Bulletin 226

DEPARTMENT OF THE INTERIOR

HUBERT WORK, SECRETARY

BUREAU OF MINES

H. FOSTER BAIN, DIRECTOR

THE
TREATMENT OF MANGANESE-SILVER ORES

BY

GALEN H. CLEVINGER and MARTINUS H. CARON

WASHINGTON
GOVERNMENT PRINTING OFFICE
1925

The Bureau of Mines, in carrying out one of the provisions of its organic act—to disseminate information concerning investigations made—prints a limited free edition of each of its publications.

When this edition is exhausted, copies may be obtained at cost price only through the Superintendent of Documents, Government Printing Office, Washington, D. C.

The Superintendent of Documents *is not an official of the Bureau of Mines*. His is an entirely separate office and he should be addressed:

SUPERINTENDENT OF DOCUMENTS,

Government Printing Office,

Washington, D. C.

The general law under which publications are distributed prohibits the giving of more than one copy of a publication to one person. The price of this publication is 20 cents.

First edition. March, 1925.

CONTENTS

	Page
Introduction.....	1
Cooperation with the Netherlands Government.....	2
Status of patents.....	3
Acknowledgments.....	4
Occurrence of manganese-silver ores.....	5
Nature of refractory silver minerals in association with manganese.....	9
Experiments.....	13
Manganese dioxide and metallic silver.....	14
Silica and metallic silver.....	16
Manganese dioxide, silica, and metallic silver.....	17
Conclusions.....	19
Possibility of mechanical separation of refractory silver minerals from manganiferous ores.....	20
Segregation by screening.....	21
Gravity concentration.....	21
Flotation.....	22
Magnetic separation.....	22
Summary.....	25
Treatment of manganese-silver ores by chemical methods other than caron process.....	26
Chloridizing roast.....	26
Chloridizing roast in a reducing atmosphere.....	29
Volatilization tests.....	30
Wet chloridizing.....	31
Wet sulphidizing.....	32
Treatment with sulphurous acid.....	32
Treatment with sulphuric acid.....	33
Vermaes process.....	34
Cyanide treatment.....	47
Introduction of air.....	47
Effect of the presence of base metals.....	48
Methods of making small-scale tests.....	48
Special apparatus required.....	48
Operating the experimental equipment.....	50
Operating the gas producer.....	50
Operating the reducing drum.....	51
Important factors to be determined by reducing tests.....	52
Size of ore.....	52
Temperature of reduction.....	52
Period of reduction.....	52
Method for determining higher oxides of manganese.....	52
Apparatus for cyanide tests.....	53
Making cyanide tests.....	54
Development of working-scale equipment for operating the Caron process.....	55
Rotary furnace.....	57
Operation of furnace.....	59
Externally heated furnace.....	59
Application of the Caron process to ore from the Gedang Ilir mine, Sumatra.....	61
Miscellaneous tests of ores from the United States and Mexico.....	74
Ore from Butte, Mont.....	74
Ore from El Favor mine.....	74
Elkoro ore.....	76
Cyanide tests.....	77
Discussion of results.....	79
Buffalo-Hunter concentrate.....	80

	Page
Working-scale tests at Pachuca, Mexico.....	88
Clevenger reducing furnace.....	88
Units of furnace.....	88
Preheating unit.....	89
Reducing unit.....	89
Cooling unit.....	90
Method of making temperature measurements in the reducing furnace.....	91
Results of large-scale reduction tests of three Mexican ores.....	93
Ore from Purisima mine.....	94
Ore from Guanacevi mine.....	94
Ore from San Juan de Pachuca.....	95
Heat requirement.....	95
Treatment of flue dust.....	97
General conclusions regarding the Mexican ores.....	98
General conclusions and summary.....	100
Bibliography of the treatment of manganese silver ores.....	102
Index.....	106

TABLES

	Page
TABLE 1. Solubility of the remaining silver in refractory manganese-silver ores from the Gedang Ilir mine, Sumatra, after removal of the higher oxides of manganese.....	11
2. Solubility of silver compounds in different reagents.....	11
3. Behavior of synthetic manganese-silver compounds at different temperatures.....	15
4. Behavior of synthetic silver-silica compounds at different temperatures.....	17
5. Behavior of synthetic manganese dioxide-silica-silver compounds at different temperatures.....	18
6. Sizing analysis of Sumatra ore.....	21
7. Flotation and table concentration of Gedang Ilir ore.....	23
8. Separation of manganese dioxide from the gangue of Gedang Ilir ore by Wetherill magnetic separator.....	24
9. Volatilization losses during chloridization.....	28
10. Recovery of silver from chloridized ore.....	28
11. Results of tests on Gedang Ilir ore by a reducing chloridizing roast.....	29
12. Volatilization tests on manganese-silver ore from Sumatra.....	30
13. Temperatures at which reduction begins with oxides of manganese in hydrogen, carbon monoxide, and carbon.....	39
14. Successive stages in the reduction by dry carbon monoxide of the manganese dioxide contained in refractory silver ore from Sumatra.....	39
15. Successive stages in the reduction by dry hydrogen of the manganese dioxide contained in refractory silver ore from Sumatra.....	40
16. Gas analyses at rising temperatures.....	43
17. Gas analyses at rising temperatures.....	43
18. Conditions for reoxidation of manganous oxide after reduction, and influence on silver extraction.....	44
19. Effect of exposure to air on reduced ore.....	45
20. Effect of temperature of reduction reoxidation and period between reduction and cyanidation on silver extraction.....	46
21. Analyses of ores from the Gedang Ilir mine.....	61
22. Data on reduction test No. 9 of low-grade silver and manganese ore in externally heated rotary furnace.....	62
23. Data on reduction test No. 10 in externally heated rotary furnace (27 kilograms per hour).....	64

	Page
TABLE 24. Data on reduction test No. 10 (a) in externally heated rotary furnace (41 kilograms per hour)-----	65
25. Data on reduction No. 11-----	66
26. Data on reduction test No. 12-----	67
27. Data on reduction test No. 13-----	68
28. Data on reduction test No. 14-----	70
29. Data on reduction test No. 15-----	72
30. Reduction tests with El Favor ore-----	75
31. Cyanide tests with raw, dried, and reduced Elkoro ore-----	78
32. Reduction test with Buffalo-Hunter concentrate-----	80
33. Data on reduction test No. 2 with Buffalo-Hunter concentrate-----	81
34. Data on reduction test No. 3 with Buffalo-Hunter concentrate-----	83
35. Data on reduction test No. 4 with Buffalo-Hunter concentrate-----	84
36. Data on reduction test No. 5 with Buffalo-Hunter concentrate-----	86
37. Data on reduction test No. 6 with Buffalo-Hunter concentrate-----	87
38. Analysis of three Mexican manganese-silver ores-----	93
39. Results of flue-dust treatment by reduction and SO ₂ -----	98

ILLUSTRATIONS

	Page
PLATE I. Laboratory equipment for reduction tests of manganese-silver ores-----	48
II. Internally fired reducing furnace with feeder above at left, and cooler at right. Externally fired reducing furnace used for experimental purposes in foreground-----	56
III. A, Plan of internally fired reducing furnace and accessories; B, Elevation of internally fired experimental reducing furnace, feeder, and cooler-----	58
IV. A, Upper end of internally fired reducing kiln, showing disk feeder; B, Gas producer and blower-----	60
V. Experimental cyanide plant-----	61
VI. Plan and elevation of calcining plant-----	88
VII. Diagram of operation of Clevenger reducing kiln-----	90
VIII. A, Head end of preheating kiln; B, View of gas producer-----	92
IX. A, Disk feeder which discharges into shaking feeder shown in B; B, Shaking feeder inside dust chambers at end of preheating kiln-----	93
X. A, Burner connections, collector rings for thermocouples, driving gear, and riding ring; B, Lower end of cooler and discharge hopper-----	92
XI. Reducing kiln and cooler, showing burner connections-----	93
XII. Elevation and section of reducing kiln, showing details of pyrometer installation-----	94
XIII. A, Recorder for measuring temperatures in a reducing furnace; B, Recorder open for cleaning and oiling-----	96
FIGURES 1. Curves showing the solubility of silver in synthetic mixtures in cyanide solutions after heating at various temperatures-----	19
2. Curves showing comparison between hydrogen and carbon monoxide as reducing agents at various temperatures-----	41
3. Details of discharge end of cooler-----	58
4. Flow sheet of experimental plant At Colorado Springs, Colo.-----	60

THE TREATMENT OF MANGANESE-SILVER ORES.

BY GALEN H. CLEVINGER AND MARTINUS H. CARON.

INTRODUCTION.

Although there are exceptions, oxidized silver ores containing the higher oxides of manganese are generally refractory to hydrometallurgical methods of treatment. When these ores are of high enough grade they can be smelted; indeed, some rather low-grade ores of this type have been smelted at a profit because of their fluxing value. In the past, when these ores could not be smelted, they either were not treated or were treated at low efficiency, generally by cyanidation. The need for thorough investigation of the problem was therefore evident for some time before the writers began their research.

The problem of treating manganese-silver ores seems to have been recognized first about 35 years ago by C. W. Goodale in applying pan amalgamation at Tombstone, Ariz. He attributed the low extraction of silver to the fouling of the mercury by manganese rather than to the presence of a refractory compound of manganese and silver. Although definite knowledge as to the cause of the poor extraction of silver was lacking, a more or less effective preliminary treatment, that is, a chloridizing roast, was applied.

E. M. Hamilton, in 1909, was perhaps the first to define clearly the problem as it affects the cyanidation of silver ores and to suggest possible methods of preliminary treatment. Most of the work done in the interval between the appearance of Hamilton's paper and the assumption of the investigation by the authors was in the nature of routine tests covering suggestions already made rather than of research directed to a fundamental study of the problem. No practical application has so far been made of any of these proposed processes.

The investigation described in this bulletin has proved that there is a refractory compound of manganese and silver—probably a manganite—insoluble in cyanide solution and other common solvents for silver. Although this compound has not been isolated from natural ores, it has been made synthetically, and shows all the characteristics of the natural product. Furthermore the authors have shown definitely that heating in air a relatively small amount of a silver compound with a large excess of silica (in the proportions ordinarily occurring in a commercial silver ore) renders

increasing percentages of the silver, depending on the temperature, insoluble in cyanide solution. Whether this is a physical or a chemical effect may be debatable, but the evidence the writers can offer seems to favor the formation of a chemical compound, such as silver silicate. The behavior of silver with silica, as will be pointed out later, has an important bearing on the problem.

The Caron process is based on the discovery that when oxidized ores containing a refractory compound of silver and manganese are heated in a reducing atmosphere—so as to reduce completely the higher oxides of manganese to manganous oxide—and are cooled under conditions that will prevent reoxidation, the refractory compound is decomposed and the silver is rendered amenable to cyanidation. Similar treatment has also been found effective for decomposing refractory combinations of silver and silica. This process, in combination with cyanidation, has been demonstrated through tests of typical samples from widely separated localities to be the most effective treatment for the majority of manganese-silver ores. The presence of antimony has under certain conditions been found to interfere seriously with the process, but its precise behavior has not been established.

The Clevenger furnace and cooler unit has been developed, whereby reduction can be obtained with high fuel economy and reversion to the refractory state can be prevented. This furnace embodies the new feature of progressive combustion of gas in the reducing zone with, finally, complete combustion at the foot of the preheating zone, and renders possible the obtaining of highly reducing conditions when required, with the heat necessary for carrying forward endothermic reactions and complete utilization of the calorific value of the fuel. Formerly, even an imperfect reducing roast in existent types of furnaces was obtained with high consumption of fuel and without provision for preventing reversion.

COOPERATION WITH THE NETHERLANDS GOVERNMENT.

The reason for cooperation between the United States Bureau of Mines and the Netherlands East Indies Government was the need for the development of a process to treat manganese-silver ores found in each of the two countries. In June, 1917, Ridder van Rappard, envoy extraordinary and minister plenipotentiary of the Netherlands Government, requested through Franklin K. Lane, then Secretary of the Interior, that R. J. van Lier and M. H. Caron, engineers in the Government Mines Service of the Netherlands East Indies, be given such assistance as might be possible through suitable governmental channels in further developing a process, invented by Mr. Caron, for the treatment of manganese-silver ores. The matter was referred

to Van. H. Manning, then director of the United States Bureau of Mines, who in turn brought it to the attention of Galen H. Clevenger, at that time metallurgist in charge of investigations of the hydro-metallurgy of gold and silver.

