The 74.9 tons of quicklime required to treat the ammonia liquors to effect the complete stripping cost \$375.00 daily, providing a lime-burning plant is constructed to supply this product. Such a plant, incorporating the latest modern devices and burning natural gas for fuel, represents an investment of \$800 per ton-day capacity, or a total of \$60,000.

Maintenance and supplies.—The cost of these items is estimated at \$35.00 per day.

The operating costs for the ammonia-recovery plant are summarized as follows:

<i>Costs of operating ammonia-recovery plant</i>	
<i>Item:</i>	<i>Cost per day (24 hours)</i>
Power—960 kw.-hr. at \$0.003.....	\$ 2.88
Labor—48 man-hours at \$0.75.....	36.00
Steam—3,600,000 pounds at \$0.40 per M.....	1,440.00
Cooling water—1,344,000 gallons at \$0.02 per M.....	26.88
Lime—75 tons at \$5.00 per ton.....	375.00
Maintenance and supplies.....	35.00
Direct operating cost.....	1,914.76

APPENDIX B

Additional information has been collected on the various salt-system equilibria and on the patents and publications covering the extraction treatment of polyhalite and is presented in this appendix. A list of the publications by the potash research staff of the Bureau of Mines, as released at various intervals during the progress of the investigations, is included also.

EQUILIBRIUM DATA ON THE SALT SYSTEMS

In this section some of the equilibrium data pertaining to the salt systems believed to be of interest in connection with the processes for extraction and recovery of the potassium compounds have been tabulated. Likewise, these data have been plotted in the form of curves in the various instances, in the hope that this information will prove of value to those working with these salt mixtures.

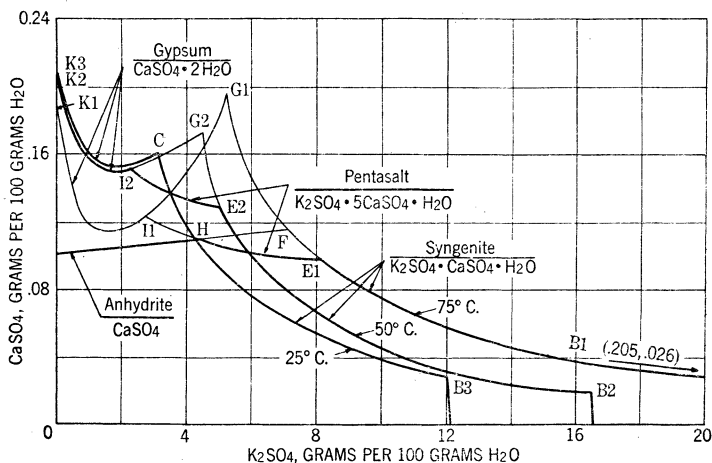


FIGURE 54.—Equilibrium isotherms for system K_2SO_4 — $CaSO_4$ — H_2O at 25°, 50°, and 75° C.

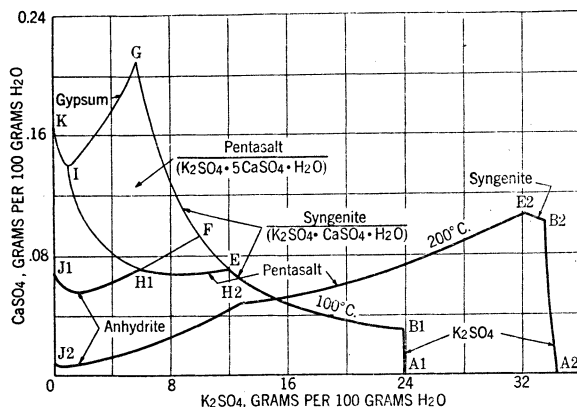


FIGURE 55.—Equilibrium isotherms for system K_2SO_4 — $CaSO_4$ — H_2O at 100° and 200° C.