The Caron process had only been tried on a laboratory scale, and there still remained the problem of working out various features of the process and developing working-scale equipment for its application, but the process gave evidence of enough promise of developing into a commercial success to justify the investigation contemplated.

STATUS OF PATENTS.

A serious complication in effecting a satisfactory arrangement for carrying forward the investigation arose from the fact that Mr. Caron¹ had patented the process in the United States and in other countries. He had given the Netherlands Government free use of the process at all of its Government-owned mines, but it had conceded to him the patent rights in so far as they concerned privately owned mines in Holland and its possessions. Mr. Caron was also at liberty to take out foreign patents in his own right.

The relationship of the Netherlands Mines Service to the home Government and the industry of that country differs from that of the Bureau of Mines to the Federal Government in that the Netherlands Government actually owns and operates mines on its own account, and the Mines Service was therefore engaged in directing these governmental operations, as well as in performing the general functions of a mining bureau; whereas in the United States there are practically no Government owned or operated metal mines, and therefore the function of the Bureau of Mines is solely to make investigations for the benefit of the whole mining industry. This being true, there always arises the question as to how far the bureau should go in developing privately owned patented processes, especially in their earlier stages, unless there is good reason for doing so. This problem at first appeared to prevent the bureau from taking an active part in the investigation and development of the Caron process, so long as title to the United States patent remained in the hands of a single individual—Mr. Caron. When this situation arose, Mr. Caron proposed to renounce all personal return from his American patents and to turn them over to a Government official as trustee for the public in such manner as had been officially under consideration with regard to other patents not connected with his process.

This proposal seemed to be more drastic than was fair or equitable to Mr. Caron, and the alternative adopted was that Mr. Caron assign his American patent rights to the Research Corporation of New York,

¹ Caron, M. H., Process for extracting gold and silver from ore containing gold, silver, and manganese dioxide. U. S. Patent 1232216, July 3, 1917.

leaving it to decide what would be a just and equitable return to him personally after the practical value of the process had been clearly established. The Bureau of Mines then entered into a cooperative agreement, covering the development of the process, with the Research Corporation. Mr. Clevenger also turned over the patents for his reducing kiln² to the Research Corporation.

After the patent situation had been satisfactorily adjusted arrangements were effected for proceeding with the investigation at the Golden, Colo., experiment station of the Bureau of Mines, which at the time was best equipped for the particular work contemplated.

The investigation was placed under the general supervision of Mr. Clevenger. R. J. van Lier remained in America until January, 1918, as representative of the Government Mines Service of the Netherlands East Indies, and was succeeded in May of that year by A. H. J. Thie. Mr. Caron took an active part in the experimental work throughout the whole period.

Work was begun at Golden, Colo., in August, 1917, and continued there until June, 1918. Later developments required better facilities for large-scale experiments, so the work was transferred to the Portland mill at Colorado Springs.

ACKNOWLEDGMENTS.

F. S. Mulock, formerly of the Research Corporation, New York, and later on the staff of the United States Smelting, Refining & Mining Co., was with us throughout the investigation. He assisted in developing the mechanical features of the process and showed much ingenuity in adapting old equipment to new uses. He was in responsible charge of the large experimental unit at Pachuca, Mexico. H. W. Young also rendered efficient service during 10 months of the investigation.

Various suggestions were made and assistance was given by members of the Bureau of Mines, particularly by R. B. Moore, former chief chemist of the bureau. M. W. von Bernewitz arranged and revised the manuscript for publication.

At Colorado Springs the Portland Gold Mining Co. of Cripple Creek permitted the free use of its equipment and machine shops, and of discarded apparatus that could be altered and rebuilt into that necessary for carrying out the many experiments. G. M. Taylor, then general manager, J. M. Tippet, then mill superintendent, and S. J. Connolly, engineer of the company, rendered substantial assistance.

In the earlier stages of the investigation the Colorado School of Mines at Golden permitted the free use of the gas producer in its power house and the assembling of such equipment as was necessary in connection with the producer.

² Clevenger, G. H., Apparatus for treating ores or the like. Twenty claims. U. S. Patent 1379083, May 24, 1921.

Many practical suggestions were made by Messrs. van Lier and Thie, who effectively administered the investigation in behalf of the Netherlands East Indies Mines Service.

The Cia de Real Del Monte y Pachuca and the United States Smelting, Refining & Mining Co. gave liberal support in connection with the large-scale demonstration of the process and kindly permitted publication of the results. Among the men connected with these companies who gave their support to the work at Pachuca or participated in it are: D. S. Calland, C. F. Moore, J. E. Smith, G. S. Embury, W. J. Fischer, E. J. Harrison, M. H. Kuryla, and G. W. Harris.

OCCURRENCE OF MANGANESE-SILVER ORES.

Manganese-silver ore most frequently occurs as a deposit in fissure veins in acid eruptive rocks, chiefly rhyolite and dacite flows of late Tertiary age. Adular (potassium-aluminum silicate) is a characteristic vein mineral in many deposits, and the vein quartz is in places pseudomorphic after calcite, indicating that the composition of the mineral-bearing solutions had changed while the fissure was being filled.

In addition to these deposits there are doubtless others of different origin and of different characteristics. Most of the manganese dioxide in the deposits associated with acid eruptives is generally of secondary origin, and is formed through oxidation of the ore by atmospheric agencies. As oxidation proceeds from the surface of a deposit downward, the ores that are most refractory to treatment for recovery of silver extend, as is to be expected, from the surface downward through the zone of oxidation. Many deposits show a gradual change from the oxidized refractory ores near the surface to the amenable unoxidized ores at greater depths. The metallurgical behavior of this type of ore and the effects of depth on the character of the ore have been discussed both by Hamilton³ and Neal.⁴

The primary manganese minerals, such as rhodonite and rhodochrosite, are decomposed in the zone of oxidation, therefore in typical refractory manganese-silver ores the manganese is all present as the higher oxides, wad being the form most commonly found. As is well known, wad is an impure mixture of manganese and other oxides, and may contain any one or more of many impurities, such as barium oxide, calcium oxide, magnesium oxide, lead oxide, copper oxide, cobalt oxide, aluminum oxide, ferric oxide, and silica. Our study of the subject clearly indicates that in these secondary processes of vein

³ Hamilton, E. M., Cyanidation of Mexican manganese-silver ores: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 10, 1909, pp. 65-67.

⁴ Neal, Walter, The manganese-silver problem: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 17, 1916, pp. 9-18.

formation the higher oxides of manganese, more particularly manganese dioxide, have functioned as precipitating agents of the silver-bearing solutions, similarly to the generally accepted function of manganese dioxide in connection with the deposition of copper, cobalt, lead, etc., therefore a considerable portion of the silver in such deposits may be present as a more or less indefinite compound of the precipitated silver in the higher oxides of manganese. The nature of the silver minerals in such ores is discussed more fully on pages 9 to 20.

In discussing the relation of manganese to gold, Emmons⁵ says that in many gold deposits manganese oxides and gold are intimately associated, and without doubt were deposited together. The Camp Bird, Tomboy, and Amethyst mines in Colorado, the Dahlonega mines in Georgia, and the mines of Philipsburg, Mont., yielded such ores. The theory is that the gold has been precipitated with manganese oxides in a reducing environment; both of the minerals were held in an acid solution descending through the ore, but in depth, by the continued reaction with alkaline minerals of the gangue and wall rock, the solution lost its acidity, precipitating the manganese and gold. This was proved by experiment.

According to Harder,⁶ manganese silver ores occur abundantly in the oxidized parts of many of the silver deposits of the Western States. These ores consist of manganese and iron oxides, carrying silver chloride and lead carbonate. The manganese is present as wad. These ores have been principally used as fluxes, for their silver and lead, and in the manufacture of spiegeleisen and ferromanganese.

In the Butte, Mont., district, the veins traverse both granite and aplite, and in some places the porphyry. Near the surface the ores are oxidized and the vein filling is chiefly quartz and manganese oxide, probably wad, carrying silver. Analyses of the ores show 21 to 88 per cent manganese oxides, 3 to 8 per cent iron oxides, 7 to 66 per cent silica, up to 4 per cent alumina, and 9 to 80 ounces of silver per ton. The oxidized parts of the veins have a black appearance, caused by manganese oxide, the result of oxidation of rhodonite and rhodochrosite, which were originally white to pink.

A considerable quantity of manganese silver ores has been shipped from the Leadville, Colo., district, largely as a flux and for the silver content. Samples from 20 mines showed the ore carried 6 to 33 per cent manganese, 15 to 45 per cent iron, 4 to 15 per cent silica, and 1.2 to 12.7 ounces of silver per ton. The ore is brownish-black.

Ore similar to that at Leadville occurs at Neihart, Cascade County, and at Castle, Meagher County, Mont., although at the former place it carries 4 to 8 per cent lead and has been mined for fluxing purposes.

⁵ Emmons, W. H., Enrichment of ore deposits: U. S. Geol. Survey Bull. 625, 1917, 530 pp.

⁶ Harder, E. C., Manganese deposits of the United States: U. S. Geol. Survey Bull. 427, 1910, 298 pp.

The manganese content averages 7 per cent, and the silver from 54 to 128 ounces per ton.

There is some manganese-silver ore in Eagle County and in the San Juan region of Colorado; also at Silver City, Grant County, and at Kingston and Lake Valley, Sierra County, N. Mex., and at Tombstone, Ariz.

The silver ore of the Commonwealth mine at Pearce, Ariz., contains varying amounts of manganese which hinder cyanidation of the ore.

The following table⁷ shows the amount of manganiferous silver ore shipped in the United States during the last six years:

Manganiferous silver ore shipped.

[In long tons.]

Year.	Arizona.	Colorado.		Nevada.	New Mexico.	Utah.
		For fluxing.	For other purposes.			
1915.....	a 1,452	14,965	15,956	104,498		55
1916.....	a 7,392	16,263	90,600	122,329		27
1917.....	a 32,000	20,546	104,169	122,872		100
1918.....	a 10,854	24,931	99,110	80,896	475	
1919.....	a 1,964	29,769	11,055	77,815	250	
1920.....	345	34,670	11,056	95,142	541	

^a Ore containing more than 36 per cent Mn sent to makers of manganese alloys not included.

Some of the oxidized manganiferous silver ores of the United Comstock mine in Nevada contain refractory silver minerals not amenable to simple cyanidation. Some of this silver is soluble only after complete reduction of the higher oxides of manganese.

The ores of the Candelaria district, Mineral County, Nev., are thoroughly oxidized, easily pulverulent material, which is black where manganese oxide predominates, yellowish-red where limonite predominates, and brownish where these compounds are more evenly distributed. Recognizable minerals are rare. The manganese is present as the soft, earthy, black dioxide wad; the iron as limonite; and zinc is revealed in places by the occurrence of calamine (the hydrous silicate) in glassy crystals. The silver is present in "unrecognizable form," to quote Knopf.⁸ The silver is frequently reported to be present as chloride, but since the rich ore of the early days required chloridizing roasting, it is certain that much of the silver was not in this form; and recent tests of ore from the Lucky Hill mine failed to show any silver chloride. Ore from Potosi Mountain carries considerable bindheimite, the so-called hydrous antimonate of lead, which is

⁷ Jenison, H. A. C., Manganese and manganiferous ores in 1920: U. S. Geol. Survey Advance Chapter of Mineral Resources of the United States, 1920, Part I.

⁸ Knopf, Adolph, The Candelaria silver district, Nevada: U. S. Geol. Survey Bull. 735-A, January, 1922, 22 pp.

deep brownish yellow, has a pitchy luster, and carries up to 21 per cent of lead and 25 ounces of silver per ton. That the typical manganiferous silver ore of the district carries bindheimite is highly probable, as the unoxidized ore carries jamesonite, which on oxidation generally yields bindheimite. This bindheimite is masked by the prevalence of the deeply colored oxides of iron and manganese. The chemical composition of three representative ores from the district are shown below, from analyses made by J. A. Carpenter:

Analysis of ores from the Candelaria district.

Mineral.	1	2	3
Fe ₂ O ₃	13.1	12.9	12.1
CaO.....	9.6	10.8	4.0
MgO.....	2.6	4.8	0.7
Zn.....	4.6	8.3	2.3
Mn.....	1.7	3.5	2.0
S.....	Trace.		0.2
Insoluble, mostly SiO ₂	48.4	48.0	70.4
Moisture.....	1.0		1.0

Sulphides are uncommon. The high zinc content noted in the analyses suggests that part of the zinc may be present as carbonate.

The Candelaria silver deposits differ notably from those of Tonopah and the Comstock and their closest analogues are in the Rochester district; but the latter are highly siliceous and not manganiferous like those of the Candelaria district. They somewhat resemble the deposits of the Arabia district. The Candelaria ores are practically straight silver ores, and although others of the same age and general character are known to occur in Nevada, the tourmaline content of the Candelaria ores, coupled with their manganiferous ferrodolomite gangue, sets them apart from all others.

A microscopic study of two large samples of Candelaria ores was made during 1922 by R. E. Head and G. S. Oldright at the Salt Lake experiment station of the Bureau of Mines.

They report that the two samples examined were almost completely oxidized and contained some cerargyrite (silver chloride). The softer of the two ores was colored dark brown to black by oxides of iron and manganese. This investigation throws no new light upon the occurrence or composition of the refractory silver mineral.

The ore is of particular interest on account of the fact that it is typical of a special class of manganese-silver ores that is not amenable to the Caron process. The unusual behavior of this and other manganese-silver ores containing antimony is discussed elsewhere in this bulletin.

Tests were made of manganese-silver ores from Arizona, Colorado, and Nevada. In Mexico such ores occur in a number of widely separated localities, and experiments have been made on ores from the

Pachuca, Guanacevi, and El Favor districts in the States of Hidalgo, Durango, and Jalisco, respectively. In Sumatra, Dutch East Indies, these ores are also of general occurrence, and many tests were made of ore from the Gedang Ilir mine which is near Benkoelen. Torarchi Miyazaki, professor of metallurgy in the Imperial University of Tokyo, has called our attention to ores of this character in Izu Province, main island of Japan. Deposits of these ores in Bolivia, Chile, and Peru have also been brought to our attention. In the Hauraki Peninsula of the North Island of New Zealand are some manganese-gold ores (with a little silver) that are earthy, but gave good recoveries of the gold on being dried in a reverberatory-type furnace, crushed to 30 mesh, and amalgamated in pans similar to the old Washoe process. On the other hand, at the Waihi silver-gold mine in the same region, the silver content of the tailings invariably increased when manganese was present in the ore.

The deposits mentioned include only those whose ores we have investigated, or which have been brought directly to our attention, so it seems likely that manganese-silver ores are probably commoner than was previously supposed.

Ores of this type do not necessarily contain a high percentage of manganese, as one ore that was investigated contained only 0.25 per cent manganese dioxide, and would only yield about 18 per cent of its silver content by direct cyanidation. Furthermore, we are convinced that for some ores where this difficulty is not suspected, and from which only 60 to 80 per cent of the silver is being obtained, the causes discussed later in this paper are the real reason why a higher extraction can not be had by ordinary methods.

NATURE OF REFRACTORY SILVER MINERALS IN ASSOCIATION WITH MANGANESE.

Because of the intimate association of the refractory silver with the relatively large proportion of higher oxides of manganese, the general experience of earlier investigators, and of ourselves, has been that the silver mineral can not be isolated for identification, as other silver minerals frequently can be. For the same reason attempts to study these ores microscopically have not been successful.

As pointed out in the next chapter, on mechanical separation, some of the ores, particularly the Gedang Ilir (Sumatra) and the Buffalo-Hunter (Colorado) ores, show a more or less constant ratio between the manganese and the silver content of the various products from screening or concentration, indicating that the silver compound is uniformly disseminated throughout the body of the manganese mineral. On the other hand, other ores which we examined do not show this fixed relationship. Our experience, however, is

that, whether or not the manganese present has a fixed ratio to the silver, it is necessary to dissolve all of the manganese; or if reduction is practiced, all the higher oxides must be reduced to manganous oxide in order to obtain the highest recovery of silver. This clearly indicates that in certain of these ores although the silver has no fixed ratio to the manganese the manganese is directly related to the refractory silver.

The apparent segregation of the refractory silver mineral along the line of contact between the quartz and manganese oxide minerals is recorded by Coghill,⁹ and seems to be of significance in certain ores.

We have found that the refractory silver in the original ore is insoluble in all the common solvents for metallic silver and its salts—that is, cyanide solutions of all concentrations, dilute and concentrated nitric acid, dilute sulphuric acid, salt solution, alkaline thiosulphates, ammonia, mercury, and other reagents. This conclusion harmonizes with all previous work on the problem.

It seemed possible that additional light on the constitution of the silver mineral could be had by the use of solvents that would dissolve the excess of manganese, leaving the silver radical unaltered. Unfortunately we can not be certain that the silver radical has not been altered during dissolution of the manganese; however, the results of a number of experiments showing the behavior of the silver with different solvents after removal of the manganese are given in detail in Table 1 (p. 11).

Dilute sulphuric acid, in the presence of reducing agents such as oxalic acid, alkaline oxalates, ferrous sulphate, and hydrogen peroxide, readily dissolves the higher oxides of manganese without dissolving the silver. Sulphurous acid is also a solvent for the higher oxides of manganese, but does not dissolve the silver. Both sulphuric acid, in the presence of sodium oxalate, and sulphurous acid have been used for removing the manganese.

Since our work was done, L. W. Austin¹⁰ has proposed the use of dilute sulphuric acid (H_2SO_4) in conjunction with pyrite (FeS_2) as a preliminary treatment. The equation given by the inventor in the patent specification shows the reduction of MnO_2 to MnO without solution of the Mn. As will be shown later, whatever effect is obtained is the result of solution of the Mn from the MnO_2 as $MnSO_4$ by the H_2SO_4 in the presence of a reducing agent, here pyrite.

More recently M. F. Fairlie and J. J. Denny¹¹ have proposed the use of H_2SO_4 in conjunction with metallic iron as a preliminary treatment. Again, the manganese is dissolved by H_2SO_4 in the presence of a reducing agent, metallic iron.

⁹ Coghill, W. H., *Refractory manganese-silver ores*: Min. and Sci. Press, vol. 104, 1912, p. 794.

¹⁰ Austin, L. W., *Treating manganese-silver ores*. U. S. Patent 1327974, Jan. 13, 1920.

¹¹ Fairlie, M. F., and Denny, J. J., *Process of treating manganiferous ores of the precious metals*. U. S. Patent 1417153, May 23, 1922.

Experience at Pachuca, Mexico, shows that long-continued treatment with sulphur dioxide (SO_2) does dissolve some silver, probably through the action of iron salts. This did not happen in the presence of lead, but did to a certain extent with iron pumps.

The data given in Table 1 are the result of tests made on high-grade ore from the Gedang Ilir mine, Sumatra. Each of the samples was ground to pass 200 mesh and treated with hot dilute sulphuric acid and sodium oxalate, with the exception of the last sample, which was treated with sulphurous acid. Care was taken to dissolve all the manganese and thoroughly wash the remaining pulp before treatment with the different solvents.

TABLE 1.—*Solubility of the silver remaining in refractory manganese-silver ores from the Gedang Ilir mine, Sumatra, after the removal of the higher oxides of manganese.*

Size of ore mesh.	MnO ₂ in original sample, per cent.	Solvent used for MnO ₂ .	Ag content after removal of MnO ₂ .		Solvent used for Ag.	Ag dissolved, per cent.	Remarks.
			Grams per metric ton.	Ounces per short ton.			
200	29.62	Dilute H ₂ SO ₄ and Na ₂ C ₂ O ₄ (sodium oxalate).	3,060	89.0	Boiling 1 to 5 dilute H ₂ SO ₄ .	Trace.	
200	29.62	do.....			Boiling 1 to 10 dilute HNO ₃ .	None.	
200	29.62	do.....			Boiling concentrated HNO ₃ .	None.	
200	29.62	do.....			Wood alcohol.....	None.	Solution changed twice in 3 days.
200	29.62	do.....			Strong NH ₄ OH.....	9.7	
200	29.62	do.....			Hot concentrated NaCl solution.	95.5	
200	29.62	do.....			Strong boiling Na ₂ S ₂ O ₃ solution.	35.5	After dissolving the MnO ₂ reduced by metallic Zn and H ₂ SO ₄ (H).
120	12.70	do.....	2,810	81.8	2½ per cent Na ₂ S ₂ O ₃ solution.	92.5	Ground 1 hour in small porcelain ball mill.
48	18.00	SO ₂ in water solution.	3,851	112.0	0.235 per cent KCN solution.	96.5	Ground 2 hours in small porcelain ball mill.

The solubility of various silver compounds in the common solvents for silver and its compounds is given in Table 2.

TABLE 2.—*Solubility of silver compounds in different reagents.*

Silver compounds.	Reagent.	Solubility.	Remarks and reference.
AgCl.....	H ₂ O.....	Almost insoluble.....	Corney, A. M., Dictionary of chemical solubilities, inorganic. 1896, pp. 371-373.
Do.....	(NH ₄) OH.....	Readily soluble.....	
Do.....	Brine solution.	do.....	
Do.....	Na ₂ S ₂ O ₃	do.....	
Do.....	KCN.....	do.....	
Do.....	Hg.....	do.....	
Metallic Ag.....	(Dilute) KNO ₃	do.....	MacLaurin, J. S., Action of potassium cyanide on New Zealand gold and silver: Jour. Chem. Soc., vol. 67, 1895, pp. 199-212.
Do.....	(Strong) KCN+O.....	do.....	

TABLE 2.—*Solubility of silver compounds in different reagents—Continued.*

Silver compounds.	Reagent.	Solubility.	Remarks and reference.
Metallic Ag....	(NH ₄)OH+O.....	Readily soluble.....	Matignon, C., and Desplantes, G., <i>Oxydation des métaux à froid en présence de l'ammoniaque: Comp. rend., t. 140. 1905, pp. 853-855.</i>
Do.....	Concentrated, H ₂ SO ₄	do.....	
Do.....	Hg.....	do.....	
Ag ₂ O.....	H ₂ O.....	Insoluble.....	Comey, A. M., work cited, p. 374.
Do.....	Acids.....	Decomposed into Ag and Ag ₂ O.	
Do.....	(NH ₄)OH.....	Insoluble.....	
Ag ₂ O.....	H ₂ O.....	Somewhat soluble.....	Comey, A. M., work cited, pp. 374-375.
Do.....	Acids.....	Readily soluble.....	
Do.....	(NH ₄)OH.....	do.....	
Do.....	KCN.....	do.....	
Do.....	Na ₂ S ₂ O ₃	do.....	
Do.....	Brine.....	do.....	
Do.....	Hg.....	Soluble when triturated with Hg.	Moissan, Henri, <i>Traité de chimie minérale (Propriétés chimiques, pp. 542-545): t. 5, 1906, p. 544.</i>
Ag ₄ O ₃	(After Baeyer and Villiger) is formed only in alkaline solutions.		Baeyer, Adolf, and Villiger, Victor, <i>Ueber die Einwirkung von Hydroperoxyd auf Silberoxyd: Ber. Deut. chem. Gesell., Jahrg. 34, 1901, Bd. 1, p. 749 and Bd. 2, p. 2769.</i>
Ag ₂ O ₂	Conc. H ₂ SO ₄	Readily soluble.....	Comey A. M., work cited, p. 374.
Do.....	Pure HNO ₃	do.....	
Do.....	(NH ₄)OH.....	do.....	
Ag ₂ S.....			
Ag ₂ S ₂ O ₃	H ₂ O.....	Almost insoluble.....	Comey, A. M., work cited, p. 475.
Do.....	Na ₂ S ₂ O ₃	Readily soluble.....	
Do.....	(NH ₄)OH.....	do.....	
Ag ₂ SO ₃	H ₂ O.....	Almost insoluble.....	Comey, A. M., work cited, p. 464.
Do.....	(NH ₄)OH.....	Easily soluble.....	
Do.....	Alkali sulphides.....	do.....	
Do.....	H ₂ SO ₃ +H ₂ O.....	Insoluble.....	
Do.....	Strong acids.....	Decomposed.....	
Do.....	Na ₂ S ₂ O ₃	Easily soluble.....	
Do.....	HNO ₃ +H ₂ O.....	Insoluble.....	

Coghill¹² says that the silver contained in the residue from sulphurous acid treatment is insoluble, or only slightly soluble in ammonia, and that a high percentage of it can be extracted by amalgamation. In his conclusions he refers to the striking similarity of the residual silver to cement silver. We have definitely proved that the silver is not in the form of cement or metallic silver, for it is insoluble either in boiling dilute (1 to 10) or concentrated nitric acid; furthermore, its solubility in sodium thiosulphate solution confirms the fact that the silver is not in metallic form, for metallic silver is not soluble in solutions of the alkaline thiosulphates.