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TABLE 45.— K_2SO_4 — $CaSO_4$ — H_2O isotherms

[See figs. 54 and 55]

Point	K ₂ SO ₄		CaSO ₄		Solid phases
	Grams per 100 grams H ₂ O	Moles per 1,000 moles H ₂ O	Grams per 100 grams H ₂ O	Moles per 1,000 moles H ₂ O	
25° C.					
A.....	12.1	12.50	K ₂ SO ₄
B.....	12.0	12.39	0.031	0.041	K ₂ SO ₄ + syngenite
C.....	3.2	3.31	.160	.212	Syngenite + gypsum
D.....208	.275	CaSO ₄ · 2H ₂ O
50° C.					
A.....	16.5	17.05	K ₂ SO ₄
B.....	16.5	17.05	0.019	0.025	K ₂ SO ₄ + syngenite
E.....	5.0	5.16	.131	.173	Syngenite + pentasalt
F.....	4.75	4.91	Syngenite + anhydrite
G.....	4.50	4.65	.175	.231	Syngenite + gypsum
H.....	3.50	3.62	Pentasalt anhydrite
I.....	2.25	2.32	.156	.206	Pentasalt + gypsum
J.....	Anhydrite
K.....208	.275	Gypsum
75° C.					
A.....	20.6	21.3	K ₂ SO ₄
B.....	20.5	21.17	0.026	0.034	K ₂ SO ₄ + syngenite
E.....	8.2	8.47	.098	.130	Syngenite + pentasalt
F.....	7.1	7.33	.115	.152	Syngenite + anhydrite
G.....	5.2	5.37	.195	.258	Syngenite + gypsum
H.....	4.5	4.65	.110	.145	Pentasalt + anhydrite
I.....	2.8	2.89	.125	.165	Pentasalt + gypsum
J.....102	.135	Anhydrite
K.....190	.251	Gypsum
100° C.					
A.....	24.0	24.79	K ₂ SO ₄
B.....	23.95	24.74	0.032	0.042	K ₂ SO ₄ + syngenite
E.....	11.89	12.28	.074	.098	Syngenite + pentasalt
F.....	10.02	10.35	.093	.123	Syngenite + anhydrite
G.....	5.68	5.87	.212	.280	Syngenite + gypsum
H.....	5.78	5.97	.071	.094	Pentasalt + anhydrite
I.....	1.10	1.14	.138	.182	Pentasalt + gypsum
J.....067	.089	Anhydrite
K.....170	.225	Gypsum
200° C.					
A.....	34.4	37.5	K ₂ SO ₄
B.....	33.6	34.71	0.098	0.130	K ₂ SO ₄ + syngenite
E.....	32.3	33.36	.107	.141	Syngenite + pentasalt
H.....	13.3	13.74	.050	.066	Pentasalt + anhydrite
I.....0078	.0103	Anhydrite

TABLE 46.— K_2SO_4 — $CaSO_4$ — $NaCl$ — H_2O ¹ isotherm, 25° C.

[See fig. 56]

K_2SO_4		$CaSO_4$		$NaCl$		Solid phases
Grams per 100 grams H_2O	Moles per 1,000 moles H_2O	Grams per 100 grams H_2O	Moles per 1,000 moles H_2O	Grams per 100 grams H_2O	Moles per 1,000 moles H_2O	
.....	0.238	0.315	0	0	$CaSO_4 \cdot 2H_2O$
.....430	.569	2	6.16	Do.
.....610	.807	5	15.40	Do.
.....74	.979	10	30.80	Do.
.....80	1.058	15	46.19	Do.
.....81	1.071	20	61.59	Do.
3.22	3.33	.223	.295	0	0	$CaSO_4 \cdot 2H_2O$ + syngenite
3.75	3.87	.20	.264	2	6.16	Do.
4.75	4.91	.235	.311	5	15.40	Do.
5.20	5.37	.273	.361	10	30.80	Do.
5.80	5.99	.26	.344	15	46.19	Do.
6.25	6.46	.23	.304	20	61.59	Do.

¹ Data from D'Ans (9) and Hill (14).

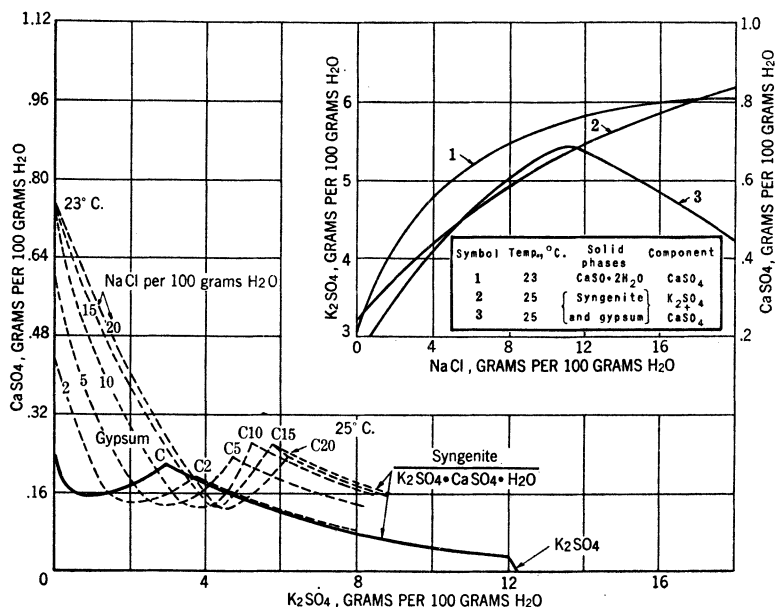


FIGURE 56.—Equilibrium diagram for system $\text{K}_2\text{SO}_4\text{—CaSO}_4\text{—H}_2\text{O}$ with added NaCl (lower); effect of NaCl on solubility of gypsum (upper 1) and syngenite-gypsum equilibrium (upper 2 and 3).

TABLE 47.— $\text{K}_2\text{SO}_4\text{—CaSO}_4\text{—H}_2\text{O}^1$ polytherm

[See fig. 57]

Point	Temperature, °C.	K_2SO_4		CaSO_4		Solid phases
		Grams per 100 grams H_2O	Moles per 1,000 moles H_2O	Grams per 100 grams H_2O	Moles per 1,000 moles H_2O	

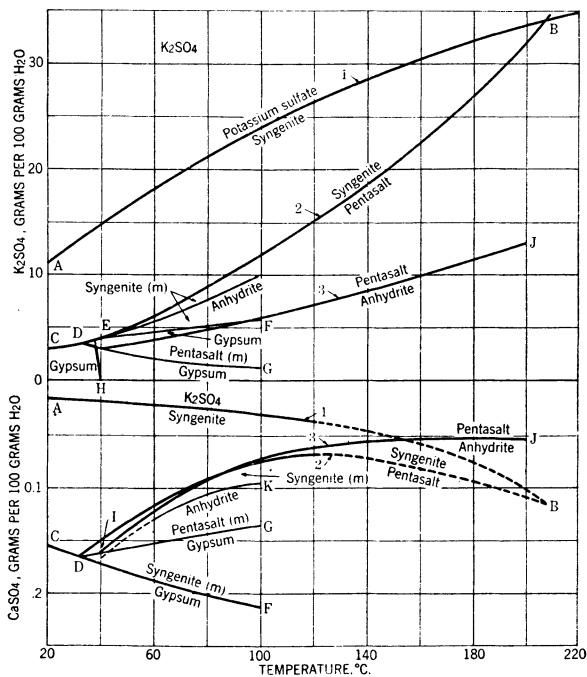
STABLE EQUILIBRIA

A.....	20	11.0	11.36	0.016	0.021	K_2SO_4 + syngenite
B.....	206	34.0	35.12	.115	.152	K_2SO_4 + syngenite + pentasalt
C.....	20	3.0	3.10	.155	.205	Syngenite + gypsum
D.....	32	3.5	3.62	.165	.218	Syngenite + gypsum + pentasalt
H.....	40					Anhydrite
I.....	38	3.2	3.31	.162	.214	Pentasalt, gypsum + anhydrite
J.....	200	13.2	13.63	.052	.069	Pentasalt and anhydrite
1.....	100	23.95	24.74	.032	.042	K_2SO_4 and syngenite
2.....	100	11.89	12.28	.074	.098	Syngenite and pentasalt
3.....	100	5.78	5.97	.071	.094	Pentasalt and anhydrite

METASTABLE EQUILIBRIA

E.....	38	3.8	3.93	Syngenite, anhydrite, and pentasalt
F.....	100	5.68	5.87	0.211	0.279	Syngenite and gypsum
G.....	100	1.10	1.14	.138	.182	Pentasalt and gypsum
K.....	100	10.02	12.40	.093	.123	Syngenite and anhydrite

¹ Transition points obtained by extrapolation of data and curves representing experimental and collected data of Hill (14) and Clarke and Partridge (reference 2, p. 248).

FIGURE 57.—Equilibrium polytherms for system K_2SO_4 — $CaSO_4$ — H_2O .TABLE 48.— K_2SO_4 — $MgSO_4$ — H_2O isotherms

[See figs. 58 and 59]

[See figs. 48 and 49.]