The high solubility of the silver in brine (NaCl) and sodium thiosulphate solutions suggests that it may be present as AgCl; but this is not true, as only a little of the silver is soluble in strong ammonia. By process of elimination it seems that the silver radical may be an oxide, particularly as the Ag after preliminary reduction with Zn and H₂SO₄, and following the removal of the Mn, was considerably less soluble in sodium thiosulphate solution.

On the other hand, consideration of the solubilities of the well-known silver oxides—argentous oxide (Ag₂O), silver oxide (Ag₂O),

¹² Coghill, W. H., *Refractory manganese-silver ores; Part II: Min. and Sci. Press, vol. 104, 1912, p. 794.*

and silver peroxide (Ag_2O_2)—leads to the belief that the silver radical is not one of these oxides. Time was not available for pursuing further this apparently unpromising line of investigation.

Our previous study of the problem led to the conclusion that the higher oxides of manganese could form refractory double oxide compounds with silver under the conditions of ore deposition and alteration.

Gorgeu¹³ has shown that silver manganite ($\text{Ag}_2\text{Mn}_2\text{O}_5$) is formed in the cold from silver acetate solution and manganese dioxide (MnO_2).

Rose¹⁴ found that silver oxide (Ag_2O) at room temperature reacts with manganese sulphate (MnSO_4) to form a black compound having the composition $\text{Ag}_4\text{O} \cdot 2\text{Ag}_2\text{O} \cdot \text{Mn}_2\text{O}_3$.

The possibility of silver silicate being formed during roasting or under certain conditions of ore deposition had not to our knowledge been previously considered as having a possible effect upon the metallurgical treatment of ores containing silver until it was revealed by some work of Clevenger in 1910.

Percy¹⁵ refers to a supposed silver silicate and the conclusion of Stas¹⁶ that silver in contact with even very refractory glass above the softening temperature absorbs oxygen and forms silver silicate, but concludes his remarks by advancing the theory that the yellow color of such glass may be due to the diffusion of extremely finely divided metallic silver, since Faraday had proved that the ruby color of glass colored with gold is caused by the finely divided metal.

Ebell¹⁷ says that silver oxide dissolves in molten glass to form silver silicate, but silver silicate has not been obtained in a pure state.

The above investigators consider only the formation of silver silicate through reaction of metallic silver or silver oxide with alkaline silicates (glass), and so far as we are aware the behavior of metallic silver or other silver compounds when heated with silica had not been definitely investigated prior to 1917, when our investigation was undertaken.

EXPERIMENTS.

In order to ascertain whether it was possible to form refractory compounds of Ag with MnO_2 and with SiO_2 , as well as with mixtures

¹³ Gorgeu, A., Action de l'eau oxygénée sur les combinaisons oxygénées du manganèse: *Compt. rend.*, t. 110, 1890, p. 958.

¹⁴ Rose, H., Ueber das Verhalten des Silberoxyds gegen andere Baden: *Ann. phys. Chem.*, Pogg., Bd. 101, 1857, p. 229.

¹⁵ Percy, John, *Metallurgy of gold and silver*. 1st ed., 1880, pp. 132-133.

¹⁶ Stas, Jean-Servais, Nouvelles recherches sur les lois des proportions chimiques sur les poids atomiques et leurs rapports mutuels (*Mémoires de l'Académie de Belgique*, t. 35, 1865, p. 176): *Œuvres Complètes*, t. 1, 1894, pp. 419-445.

¹⁷ Ebell, P., Ueber die Aehnlichkeit des Verhaltens von Ultramarin hoher Vertheilung und Schlemmbarkeit, verglichen mit dem der Metallsulfide im Colloidalzustand: *Ber. Deut. chem. Gesell.*, Jahrg. 16, 1883, Bd. 2, p. 2429.

of MnO_2 and SiO_2 , the experiments recorded in Tables 3, 4, and 5 were made with reagents prepared as described below.

Manganese dioxide was prepared by treating a concentrated solution of MnSO_4 with HNO_3 and KClO_3 . The precipitated MnO_2 was thoroughly washed and kept wet for use in the various mixtures. Although chemically pure reagents were used, the precipitate after drying at 110°C . showed but 85.8 per cent of MnO_2 . There was present in the dried precipitate approximately 3 per cent combined water, therefore the remainder of the difference is due to the presence of lower oxides of manganese. Morse¹⁸ has shown that MnO_2 precipitated from solution is only stable in the presence of KMnO_4 or Mn_2O_7 , or other strong oxidizing agents; otherwise it loses part of its oxygen and reverts gradually to a lower oxide.

Chemically pure Ag was prepared from a weak ammoniacal solution of AgNO_3 by precipitation with H_2O_2 . The very finely divided metallic silver thus formed was separated by filtration and thoroughly washed.

It was thought that there was a possibility that the finely divided silver prepared by this method would be contaminated with silver oxides, but Berthelot¹⁹ has shown that when an excess of H_2O_2 is used the precipitated silver is free from oxides. Absence of silver oxides was insured by treating part of the precipitated Ag with dilute H_2SO_4 , which readily dissolves silver oxide.

Chemically pure precipitated silica was used as a source of silica.

MANGANESE DIOXIDE AND METALLIC SILVER.

The finely divided moist MnO_2 was thoroughly mixed with the moist precipitated Ag in the proportions noted in Table 3. In all the experiments made at higher temperatures the mixture was heated in a silver dish in order to avoid any possible introduction of siliceous material.

¹⁸ Morse, H. W., Die Reduction von Uebermangansaure durch Mangansuperoxyd: Ber. Deut. chem. Gesell., Jahrg. 30, 1897, Bd. 1, p. 48.

¹⁹ Berthelot, P. M. E., Action de l'eau oxygénée sur l'oxyde d'argent et sur l'argent métallique: Ann. chim. phys., sér. 5, t. 21, 1880, pp. 164-172.

TABLE 3.—*Behavior of synthetic Mn-Ag compounds at different temperatures.*

Heated in air to temperature shown.	Composition before calcining.		Loss in weight after calcining.	Composition after calcining.		Loss in weight through dissociation.	Calculated combined H ₂ O.	Ag in mixture after calcining.	Ag soluble in dilute H ₂ SO ₄ , half-hour on hot plate.	Ag soluble in dilute HNO ₃ , 1 hour on hot plate.	Ag soluble in strong KCN solution (1 per cent) after 15 hours milling and 72 hours agitation.
	MnO ₂ .			MnO.							
	Per cent.	Per cent. (a)	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
20° (room temperature).....	77.8							1.928	23.5	32.1	c 38.2
Dried at 110°.....	85.8							1.928	22.3	26.1	d 22.4
Do.....	85.8			85.8				5.750	22.2	37.3	
3 hours at 320°.....	85.8		2.3	85.8			2.3	6.035			17.5
1 hour at 600°.....	85.8		7.8	59.0	41.0	5.13	2.67	6.375	15.9	34.4	24.5
1 hour at 850°.....	85.8		8.8	53.3	46.7	5.95	2.85	6.312	58.8	78.6	98.1
1 hour at 890°.....	85.8		9.2	51.14	48.86	6.36	2.84	6.33	61.6	79.3	
1 hour at 890°, afterwards reduced at 850° for 1 hour and cooled in gas.....	85.8		16.69	None.	100.00	14.89	1.80	6.97	None.	100.00	99.89

^a Not estimated.

^b On hot plate 1 hour.

^c Milled before KCN was added.

^d Milled 10 minutes before KCN was added.

a Not estimated.

b On hot plate 1 hour.

c Milled before KCN was added.

d Milled 10 minutes before KCN was added.

It will be noted that a large proportion of a silver compound insoluble in dilute HNO_3 , dilute H_2SO_4 , and KCN solution is formed at room temperature when freshly precipitated MnO_2 is ground wet with finely divided metallic Ag. Increase of the temperature to 320°C . renders still more of the Ag insoluble in KCN, but somewhat more soluble in the other solvents. At 850° , 98.1 per cent of the Ag is soluble in KCN. There is also a marked increase in the solubility in the other solvents, although not as great as with the cyanide solution. A mixture heated to 890° , and then reduced at 850° , showed complete solution of the Ag in dilute HNO_3 , practically complete solution in KCN, and no solution by dilute H_2SO_4 . This proves that the Ag in the reduced mixture is again in the form of metallic silver. The high solubility in KCN solution of the Ag in the mixture heated to 850° indicates that although most of the Ag is not in the metallic form, as shown by the behavior with the other solvents, yet the refractory manganite ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$) is decomposed at higher temperatures into a soluble silver compound which is stable. We had expected that if such a reaction occurred it would be reversible, and upon cooling in the air the same refractory compound would be found to a greater or less extent, as with MnO_2 reduced to MnO and cooled in the air.

The only explanation we can offer for this difference in behavior is that although the MnO_2 loses oxygen upon heating, the higher oxides of manganese formed are stable and do not absorb oxygen during cooling, whereas MnO absorbs oxygen even at low temperatures, and very rapidly at higher temperatures. This demonstrates very clearly the part that oxygen plays in the formation of the refractory manganese-silver compound.

These results indicate that manganese-silver ores could be readily treated by a straight oxidizing roast at a temperature of 850° to 900°C ., except for the fact that SiO_2 is invariably present in these silver ores, and, as will be shown later, plays an important rôle in the recovery of the silver therefrom.

SILICA AND METALLIC SILVER.

The finely precipitated SiO_2 was thoroughly mixed with water and with the damp Ag precipitate in the proportions noted in Table 4. A silver dish was used as a container for the samples in all of the experiments made at higher temperatures.

TABLE 4.—*Behavior of synthetic Ag-SiO₂ compounds at different temperatures.*

Heated in air to temperature shown.	SiO ₂ .	Ag.	Loss in weight during calcination.	Color.	Ag soluble in dilute H ₂ SO ₄ (1 to 5), 1 hour on hot plate.	Ag soluble in dilute HNO ₃ (1 to 5), 1 hour on hot plate.	Ag soluble in strong KCN solution (1 per cent) after 15 hours milling and 72 hours agitation.
°C.	Per cent.	Per cent. (16 oz.)	Per cent.		Per cent.	Per cent.	Per cent.
110.....	99.45	0.55	None.	White.....	None.	87.1	99.35
320.....	99.45	.55	0.18	do.....	Trace.	78.7	98.25
600.....	99.45	.55	.17	Faint pink.....	22	76.6	91.45
900.....	99.45	.55	.11	Bright pink.....	8.6	28.0	62.55
900 a.....	99.45	.55	(b)	Light yellow.....	41.5	91.4	97.25

a Then reduced at same temperature and cooled in producer gas.

b No loss through reduction.

At temperatures below 320° C. practically none of the silver is rendered insoluble in potassium cyanide solution through combination with the silica. The silver is insoluble in dilute sulphuric acid, which is what would be expected if it remained in the metallic state, but the fact that it is not completely soluble in dilute nitric acid throws some doubt on its form in silver-silica mixtures below 320°. At 600° there is a marked decline in the amount of silver dissolved by potassium cyanide, and 22 per cent of it becomes soluble in dilute sulphuric acid. The proportion soluble in dilute nitric acid is only 2.1 per cent less than it is at 320°. The characteristic pink color first appeared in the material heated to 600°.

At 900°, the percentage of the silver soluble in potassium cyanide fell to 62.55, in dilute sulphuric acid to 8.6, and in dilute nitric acid to 28.0. The considerable lowering in the percentage of the silver soluble in dilute sulphuric acid with an increase in temperature is probably due to the formation of silver silicate through the union of silver oxide found at the lower temperature with silica at the higher temperature. The greatly decreased solubility in dilute nitric acid and in potassium cyanide solution also strongly points to this conclusion. The color of the mixture heated to 900° was a bright pink.

It should also be noted that when the 900° product is reduced with producer gas at 900°, after very fine grinding, the silver becomes largely soluble in potassium cyanide solution but is not all dissolved by dilute nitric acid, and, furthermore, is rather highly soluble in dilute sulphuric acid. This behavior clearly indicates that the silver is not all present in metallic form in the reduced compound, as it appears to be with the manganese compound. The pink color of the silver-silica compound changes during reduction to a light yellow.

MANGANESE DIOXIDE, SILICA, AND METALLIC SILVER.

The behavior of mixtures of manganese dioxide, silica, and metallic silver heated to various temperatures has been investigated similarly to the mixtures of silver with manganese dioxide, and silver with silica. These results are recorded in Table 5.

TABLE 5.—*Behavior of synthetic MnO₂-SiO₂-Ag compounds at different temperatures.*^a

Heated in air to temperature shown.	SiO ₂ in original mixture.	MnO ₂ in original mixture.	MnO ₂ after calcining.	Ag after calcining.	Loss in weight during calcining.	Ag sol-uble in dilute H ₂ SO ₄ (1 to 5) 1 hour on hot plate.	Ag sol-uble in dilute HNO ₃ (1 to 5) 1 hour on hot plate.	Ag sol-uble in strong KCN solution (1 per cent). ^b	Remarks.
^{° C.}	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	
20°, mixed at room temperature.....	86.18	11.3	11.3	0.818				97.82	
$\frac{1}{2}$ hour at 130°.....	86.18	11.3	11.3	.82		55.9	61.8	84.75	
$\frac{1}{2}$ hour at 600°.....	86.18	11.3	8.8	.827	1.13	65.6	63.9	46.10	
$\frac{1}{2}$ hour at 900°.....	86.18	11.3	5.7	.843	2.16	50.3	59.1	78.20	
$\frac{1}{2}$ hour at 500°.....	86.18	11.3	.71	.844	2.53	94.4	92.06	99.65	After being heated to 500° C., and reduced at this temperature with producer gas for $\frac{1}{2}$ hour and cooled in the gas.
$\frac{1}{2}$ hour at 900°.....	86.18	11.3	.325	.845	3.14	90.9	95.55	98.55	After being heated to 900° C., and reduced at this temperature with producer gas for $\frac{1}{2}$ hour and cooled in the gas.

^a Chemically pure commercial 150-mesh MnO₂, 200-mesh precipitated SiO₂, and the metallic Ag were milled together in a small porcelain ball mill for $\frac{1}{2}$ hour. From this homogeneous mixture, a sample for each test was weighed.

^b All samples for cyanide treatment were milled in KCN solution for 10 minutes, followed by 72 hours of agitation.

^c Not determined.

On account of the lower content of manganese dioxide in the mixture, the reaction between it and the metallic silver is not very marked at room temperature, as is indicated by the solubility in potassium cyanide solution; however, there is a considerable decrease in the solubility of the silver in dilute nitric acid. At 130° C. the formation of insoluble silver becomes pronounced, while at 600° it reaches a maximum. After reduction in producer gas, as might be

FIGURE 1.—Curves showing the solubility of silver in synthetic mixtures in cyanide solutions after heating at various temperatures.

expected, most of the silver becomes soluble in potassium cyanide solution. The solubility in nitric acid is high, but lower than with manganese dioxide alone, while the solubility in dilute sulphuric acid is surprisingly high.

The curves in Figure 1 show the difference in the extraction of silver resulting from the heating of mixtures of silver with manganese dioxide, silver with silica, and silver with both manganese dioxide and silica.

CONCLUSIONS.

When freshly precipitated manganese dioxide is triturated with finely divided metallic silver and water, a compound of silver insoluble in potassium cyanide solution and other common solvents for this metal is formed. Heating to higher temperatures, up to 320° C., accelerates the production of the refractory silver compound; and heating to 900° almost completely converts it to compounds soluble in potassium cyanide solution. Evidently the refractory silver compound is a silver manganite of uncertain composition.

When finely ground and intimately mixed silica and metallic silver are heated in air above 320°, a compound of silver is formed which is insoluble in potassium cyanide solution. At 600°, formation of this compound is pronounced, and with a further increase in temperature the proportion of the compound formed becomes greater. The refractory compound is a silver silicate having a pink color.

It appears that in manganese-silver ores of secondary origin, formed at low temperature, the refractory silver mineral is a manganite of silver; whereas, if ore deposition has taken place at higher temperature, silver silicate may also be present. In the hydrometallurgical treatment of ores containing silver, the behavior of silver and silica at elevated temperatures becomes of the greatest importance. The uniformly low extraction by cyanidation of the silver from ores which have been given an oxidizing roast is explained, for the first time, through the formation of insoluble silver silicate.

Since this work was done, C. M. Bouton, W. C. Riddell, and L. H. Duschak,^{19a} of the Bureau of Mines, have investigated the behavior of silver in chloride volatilization and in this connection considered the possibility of the formation of silver silicate at high temperatures. They doubt the existence of silver silicate and advance the theory that the silver penetrates the particles of silica, possibly in colloidal form. If this be true, it would be expected that the silver in the silver-silica combination would be as refractory after heating in the presence of a reducing gas as before; but this is not so, as will be clear from the data given previously. This subject requires further investigation before the existence or nonexistence of silver silicate can be definitely stated.

POSSIBILITY OF MECHANICAL SEPARATION OF REFRACTORY SILVER MINERALS FROM MANGANIFEROUS ORES.

Some metallurgists have devoted much attention to the possibility of separating out the refractory silver minerals by various methods of concentration, but commercially the results of the tests have been uniformly unsatisfactory; and, unfortunately, statements regarding

^{19a} Bouton, C. M., Riddell, W. C., and Duschak, L. H., Silver in chloride volatilization: Tech. Paper 217, Bureau of Mines, 1924, 56 pp.

the behavior of the silver compound do not always harmonize. In considering these data, we find that in many analyses the manganese content in the various products has not been determined, whereas if this had been done, it is believed that much of the discrepancy in these results could be more readily explained. Another factor which also led to confusion is that no distinction was made between the amenable and the refractory silver in the ore.

SEGREGATION BY SCREENING.

Coghill ²⁰ gives the results of a sizing test of a sample designated "Arizona ore." This test shows in general an increase of silver in the finer sizes, but unfortunately no manganese determinations are given which would show the relationship between the two minerals. Below (Table 6) is a sizing test of a sample of high-grade ore from the Gedang Ilir mine, Sumatra:

TABLE 6.—*Sizing analysis of Sumatra ore.*

Mesh.	Weight, per cent.	MnO ₂ , per cent.	Au.		Ag.	
			Grams per metric ton.	Ounces per short ton.	Grams per metric ton.	Ounces per short ton.
+20.....	9.24	19.99	18.8	0.54	4,481	130.4
-20+40.....	33.97	23.17	22.8	.66	5,081	147.8
-40+60.....	13.27	25.81	25.6	.74	5,181	150.7
-60+80.....	8.21	27.43	29.6	.86	5,410	157.4
-80+100.....	7.07	28.57	31.2	.90	5,421	157.7
-100+125.....	2.60	30.00	33.4	.97	5,688	165.5
-125+200.....	18.18	33.67	38.0	1.10	6,510	189.4
-200.....	7.42	44.05	44.8	1.30	8,613	250.6

Table 6 shows that the ratio between the silver and manganese remains approximately the same for all sizes, despite the fact that both the manganese and the silver content of the different sizes vary considerably, the tendency of this ore being for the finer sizes to contain a higher percentage of both minerals. Similarly, the gold also bears an approximately fixed relationship to the manganese.

GRAVITY CONCENTRATION.

Hamilton ²¹ records the making of a concentrating test of an ore from Minas Prietas, Mexico, in which the tailing contained rather more silver than the concentrate, but no figures are given for the manganese content of the two products.

Coghill ²² calls attention to a concentration test which he made on an ore from Jalisco, Mexico. A considerable proportion of the manganese contained in the original ore was separated with the concentrate and a middling product. In this test the silver content of

²⁰ Coghill, W. H., *Refractory manganese-silver ores*; Part I: Min. and Sci. Press, vol. 104, 1912, p. 754.

²¹ Hamilton, E. M., *Cyanidation of manganese-silver ores of Mexico*: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 10, 1916, p. 66.

²² Coghill, W. H., *Refractory manganese-silver ores*; Part I: Min. and Sci. Press, vol. 104, 1912, p. 754.

these products bears no relationship to the manganese content given. In general, the silver remaining in the tailing is more amenable to cyanidation than that contained in the concentrate. On account of the high silver content, 13 ounces per ton of tailing, concentration was not considered feasible for its recovery.

Mill tests of a considerable tonnage of low-grade silver ore from the Buffalo-Hunter mine at Silver Cliff, Colo., indicate that a satisfactory recovery of the silver from this material can be obtained by water concentration. Furthermore, the ratio of silver to manganese is quite constant. The manganese mineral in the Buffalo-Hunter ore is very dense, which makes it particularly favorable to water concentration.

It has been our experience that the Gedang Ilir ore can not be concentrated satisfactorily on account of the earthy nature of the manganese dioxide. On the whole, water concentration of these ores, particularly of those of high grade, is not feasible. The Buffalo-Hunter ore apparently is one of the few exceptions to this rule, on account of the fact that the original ore is low grade, and the manganese mineral with which the silver is associated is hard and dense.

FLOTATION.

Our experience, together with the results obtained by others, has clearly indicated that plain flotation is of no benefit to this type of ore. Neal²³ has tried it extensively, and reports as a result of his experiments that silver refractory to cyanidation is also refractory to flotation, and that, on the whole, flotation gives no promise of yielding commercial results.

Four tests of Gedang Ilir ore were made by flotation and table concentration after reduction at 900° C., and the results are shown in Table 7.

The above table shows that the recovery of silver in the concentrates by flotation varied between 28.8 and 33.3 per cent. Sulphidizing did not improve the recovery. It will be observed that in test 3 the concentrate yields 28.8 per cent of the silver and 28.4 per cent of the manganese, again showing the close relationship between the two metals.

MAGNETIC SEPARATION.

As a result of tests of El Favor (Jalisco, Mexico) ore at the Massachusetts Institute of Technology, Bugbee²⁴ states that magnetic separation, followed by a chloridizing roast of the concentrate and cyanidation of the chloridized concentrate and the raw tailing, yielded a recovery of 70 to 80 per cent. From an ore containing approximately 20 ounces of silver per ton, the highest concentrate obtained assayed 78 ounces per ton of concentrate.

²³ Neal, Walter, The manganese-silver problem: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 17, 1916, p. 16.

²⁴ Bugbee, E. E., The manganese-silver problem: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 17, Aug. 1916, p. 11.

TABLE 7.—*Flotation and table concentration of Gedang Ithi ores.*

Test No.	Condition of tests.	Metal contents.						Recovery or loss, per cent.		
		Product.	Au.		Ag.		Mn.	Au.	Ag.	Mn.
			Grams per metric ton.	Ounces per short ton.	Grams per metric ton.	Ounces per short ton.				
1A	Used "Sample A" ore, 250-gram sample crushed to 65 mesh, and 2 pounds per ton of mixture containing 40 per cent coal tar, 10 per cent tar creosote, 30 per cent Yaryan pine oil, and 20 per cent cresylic acid. Treated in Janney machine, 25 minutes.	Heads..... Conc..... Tails.....	23.39 41.20 20.80	0.68 1.19 .60	3,640.0 9,462.8 2,787.2	105.9 275.4 81.1	13.64 29.66 11.29	100.00 22.60 77.40	100.00 33.30 66.70	100.00 27.80 72.20
1B	Used "Sample A" ore, 250-gram sample crushed to 65 mesh. Sample tabled on small Wilfley table, table tailing sulphidized with 2 pounds of Na ₂ S per ton, and floated, as in 2.	Heads..... Table conc..... Table tail.....	22.61 84.80 12.90	.65 2.46 .37	3,623.5 4,439.2 3,490.0	105.4 126.2 101.5	12.89 16.71 12.30	100.00 50.70	100.00 16.50	100.00 a 17.50
2	Used "Sample A" ore, 65 mesh, and 2 pounds per ton of mixture composed of 30 per cent coal tar, 30 per cent coal tar creosote, and 50 per cent Yaryan pine oil. Treated in Janney machine, 25 minutes.	Flot. conc..... Flot. tail.....	34.80 9.20	1.01 .26	9,393.2 2,503.6	273.3 72.5	30.00 9.30	19.20 30.10	32.40 51.10	b 29.90 53.30
3	Used "Sample B," 250 grams, 65 mesh, and 2 pounds per ton of mixture composed of 30 per cent coal tar, 10 per cent creosote, and 60 per cent pine oil. Treated in Janney machine, 25 minutes.	Heads..... Conc..... Tails.....	26.82 32.00 26.00	.78 .93 .75	3,860.0 8,217.6 3,178.0	112.3 238.8 92.4	13.94 29.60 11.50	100.00 16.10 83.90	100.00 28.80 71.30	100.00 28.40 71.60

a Table recovery.

b Total recovery: Au, 69.90; Ag, 48.90; Mn, 47.40.

Table 8 shows the results of a magnetic separation test of a sample of high-grade ore from the Gedang Ilir mine. It will be noted that only the 10 to 28 mesh product was used for making this test.