Point	K ₂ SO ₄		MgSO ₄		Solid phases ¹
	Grams per 100 grams H ₂ O	Moles per 1,000 moles H ₂ O	Grams per 100 grams H ₂ O	Moles per 1,000 moles H ₂ O	
25° C. ²					
A.....	12.10	12.50	K ₂ SO ₄
B.....	14.20	14.70	16.4	24.5	K ₂ SO ₄ + schönite
C.....	5.78	6.0	37.9	56.7	Schönite + MgSO ₄ .7H ₂ O
D.....	37.8	56.5	MgSO ₄ .7H ₂ O
30° C. ²					
A.....	13.11	13.53	K ₂ SO ₄
B.....	15.33	15.83	17.72	26.51	K ₂ SO ₄ + schönite
C.....	6.55	6.76	39.91	59.71	Schönite + MgSO ₄ .7H ₂ O
D.....	40.91	61.90	MgSO ₄ .7H ₂ O
85° C. ²					
A.....	22.05	22.76	K ₂ SO ₄
E.....	26.39	27.24	25.78	38.57	K ₂ SO ₄ + leonite
F.....	20.70	21.37	34.20	51.16	Leonite + langbeinite
G.....	5.10	5.26	49.5	74.05	Langbeinite + MgSO ₄ .H ₂ O
H.....	49.0	73.3	MgSO ₄ .H ₂ O
100° C. ²					
A.....	24.22	25.00	K ₂ SO ₄
I.....	28.6	29.52	20.6	30.82	K ₂ SO ₄ + langbeinite
G.....	5.5	5.68	45.0	67.32	Langbeinite + MgSO ₄ .H ₂ O
H.....	46.6	69.70	MgSO ₄ .7H ₂ O

¹ See p. 17 for chemical compositions.² Data from Von Klooster (12).³ Data from Starrs and others (references 21 and 22 in list of Bureau of Mines publications, p. 249).

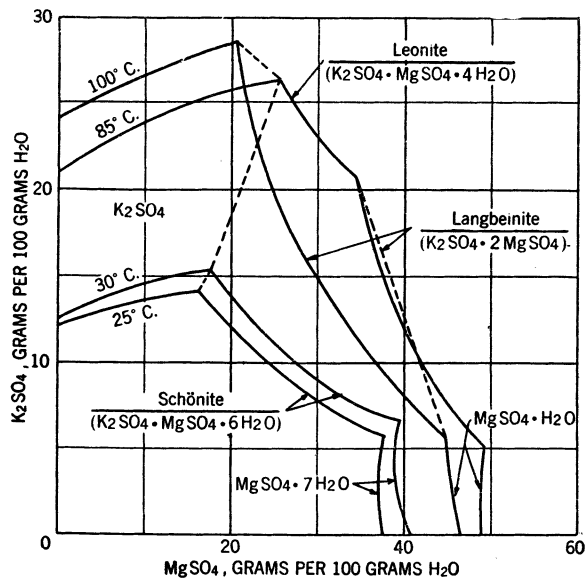
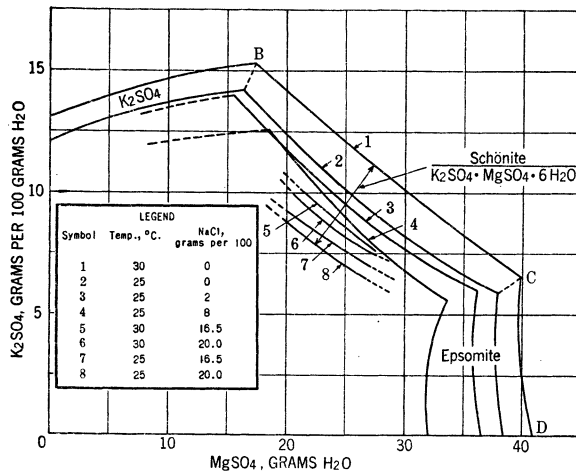
FIGURE 58.—Equilibrium isotherms for system K_2SO_4 — $MgSO_4$ — H_2O .FIGURE 59.—Equilibrium isotherms for system K_2SO_4 — $MgSO_4$ — H_2O with added NaCl.