TABLE 8.—*Separation of MnO_2 from the gangue of Gedang Ilir ore by Wetherill magnetic separator.*

Original sample, size 10 to 28 mesh.

Metal contents of ore:

MnO ₂ , per cent.....	23.3
Au—Grams.....	30
Ounces.....	0.87
Ag—Grams.....	5,003
Ounces.....	145.6

Concentrate obtained by 2.5-ampere field strength, MnO₂=64 per cent, equivalent to Mn 40.45 per cent, 2.6 per cent of total product.

Metals in concentrate—

Au—Grams.....	28
Ounces.....	0.81
Ag—Grams.....	13,017
Ounces.....	378.8

Concentrate obtained by 4-ampere field strength, MnO₂=57.5 per cent equivalent to Mn=36.35 per cent, 32.2 per cent of total product.

Metals in concentrate—

Au—Grams.....	43
Ounces.....	1.25
Ag—Grams.....	11,181
Ounces.....	325.3

Middlings obtained by 5.5-ampere field strength, MnO₂=27.3 per cent, equivalent to Mn 17.26 per cent, 3.4 per cent of total product.

Metals in middlings—

Au—Grams.....	42
Ounces.....	1.22
Ag—Grams.....	5,634
Ounces.....	163.9

Tailings from 5.5-ampere field strength, MnO₂=3.09 per cent, equivalent to Mn 1.95 per cent, 61.8 per cent of total product.

Metals in tailings—

Au—Grams.....	22.4
Ounces.....	0.65
Ag—Grams.....	1,400
Ounces.....	40.7

The ratio of manganese in the first concentrate to that in the original ore was 2.73 to 1, while the silver had a ratio of 2.63 to 1. In the second concentrate the ratios were manganese, 2.47 to 1, and silver, 2.24 to 1. The ratios in the middling to that in the original ore were manganese, 1.17 to 1, and silver, 1.31 to 1. The ratios in the tailing to that in the original ore were manganese, 1 to 7.5, and silver, 1 to 3.57. It will be noted that the ratio of silver to manganese is fairly constant in all the products, with the exception of the tailing.

Magnetic separation tests were also made of a sample of ore from a Mexican mine. The concentrate contained 34.7 per cent man-

ganese dioxide, while the original ore contained 2.88 per cent. The silver content of the original ore was 52.2 ounces, while the concentrate assayed 103.22 ounces. The original ore by direct cyanidation yielded 69.3 per cent of the silver, while the concentrate yielded 38.4 per cent. The tailing from magnetic separation yielded 82.6 per cent of the silver by direct cyanidation. In this test it will be noted that most of the refractory silver follows the manganese. Although with this ore there does not appear to be the direct ratio between the silver and the manganese that exists in the Sumatra ore, yet the refractory nature of the silver directly associated with the manganese minerals is very evident. The total percentage of silver recovered in the concentrate with a 4 to 8 mesh product amounted to only 14.4 per cent.

From the results cited it is evident that magnetic separation does not offer a commercial solution of the problem of treating these ores. On account of the limited capacity of the separators and the close sizing required—the separator not being adapted to the treatment of the finer sizes—there appears to be no chance for magnetic separation even for ores more amenable to treatment than those with which we are familiar.

Neal²⁵ cites tests made by the Huff Electrostatic Separator Co. of a sample of El Favor ore which assayed 24.8 ounces of silver per ton. The highest grade concentrate obtained was from the 20 to 60 mesh product, and assayed 55.8 ounces per ton. The concentrate obtained from all the products represented 25 per cent of the weight of the original ore and 45.5 per cent of the valuable metal content. It is stated that treatment of the tailing would probably have shown a somewhat higher percentage of recovery, since the more refractory mineral had been removed in the concentrate, but electrostatic treatment was abandoned on account of the cost of shipping the low-grade concentrate.

In the course of making our tests of the Gedang Ilir ore with the magnetic separator we tried the Huff machine on the fine sizes which, it was known, could not be treated by the magnetic separator. These tests were by no means exhaustive, but in general they showed the unsuitability of electrostatic separation for this ore.

SUMMARY.

In general, mechanical methods of separation give very poor results with manganese-silver ores, the one exception coming to our attention being the Buffalo-Hunter ore. This ore, as formerly stated, is low grade and refractory, therefore could not be treated at a profit by any known direct process. On account of the hardness and density of the manganese mineral, it is possible to obtain by water concen-

²⁵ Neal, Walter, The manganese-silver problem: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 17, August, 1916, p. 11.

tration a fairly high recovery of a product which can be profitably shipped or treated locally. It is, however, well to remember that for such treatment large ore deposits should be available, permitting large-scale operation; and, furthermore, that a satisfactory process for treating the concentrate must be available.

TREATMENT OF MANGANESE-SILVER ORES BY CHEMICAL METHODS OTHER THAN CARON PROCESS.

CHLORIDIZING ROAST.

The earliest recorded application, so far as we are aware, of a chloridizing roast for the treatment of manganese-silver ores was made by Goodale²⁶ in the Tombstone district of Arizona. He noted the interference of manganese in the pan-amalgamation process as then employed in that district and attributed most of this difficulty to fouling of the mercury by the manganese. Later experience, however, has shown that aside from this possible difficulty, refractory silver minerals are present in these ores which are not recoverable by direct amalgamation. The chloridizing roast serves to change these silver combinations to a considerable extent into silver chloride, which is readily decomposed by mercury or dissolved by cyanide solution.

Hamilton,²⁷ Coghill,²⁸ Neal,²⁹ and others who have investigated the cyanidation of manganese-silver ores made tests employing the chloridizing roast as a treatment preliminary to cyanidation. It is general experience that the recovery of silver is considerably increased thereby, but the same difficulties arise in connection with roasting as with the earlier processes of amalgamation and lixiviation. These difficulties are chiefly due to incomplete chloridization and losses of silver through volatilization.

On account of the more recent development of blast roasting, the chloridizing blast roast appears to be more promising for certain ores than the earlier methods of application, for reasons explained below.

In the chloridizing roast, as formerly carried out in various types of roasting furnaces, the ore was first given an oxidizing roast, which was followed by the addition of the sodium chloride for chloridizing. During the oxidizing roast the MnO_2 would be dissociated with the formation of the lower oxides Mn_2O_3 or Mn_3O_4 , depending upon the temperature and time of heating. Also, during this stage, as we have clearly shown elsewhere in this bulletin, a large proportion of the amenable silver compounds in the ore would combine with the Mn and SiO_2 to form additional refractory compounds. It is, therefore,

²⁶ Goodale, C. W., Occurrence and treatment of the argentiferous manganese ores of the Tombstone district, Arizona: Trans. Am. Inst. Min. Eng., vol. 17, 1889, p. 767.

²⁷ Hamilton, E. M., Cyanidation of Mexican manganese-silver ores: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 10, August, 1909, p. 66.

²⁸ Coghill, W. H., Refractory manganese-silver ores: Min. and Sci. Press, vol. 104, 1912, p. 756.

²⁹ Neal, Walter, The manganese-silver problem: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 17, August, 1916, pp. 9-18.

not unusual during an oxidizing roast of ores of this class for all of the silver to be converted into refractory compounds where originally there had been only 60 to 75 per cent of refractory silver.

On the addition of sodium chloride to the heated ore in an oxidizing atmosphere a considerable proportion of the silver is converted into silver chloride, but the conversion is never complete, as indicated by the subsequent low recovery of silver. It is, therefore, obvious that the conversion would probably be more complete if oxidation could be avoided during the earlier stages of roasting.

With the chloridizing blast roast the necessary fuel and salt are mixed directly with the ore, and, after ignition, air is either blown or drawn through the charge. Under these conditions, during the heating of the ore an excess of carbon is left which to a greater or less extent reduces the higher oxides of manganese to the lower oxides, even as low as manganous oxide (MnO). This condition, as will be clear from a consideration of other data presented herein, largely liberates the silver in a finely divided metallic condition which is ideal for chloridization. However, during this first stage, in which the conditions are reducing, no chloridization of the silver can take place at the temperature employed; but later, after the fuel is consumed, the mixture of hot ore and sodium chloride comes in contact with the air, at once giving conditions favorable to chloridization. Therefore such chloridization as is accomplished takes place during this later stage.

Under the best conditions this operation is not subject to definite control, therefore the degree of chloridization and the subsequent recovery of silver may vary decidedly. The loss of silver through volatilization may be less by the blast method than by the ordinary method of roasting. Table 9 shows the results of experiments with Gedang Ilir ore under various conditions of chloridization, while Table 10 shows the recovery obtained from this ore calcined.

TABLE 9.—Volatilization losses during chloridization.

Sample No.	Tempera- ture.	Time of roasting.	Total time of heating from 0° to maxi- mum tempera- ture.	Assay of original ore (per ton).				Salt added to ore.	Assay after chloridization (per ton).				Volatilization losses.	
				Au.		Ag.			An.	Ag.	Au.	Ag.		
				Grams.	Ounces.	Grams.	Ounces.							
1 a.....	600-650	25	1	29.3	1.00	3,793	110.4	3	Grams.	Ounces.	Per cent.	Per cent.		
2 b.....	750-780	20	1	29.3	1.00	3,793	110.4	3	3,691	107.4	8.87	2.7		
3 a.....	800-840	20	1	29.3	1.00	3,793	110.4	3	3,541	103.0	21.16	6.6		

a The sample was roasted in a fire-clay crucible in a muffle, without stirring. b No. 2 was roasted in a closed crucible to obtain better reducing effect. c Plus 2 per cent C.

TABLE 10.—Recovery of silver from chloridized ore.

Sample No.	Assay of original ore (per ton).		Assay after chloridization (per ton).		Recovery by thiosulphate.		Strength of cyanide added.		Strength of cyanide after milling.		Protective CaO added after milling.		Cyanide tailings (per ton).		Recovery by cyanide.		Total recovery by cyanide on original ore.	
	Au.		Au.		Au.		Au.		Au.		Au.		Au.		Au.		Au.	
	Grams.		Grams.		Grams.		Grams.		Grams.		Grams.		Grams.		Grams.		Grams.	
	Per cent.		Per cent.		Per cent.		Per cent.		Per cent.		Per cent.		Per cent.		Per cent.		Per cent.	
	Ounces.		Ounces.		Ounces.		Ounces.		Ounces.		Ounces.		Ounces.		Ounces.		Ounces.	
1.....	29.3	3,793	27.0	3,792	32.4	40.0	0.24	0.142	1	0.046	1	0.046	6.3	1,016	76.7	73.2	70.7	73.2
2.....	29.3	3,793	26.7	3,691	34.8	82.3	.24	.12	1	.053	1	.053	2.7	258	89.9	81.9	81.9	90.5
3.....	23.1	3,541	23.1	3,541	77.9	85.6	.24	.12	1	.080	1	.080	3.0	492	87.0	86.1	68.6	80.4

NOTE.—The samples were run for 2 hours in a porcelain ball mill in a 10 per cent Na₂S₂O₃ solution. The ratio of solution to ore for both thiosulphate and cyanide milling was 4 : 1.

CHLORIDIZING ROAST IN A REDUCING ATMOSPHERE.

Table 11 shows the results of chloridization at various temperatures, a strong reducing atmosphere being maintained throughout the operation. Precautions were also taken to cool all samples in a reducing atmosphere.

TABLE 11.—Results of tests of *Gedang Ilir* ore by a reducing chloridizing roast.

Run No.	Screen product of sample.	Salt added to ore. ^a	MnO ₂ in sample after addition of 3 per cent of NaCl.	Reduced at temperature shown.	Time of reduction.	Gas used for reduction.	Loss in weight after reduction.	MnO ₂ in sample after reduction.	MnO ₂ in sample calculated on original weight.	Content in heads after reduction.		Losses through volatilization.		Recovery by cyanide after one-half hour's milling and— ^b		Recovery by a 5 per cent thio-sulphate solution after one-half hour milling followed by 24 hours agitation.	
										Au.	Ag.	Au.	Ag.	Au.	Ag.	Au.	Ag.
		Per cent.	Per cent.	° C.	Hours.	Producer gas c.	Per cent.	Per cent.	Per cent.	Grams per ton.	Grams per ton.	Grams per ton.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	Mesh.	3	23.68	±300	±1½		5.576	9.06	8.74	61.0	5,039	+0.1	96.7	93.6	94.1	43	72.4
2	—28	3	23.68	±400	±1		6.628	8.3	7.75	61.2	5,109	+0.6	+19	96.7	93.9	50	48.9
3	—28	3	23.68	±500	±1		8.53	2.87	2.62	62.0	5,229	+1.1	Lost.	95.0	80.8	39.4	16.3
4	—28	3	23.68	±600	±1		9.786	None.	None.	63.6	5,349	+0.4	82.0	94.4	82.4	49.0	13.0
5	—28	(f)		±340	±1	Hydrogen.....				62.0	5,171		93.8		53.5	66.27	

^a The salt was added to the ore in solution to obtain a homogeneous contact between the salt and the refractory silver compounds.

^b The strength of cyanide added to ore was 0.196 per cent NaCN; dilution during milling 1 to 4, and during agitation 1 to 8.

^c An analysis showed CO₂, 6.1 per cent; O₂, 0.7 per cent; CO, 22.0 per cent; H, 1.0 per cent; N, 70.1 per cent.

^d The reduction at a temperature of 400° C. resulted in a conversion of all MnO₂ into Mn₂O₃.

^e With a longer reduction at 500° C. a total reduction from MnO₂ to MnO could have been accomplished.

^f Excess of salt.

Analysis of head sample:

	Au.	Ag.
Grams.	Grams.	
Run No. 1.....	57.6	4,826
Run No. 2.....	56.8	4,769
Run No. 3.....	56.8	4,820
Run No. 4.....	58.4	4,768
Run No. 5.....	59.2	4,785
Run No. 6 (see summary).....	57.2	4,763
Average.....	57.7	4,788
Average (ounces).....	1.67	139.3

It will be noted that at 300° C., 72.4 per cent of the silver has been converted into forms soluble in sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$). With increase of temperature, the percentage soluble in the thiosulphate decreases until at 600° only 13 per cent is soluble.

In order to determine whether reduction without sodium chloride converted any part of the silver into a form soluble in sodium thiosulphate, a sample of the same ore used for the chloridizing tests was treated directly with thiosulphate solution, and the recovery was only 0.726 per cent. Another sample reduced by producer gas at 330° was similarly treated with thiosulphate, and only 9.4 per cent was recovered. This clearly indicates, although it does not definitely prove, that some silver compound other than silver chloride is formed, which under reducing conditions is soluble in sodium thiosulphate. When chloridization is carried on in a reducing atmosphere at 300°, possibly some silver is converted to this compound, but the greater part of the silver is evidently in the form of silver chloride. As indicated by the results, the decomposition of the soluble forms of silver, in which the chloride predominates, rapidly increases with higher temperatures, metallic silver being the final product.

VOLATILIZATION TESTS.

A sample of manganese-silver ore from Sumatra submitted for test to F. G. Moses, formerly of the Intermountain experiment station of the Bureau of Mines, assayed 207.6 ounces of silver and gold per ton, 13 per cent manganese, and 72.5 per cent insoluble. Experiments were conducted to determine the applicability of chloride volatilization as a means of recovering the silver. All tests were made as follows:

A 100-gram sample was mixed with the chloridizing reagent and placed in a 6-inch roasting dish in a muffle furnace kept at the temperature of the test. An oxidizing atmosphere was maintained in the muffle. The residue was weighed and assayed. Results of seven tests are given in Table 12.

TABLE 12.—*Volatilization tests of manganese-silver ore from Sumatra.*

No.	Weight of ore.	Weight of NaCl.	Weight of CaCl_2 .	Temperature.	Time.	Weight of residue.	Silver and gold.		Silver and gold volatilized.
							Heads.	Tails.	
	Grams.	Grams.	Grams.	° C.	Hours.	Grams.	Ounces.	Ounces.	Per cent.
1.....	100	8	0	900	2	95.0	207.6	84.8	61.1
2.....	100	4	0	900	2	95.0	207.6	84.5	61.3
3.....	100	0	4	900	2	94.0	207.6	114.2	48.2
4.....	100	0	8	900	2	95.0	207.6	93.0	57.4
5.....	100	0	2	900	2	94.5	207.6	93.1	57.5
6.....	100	2	4	900	2	95.0	207.6	99.0	55.2
7.....	100	10	0	900	2	97.0	207.6	96.0	55.2

The percentage of the silver volatilized, shown in the last column, is far below that which would be necessary to make the volatilization process promising for this ore. Longer periods of heating might improve results, though in practice it would be difficult to get much longer heating at the temperature required.

WET CHLORIDIZING.

Conversion of refractory silver compounds into soluble silver chloride by wet methods has been considered by various investigators, chiefly Linton.³⁰ He mixed the required sodium chloride with the ore during grinding to 100 mesh, after adding a 5 per cent solution of sulphuric acid, and agitating the whole occasionally during a period of 24 hours. The solution was separated by filtration, and the pulp well washed and then cyanided. Linton records silver recoveries of 60 to 94 per cent. In this process the manganese is dissolved as sulphate to the extent that the active reagents (sodium chloride and sulphuric acid) are supplied. We have found that in order to attain the best results by a process of this kind it is necessary to dissolve all the manganese, and failure to do so doubtless accounts for the lower extractions recorded. Such a process is most attractive for ores low in manganese and a gangue insoluble in acid, but becomes more and more difficult to operate as the percentage of manganese to be dissolved increases. It is difficult, particularly with the higher grades of manganese-silver ores, to filter and completely wash the ore pulp. The manganese sulphate remaining in the residue is an active cyanicide. Preliminary treatment with hydrochloric acid has been suggested by various investigators, and has generally shown high recoveries when followed by cyanidation. The reactions taking place are somewhat similar to those that occur when sodium chloride and sulphuric acid are used. In the former reaction, manganese sulphate is formed and in the latter, manganese chloride; while in both reactions free chlorine is evolved. The equations for both reactions are shown below:

Hamilton³¹ has cited tests in which dry sulphidizing of the ore has been accomplished by heating the ore mixed with elemental sulphur, generally out of contact with the air. Although this treatment preliminary to cyanidation generally betters the silver recovery, there is still much room for improvement.

When manganese dioxide is heated with sulphur, a mixture of green manganous sulphide (Mn_2S_3) and manganous oxysulphide is

³⁰ Linton, Robert, Silver ore treatment in Mexico: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 9, March, 1909, p. 307.

³¹ Hamilton, E. M., Cyanidation of manganese-silver ores of Mexico: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 10, August, 1909, p. 66.

formed. There is also probably some manganous sulphate (MnSO_4) formed. Manganous oxysulphide is a powerful cyanicide, therefore it is necessary to use a preliminary acid wash to remove the oxysulphides, as far as possible, prior to cyanidation.

Brunner ³² points out that in order to form Mn_2S_3 and avoid formation of oxysulphide, it is necessary also to add carbon; the reaction taking place in the presence of carbon is as follows:

WET SULPHIDIZING.

Hamilton and Clevenger ³³ were the first to use hydrogen sulphide and alkaline hydrosulphides for preliminary treatment of manganese-silver ores prior to cyanidation, and Clevenger to point out that normal sulphide is not effective.

When hydrogen sulphide in a water solution is brought into contact with manganese dioxide, manganous sulphide is formed first. This is at once oxidized to a mixture of manganous dithiosulphate, manganous sulphite, and manganese sulphate. The reaction of manganese dioxide with alkaline hydrosulphides is somewhat similar to that with hydrogen sulphide.

In general, it has been our experience that a high consumption of cyanide results when any method of sulphidizing—either dry or wet—is used preliminary to cyanidation. This high consumption, even with carefully washed pulp, is readily understood on account of the formation of less soluble manganese compounds. The variations in silver recovery when this method of preliminary treatment is used are largely explained by the incomplete conversion of the manganese compounds into soluble forms.

TREATMENT WITH SULPHUROUS ACID.

An aqueous solution of sulphur dioxide dissolves the higher oxides of manganese with formation of a mixture of manganous dithionate and manganous sulphate.³⁴ If sufficient sulphurous acid is used, and enough contact with the finely ground ore is permitted the manganese is completely dissolved.

Hamilton ³⁵ discovered that when the manganese-silver ores of the Minas Prietas district of Mexico were given a preliminary treatment with sulphurous acid, followed by thorough washing with water, the recovery of silver by cyanidation was much higher. The consump-

³² Brunner, C., Ueber Darstellung und Eigenschaften des Mangans: Ann. Phys. Chem., Bd. 101, 1857, pp. 264-291.

³³ Hamilton, E. M., and Clevenger, G. H., Cyanidation of manganese-silver ores of Mexico: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 10, August, 1909, p. 66.

³⁴ Croasdale, Stuart, Volatilization of metals as chlorides: Eng. and Min. Jour., vol. 76, 1903, pp. 312 and 420.

³⁵ Hamilton, E. M., Cyanidation of manganese-silver ores of Mexico: Jour. Chem. Met. and Min. Soc. of South Africa, vol. 10, August, 1909, p. 66.

tion of cyanide was moderate, but perfect washing is frequently difficult to attain. Later investigators have recorded results of similar treatment of manganese-silver ores from other localities, and in general it has been indicated that a fairly satisfactory recovery of the silver can be obtained by proper manipulation. Neal³⁶ has called attention to the necessity of completely dissolving the manganese in order to obtain the best recovery of the silver. Coghill³⁷ calls attention to the importance of thorough washing for the removal of manganese salts after sulphurous acid treatment and prior to cyanidation if a high consumption of cyanide is to be avoided.

Our investigation of the process confirms Neal's statement that the manganese should be completely dissolved; also Coghill's statement that the residue must be thoroughly washed before cyanidation. Herein lie the two difficulties in connection with the application of the process on a commercial scale as well as those involving the use of sulphuric acid with a reducing agent. Both conditions can be readily attained in the laboratory, but are more difficult to accomplish in large-scale work. Moreover, high consumption of sulphurous acid is expensive unless a source of cheap sulphur, such as waste gases containing SO_2 , is available. It is apparent that as regards recovery of the silver the process is best suited to ores low in manganese. The higher the manganese content the more difficult is the efficient application of the process. Likewise, if sulphur had to be used, the consumption should be prohibitive with the ores higher in manganese.

It has been suggested that the manganese could be profitably recovered from the waste solutions resulting from the preliminary treatment; however, the cost of evaporating the large volumes of solution involved and conversion of the manganese sulphate into a marketable form would in most localities exceed the value of the manganese by-product.

TREATMENT WITH SULPHURIC ACID.

Manganese dioxide is not soluble in dilute sulphuric acid alone, but is readily soluble in the dilute acid in the presence of various reducing agents, for example, oxalic acid, ferrous sulphate, metallic iron, and hydrogen peroxide. It is well known that hydrogen peroxide (H_2O_2) may function either as an oxidizing or reducing agent, the former with alkalis and the latter with acids. Its behavior in the presence of H_2SO_4 and MnO_2 is that of a reducing agent, the reaction being according to the equation:

The H_2O_2 is able to effect energetic reductions owing to the avidity with which the oxygen atom of the H_2O_2 combines when liberated with

³⁶ Neal, Walter, The manganese-silver problem: Jour. Met. and Min. Soc. of South Africa, vol. 17, August, 1916, p. 13.

³⁷ Coghill, W. H., Refractory manganese-silver ores: Min. and Sci. Press, vol. 104, 1912, p. 797.

another atom of oxygen of an oxygenated substance, thus being transformed into the more stable molecular O_2 . The dissolution of the Mn by dilute H_2SO_4 in the presence of H_2O_2 goes on with astonishing rapidity, even with cold solutions. This reagent could not of course be used commercially. Nascent hydrogen in the presence of dilute H_2SO_4 dissolves MnO_2 slowly.

In the Austin process, referred to previously, the manganese dioxide is dissolved by sulphuric acid in the presence of a reducing agent—here pyrite (FeS_2). The reaction given is as under:

The inventor claims that the manganese dioxide is probably reduced to manganous oxide, and sulphuric acid is formed by oxidation of the pyrite as shown by the above equation. The fact should, however, be noted that a strong base like manganous oxide can not exist in the presence of free acid. Reaction could go forward in the presence of acid and then with formation of manganese sulphate. The inventor states that under certain conditions the ferric sulphate hydrolyzes, forming free sulphuric acid according to the equation $Fe_2(SO_4)_3 + 3H_2O = Fe_2O_3 + 3H_2SO_4$. It is true that hydrolysis can take place under certain conditions, but only when there is no free acid present, and acid is essential for the process. The balanced equation for a ferric salt split by hydrolysis is as follows:

In dilute sulphuric acid this reaction ceases, as the high concentration of the SO_3 ions from the acid will force back the reaction from the right to the left. All basic ferric sulphates are therefore changed into normal salts in the presence of free acid.