TABLE 49.— K_2SO_4 — $MgSO_4$ — H_2O ¹ polytherm

[See fig. 60]

Point	Temp., ° C.	K_2SO_4		$MgSO_4$		Solid phases ²
		Grams per 100 grams H_2O	Moles per 1,000 moles H_2O	Grams per 100 grams H_2O	Moles per 1,000 moles H_2O	
A.....	25	12.10	12.50	K_2SO_4
B.....	25	14.20	14.70	16.4	24.5	K_2SO_4 + schönite
C.....	25	5.78	6.0	37.9	56.7	Schönite + $MgSO_4 \cdot 7H_2O$
D.....	25	37.8	56.5	$MgSO_4 \cdot 7H_2O$
I.....	41	7.0	7.2	48.2	72.1	Schönite + leonite + $MgSO_4 \cdot 7H_2O$
2.....	47.2	7.0	7.2	50.3	75.3	Schönite + leonite + K_2SO_4
3.....	47.5	18.2	18.8	24.3	36.3	Leonite + $MgSO_4 \cdot 7H_2O$ + $MgSO_4 \cdot 6H_2O$
4.....	48.2	48.2	73.4	$MgSO_4 \cdot 7H_2O$ + $MgSO_4 \cdot 6H_2O$
5.....	61.0	7.1	7.3	57.4	85.9	Leonite + langbeinite + $MgSO_4 \cdot 6H_2O$
6.....	66.5	7.0	7.2	59.3	88.8	Langbeinite + $MgSO_4 \cdot 6H_2O$ + $MgSO_4 \cdot H_2O$
7.....	67.5	58.7	87.8	$MgSO_4 \cdot 6H_2O$ + $MgSO_4 \cdot H_2O$
8.....	89	26.1	27.0	27.4	41.0	Leonite + langbeinite + K_2SO_4
A1.....	100	24.2	25.0	K_2SO_4
I.....	100	28.6	29.52	20.6	30.82	K_2SO_4 + langbeinite.
G.....	100	5.5	5.68	45.0	67.32	Langbeinite + $MgSO_4 \cdot H_2O$
H.....	100	46.6	69.70	$MgSO_4 \cdot 7H_2O$.

¹ Data for points A-H from Starrs; see reference 21 in list of Bureau of Mines publications (p. 249); data for points I to 8 from D'Ans (9).

² See p. 17 for solid-phase compositions.

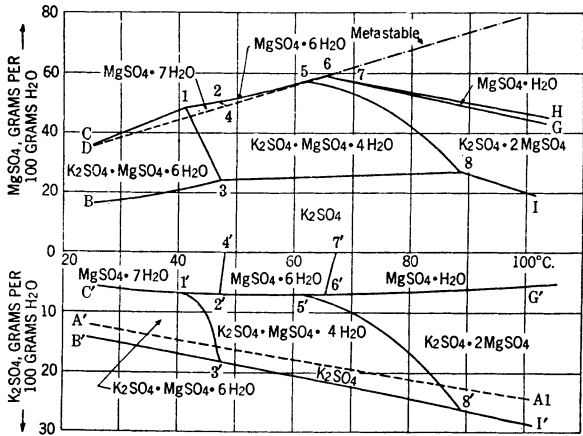


FIGURE 60.—Equilibrium polytherm for system K_2SO_4 — $MgSO_4$ — H_2O .

TABLE 50.— K_2SO_4 — $MgSO_4$ — $CaSO_4$ — H_2O ¹ isotherm, 25° C.

[See fig. 61]

Point	K_2SO_4 , grams per 100 grams H_2O	$MgSO_4$, moles per 1,000 moles H_2O	Solid phases ²
K.....	3.27	0.0	Syngenite, gypsum
A.....	12.00	0	K_2SO_4 , syngenite
B.....	15.5	14.8	K_2SO_4 , syngenite, schönite
C.....	14.0	16.6	K_2SO_4 , schönite
D.....	5.8	37.9	Schönite, $MgSO_4 \cdot 7H_2O$
E.....	5.1	39.0	Syngenite, schönite, $MgSO_4 \cdot 7H_2O$
F.....	4.9	38.9	Syngenite, polyhalite, $MgSO_4 \cdot 7H_2O$
G.....	3.5	37.3	Gypsum, polyhalite, $MgSO_4 \cdot 7H_2O$
H.....	3.4	37.0	Syngenite, gypsum, polyhalite

¹ No data available on concentrations of $CaSO_4$; other data from International Critical Tables, vol. IV, p. 349.

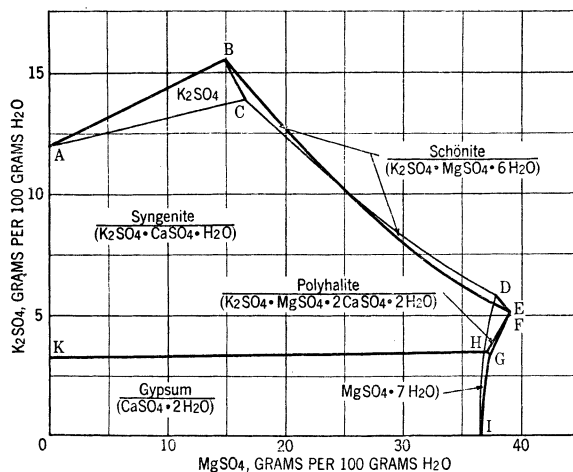
² See page 17 for composition of solid phases.

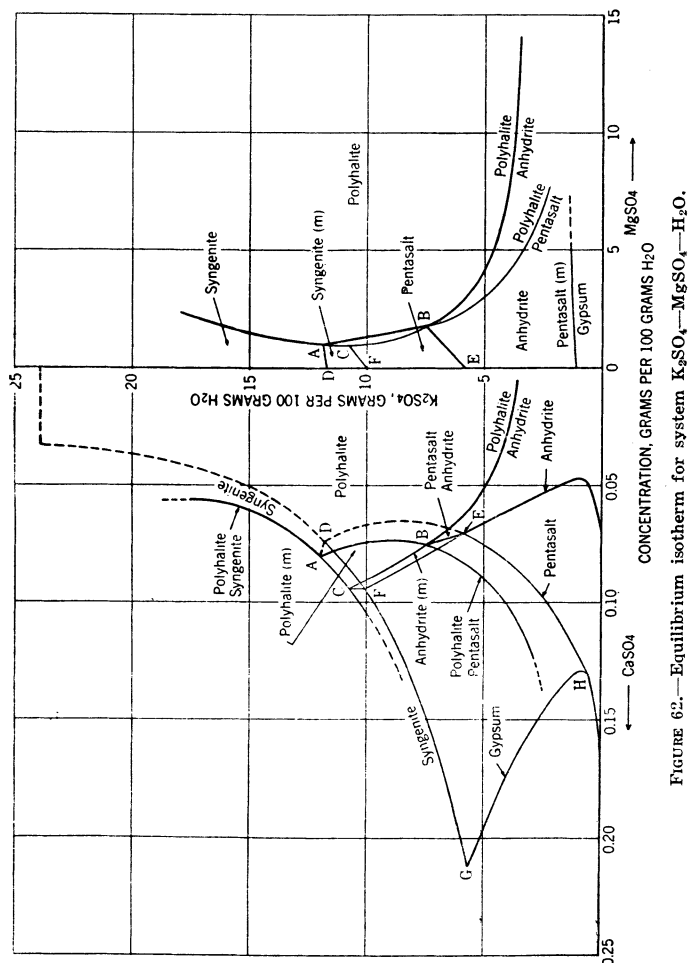
TABLE 51.— K_2SO_4 — $MgSO_4$ — $CaSO_4$ — H_2O ¹ isotherm, 100° C.

[See fig. 62]

Point	K_2SO_4 , grams per 100 grams H_2O	$MgSO_4$, grams per 100 grams H_2O	$CaSO_4$, grams per 100 grams H_2O	Solid phases
A.....	12.00	1.00	0.080	Polyhalite, syngenite, pentasalt
B.....	7.5	1.75	.075	Polyhalite, anhydrite pentasalt
C (m).....	10.7	.90	.093	Polyhalite, syngenite, anhydrite
D.....	11.8	0	.074	Pentasalt, syngenite
E.....	5.8	0	.071	Pentasalt, anhydrite
F (m).....	10.0	0	.093	Syngenite, anhydrite
G (m).....	5.7	0	.211	Syngenite, gypsum
H (m).....	1.1	0	.138	Pentasalt, gypsum

¹ Data from equilibrium curves from experimental and compiled data of Conley, Gabriel, and Partridge (7); (m)-metastable.

FIGURE 61.—Equilibrium isotherm for system K_2SO_4 — $MgSO_4$ — $CaSO_4$ — H_2O at 25° C.

FIGURE 62.—Equilibrium isotherm for system K_2SO_4 — $MgSO_4$ — H_2O .TABLE 52.— K_2SO_4 — $MgSO_4$ — H_2O (with added NaCl)
isotherms, 25° and 30° C.

[See fig. 59]

Curve ¹	Point	Temp., ° C.	K_2SO_4		$MgSO_4$		NaCl	
			Grams per 100 grams H_2O	Moles per 1,000 moles H_2O	Grams per 100 grams H_2O	Moles per 1,000 moles H_2O	Grams per 100 grams H_2O	Moles per 1,000 moles H_2O
3 ²	B	25	15.5	16.0	14.0	20.9	2.0	3.1
	C	25	5.7	5.9	36.2	54.1	2.0	3.1
	D	25	36.4	54.4	2.0	3.1
4 ²	B	25	12.6	13.0	18.7	28.0	8.0	12.3
	C	25	5.6	5.8	33.6	50.2	8.0	12.3
	D	25	32.0	47.8	8.0	12.3

¹ See table 49 (p. 244) for data on curves 1 and 2 and reference 17 in list of Bureau of Mines publications (p. 249) for data on curves 6 to 8.

² Previously unpublished data obtained by Loyal Clarke, now at Pittsburgh Experiment Station, Bureau of Mines.

PATENTS RELATING TO TREATMENT OF POLYHALITE

In the following section a list of general patents, including most of the United States and foreign patents dealing with methods for the treatment of polyhalite, has been recorded. This list is not complete but is believed to include the majority of the patents relating to this mineral.

**UNITED STATES PATENTS RELATING TO POLYHALITE.
ISSUED TO BUREAU OF MINES INVESTIGATORS**

1. PARTRIDGE, EVERETT P., AND FRAAS, FOSTER. Process for Recovering Potassium Salts from Minerals. U. S. Patent 1,975,798, October 9, 1934; assigned to Secretary of Commerce. 11 claims.
2. PARTRIDGE, EVERETT P., AND FRAGEN, NATHAN. Process for the Recovery of Potassium Salts from Minerals. U. S. Patent 2,033,149, March 10, 1936; assigned to U. S. Department of Commerce. 9 claims.
3. STORCH, H. H., AND FRAGEN, NATHAN. Method of Recovering Potassium Sulfate from Syngeinite. U. S. Patent 2,033,159; assigned to U. S. Department of Commerce. 9 claims. March 10, 1936.

GENERAL PATENTS RELATING TO TREATMENT OF POLYHALITE⁴³

1. BERLINER, JULIUS F. Mineral Conversion. U. S. Patent 1,909,606, May 13, 1933; assigned to E. I. duPont de Nemours & Co.
2. BUCHNER, KARL. (Extraction and Manufacture of Potassium Sulfate from Calcium-Containing Sulfates.) U. S. Patent 1,854,687, April 19, 1932; assigned to Preussische Bergwerks- und Hütten Aktiengesellschaft, Berlin, Germany.
3. CASHMORE, ALBERT E., CLIFFORD, IVOR L., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Potassium Sulfate and Calcium-Potassium Sulfate. British Patent 437,652, November 4, 1935.
4. CHEMISCHE FABRIK BUCHAU. (Process for the Decomposition of Complex Salts Composed of the Sulfates of the Alkalies and Alkaline Earths.) French Patent 733,985, July 19, 1932; British Patent 386,854, January 26, 1933.
5. CLIFFORD, IVOR L., CASHMORE, ALBERT E., AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Potassium Sulfate from KCl and Na₂SO₄. British Patent 439,287, November 25, 1935.
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9. ———. (Method of Making Potassium Sulfate.) French Patent 790,363; see British Patent 410,830, November 20, 1935.
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12. MOND, ALBERT L. Process for the Decomposition of Complex Salts Composed of the Double Sulfates of Potassium and Calcium. British Patent 386,854, January 26, 1933; assigned to Chemische Fabrik Buchau, Germany.
13. RACZKOWSKI, HENRY E. L. Process for Potassium Sulfate and Syngeinite. British Patent 435,772, September 27, 1935; see French Patent 776,937; assigned to Palestine Potash, Ltd.
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19. ———. Process of Treating Polyhalite with Calcium Carbonate. U. S. Patent 1,956,930, May 1, 1934.
20. ———. Process of Treating Polyhalite. U. S. Patent 1,981,125, November 20, 1934.
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