Another process, belonging to the class employing sulphuric acid in the presence of a reducing agent and more or less similar to the Austin, is that of Fairlie and Denny, previously mentioned. The finely crushed ore is subjected to a preliminary wet treatment with sulphuric acid of 3 to 5 per cent strength in the presence of scrap iron, whereby the manganese dioxide is dissolved and manganese sulphate is formed. The following reaction is claimed by the inventors:

The solution and ore are separated by usual methods, and the ore is neutralized and treated by standard methods for the recovery of the precious metals.

VERMAES PROCESS.

The Vermaes process³⁸ consists of mixing the crushed ore with organic matter (such as sugar, corn, coconut shells, cotton seed, wood.

³⁸Vermaes, Stefanus Johannes, Treatment of refractory manganese ores containing precious metals or silver alone. U. S. Patent 1234426, July 24, 1917.

bark, peat) and sodium chloride. This mixture is heated to a temperature of 320 to 330°C., after which the ore is cyanided. The inventor claims that by his process the silver and gold losses that occur during the ordinary chloridizing roast are avoided because of the low temperature employed.

In the Vermaes process the organic matter is added for the purpose of breaking up the manganese-silver compounds. As we have shown elsewhere, reduction of natural manganese dioxide begins at a temperature of approximately 90° C. in an atmosphere of hydrogen or carbon monoxide. In the dry distillation of organic material hydrogen, carbon monoxide, and hydrocarbons are readily formed at temperatures of 180° to 200° C., and the reducing gases so formed will react with the higher oxides of manganese, reducing them to a lower oxide—generally, in this process, to mangano-manganic oxide (Mn_3O_4). According to Vermaes, the silver will then combine with the sodium chloride present, forming silver chloride. He specifies that sodium chloride be added as a solution to the ore to be decomposed in order to obtain the necessary intimate contact. As the temperature in this process generally does not rise above 330°, all the charcoal resulting from the distillation of the wood remains unacted upon and finely divided throughout the ore.

During the heating, part of the gold is transformed into aurous chloride, as indicated by its solubility in sodium thiosulphate solution. As auric chloride is completely decomposed into aurous chloride at temperatures above 180°, it is evident that none of the former compound would be present; and as aurous chloride is to a certain extent volatile at low temperatures, some loss of gold may be expected. On the other hand, Vermaes claims that no volatilization of either gold or silver takes place. However, in our study of the chloridizing roast, as carried out in a reducing atmosphere at 300°, we have shown that while there is no loss of silver there is a small loss of gold. Furthermore, the silver is not all present as chloride, a small part being in the metallic state, since decomposition of silver chloride begins in a reducing atmosphere at 300°. Evidently it is necessary to regulate carefully the proportion of organic material added in accordance with the percentage of higher oxides of manganese present in the ore. It is therefore obvious that with ores containing a high percentage of manganese an excessive amount of organic material would be required. The amount of sodium chloride required, according to Vermaes, depends on the proportion of silver present, and is 1 to 3 per cent.

CHEMISTRY OF THE CARON PROCESS.

Our own experience with manganese-silver ores, confirmed by the recorded results of others, led to the conclusion that the manganese in the refractory ores occurs as higher oxides, principally dioxide; and, furthermore, that below the zone of oxidation, where the manganese is chiefly present as compounds, generally represented by the minerals rhodonite (MnSiO_3) and rhodocrosite (MnCO_3), the silver is amenable to direct cyanidation. This indicates that refractory manganese-silver compounds are not present in the ore when originally deposited, and therefore it is probable that if the higher oxides of manganese were reduced to the manganous state the silver would be liberated in a form amenable to cyanidation.

The well-known fact that the higher oxides of manganese could be readily reduced to manganous oxide (MnO) by heating in various reducing gases led to the first experiments embodying the use of such gases for preliminary treatment of the ore prior to cyanidation or other processes for recovering the silver.

In general, these earlier tests indicated that it was necessary to reduce the higher oxides of manganese completely to MnO in order to obtain the best silver recovery; furthermore, it was established that there were certain temperature limits within which reduction should be carried on to obtain the best results. Reduction at a temperature above the upper limit gives an oxide which is more stable, but on the other hand there is the disadvantage of a lower recovery of silver, which more than outweighs this advantage. When reduction is carried on below the lower temperature limit, conversion of the higher oxides of manganese to MnO proceeds more slowly, and the resulting MnO is less stable, so that it is not advantageous to employ too low a temperature. In general, it was later ascertained that most ores yield the best results when reduction is accomplished at temperatures of 500 to 700°C . (932 to $1,292^\circ \text{F}$.), the best temperature for most ores being approximately 600°C . ($1,112^\circ \text{F}$.). When reduction is carried on at 900°C . ($1,652^\circ \text{F}$.), or above, a very stable form of MnO results, but the recovery of silver by cyanidation is considerably lower; also, in actual practice, the employment of a high temperature would necessitate a greater fuel consumption and more wear and tear on the furnace equipment.

During the first tests it was also noted that unless the reduced ore was cooled in a reducing atmosphere, the MnO was at once reoxidized to a greater or less degree to the higher oxides of manganese (Mn_3O_4) on coming in contact with the air in a heated condition. Coincident with this reversion of MnO to Mn_3O_4 , the silver which had been rendered amenable through reduction reverts in part to the refractory form; probably the same compound is formed as that origi-

nally present in the ore. It was, therefore, clearly established that in order to obtain the best results in the subsequent cyanide treatment for recovery of the silver all of the higher oxides of manganese should be completely reduced to MnO ; furthermore, the reduced ore must be cooled either in a reducing atmosphere or by quenching in water to avoid reoxidation of the manganese and reversion of silver to the refractory form. Moreover, the temperature of reduction should be between 500 and 700°C . (932 to $1,292^{\circ}\text{F}$.) in order to render the highest percentage of the silver amenable to cyanidation.

SIZE OF ORE PARTICLES.

These preliminary tests also showed that the size of the ore particles subjected to reduction has an important bearing on the final results. Strangely enough, with most of the ores investigated and particularly that from Sumatra, it was found that the best results were obtained when reduction was performed on ore which had been crushed to approximately 1-inch size. A sample of this ore in 4 or 5 inch lumps was reduced in the same manner as the finer material, and yielded by cyanidation a silver recovery only a little lower than the highest possible recovery under the most favorable conditions established for this lot of ore. However, it should be remembered that there are certain ores in which the higher oxides of manganese are present in very dense form, and require grinding. Notable among these is the Buffalo-Hunter (Colorado) concentrate, the treatment of which is referred to later. It was also found that the Hardshell (Arizona) ore could not be efficiently treated until crushed to 4 mesh or finer. The Buffalo-Hunter ore yielded the best results from a 30-mesh product.

We have found that both size of the ore and temperature of reduction may have an important influence upon the solubility of the silver in cyanide solution. For instance, the recovery from a 2 to 10 mesh product when reduced at 900°C . ($1,625^{\circ}\text{F}$.) was 95 per cent, while recovery from the same sample crushed to minus 48 mesh and reduced at the same temperature was 86.3 per cent. It has been found that at a lower temperature, 600°C . ($1,112^{\circ}\text{F}$.), the difference in recovery due to size of ore particles is not so marked. A plus 48-mesh product, the largest particles of which were one-half inch, showed a recovery of 98.15 per cent. A minus 48-mesh product from the same sample, under the same conditions, gave 94.6 per cent. With the first product, the reduction at a higher temperature resulted in a difference of 8.7 per cent of the silver recovered, whereas with the latter this difference was only 3.55 per cent.

It has also been observed that ore reduced at a low temperature, 500 to 700°C . (932 to $1,292^{\circ}\text{F}$.), does not need to be ground so fine prior to cyanidation as when reduced at a higher temperature.

PRODUCTS OF REDUCTION.

The possibility of silver silicate being formed during an oxidizing roast, or even during reduction, has been mentioned in the previous discussion of the nature of silver minerals. We believe that the explanation of the more favorable results obtained when reduction is carried out on larger ore particles is to a considerable extent explained by this fact. For example, if the ore is not crushed, there is less contact between the silver particles and the silica; therefore, the conditions for forming silver silicate are not so favorable as in the finely ground ore. Although silver silicate is decomposed by reducing gases somewhat similarly to the manganese compounds of silver, yet such decomposition is not so readily effected, nor is it so complete, as with the manganese compounds. Accordingly, if conditions are favorable to formation of silver silicate during reduction, there will always be a certain part of the silver which is not completely decomposed and rendered amenable to cyanidation, and which will lower the final extraction correspondingly. This refractory behavior also explains why the results in general, particularly with the fine ore, are not so good when reduction is carried on at a higher temperature, on account of the greater tendency for this compound to form at higher temperatures.

Below are given typical equations showing the reductions of higher oxides of manganese (here MnO_2 has been taken as typical) by various reducing gases:

These equations indicate that the products of the reducing action of the gases are manganous oxide, carbon dioxide, and water. Under the conditions of operating the process, carbon dioxide in any concentration apparently does not reoxidize manganous oxide. To prove this point, pure manganous oxide, which had been prepared from pure manganese dioxide by reduction with hydrogen, was cooled from a temperature of 800°C . ($1,472^\circ \text{F}$.) to room temperature in an atmosphere of pure carbon dioxide. There was no alteration whatever of the manganous oxide by this treatment. It was further observed throughout all of the tests which have been made, both on a small and large scale, that carbon dioxide in any reasonable concentration did not interfere with reduction any more than to act as a diluent of the reducing gases. That carbon dioxide does not oxidize manganous oxide is further confirmed by the fact that at high temperatures elemental manganese is only oxidized by carbon dioxide to manganous oxide.³⁹

³⁹ Moissan, H., Sur les oxydes métalliques de la famille du fer: *Ann. chem. phys.*, sér. 5, t. 21, 1880, p. 231.

Although this point has not been definitely investigated, it has also been observed that water vapor in any reasonable quantity does not appear to interfere with the process. The fortunate circumstance that the products of the reaction of reduction do not interfere with reduction renders the commercial application of reduction on a large scale a comparatively simple matter with the equipment we have developed.

REDUCTION TEMPERATURE.

Table 13 shows the temperature at which reduction begins with oxides of manganese in hydrogen, carbon monoxide, and carbon.

TABLE 13.—*Temperatures (° C.) at which reduction begins with oxides of manganese in hydrogen, carbon monoxide, and carbon.^a*

	Manganese dioxide.		Manganomanganic oxide.		Manganous oxide.
	Precipitated.	Pyrolusite.			
Composition by analysis of substance regarded as anhydrous.	Mn ₇ O ₁₅	Mn ₁₅ O ₂₈	Mn ₅ O ₇	Mn ₃ O ₄	MnO.
Physical texture.....	Fine powder, amorphous.	Very compact, crystalline.	Fine powder, amorphous.	Fine powder, amorphous.	Amorphous.
Temperatures, ° C.:					
Carbon monoxide.....	Below 15.....	87.....	97.....	240.....	No action at 600. Do.
Hydrogen.....	Near 145.....	Near 190.....	Near 240.....	255.....	
Carbon.....	260.....	390.....	410.....	430.....	

^a Wright, C. R. Adler, and Luff, A. P., *Researches on some points in chemical dynamics*: Jour. Chem. Soc. (London), vol. 33, 1878, pp. 1-27.

The temperature of initial reduction was lower with carbon monoxide than with hydrogen, and lower than with carbon in all tests. Time and pressure may bring about reduction at lower temperatures.

Table 14 shows the effect of temperature on reduction in pure dry carbon monoxide, and Table 15 shows the effect of temperature on reduction in pure dry hydrogen.

TABLE 14.—*Successive stages in the reduction by dry carbon monoxide of the manganese dioxide contained in refractory silver ore from Sumatra.*

MnO ₂ in original sample.	Time of reduction.	Temperature of reduction.	Loss in weight after reduction.	MnO ₂ after reduction, calculated on original weight.	Manganous-manganite compound obtained through reduction.	
					MnO.	MnO ₂ .
<i>Per cent.</i>	<i>Hours.</i>	<i>° C.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
16.064.....	2	110	0.98	14.20	11.60	88.40
16.064.....	2	147-150	2.43	8.44	47.44	52.56
16.064.....	2	215	3.77	2.95	81.58	18.42
16.064.....	2	300	4.70	1.29	91.97	8.03
16.064.....	2	465	5.93	None.	100.00	None.

NOTE.—Carbon monoxide was prepared by treating formic acid with concentrated sulphuric acid. After reduction, amorphous carbon was deposited in the ore.

TABLE 15.—*Successive stages in the reduction by dry hydrogen of the manganese dioxide contained in refractory silver ore from Sumatra.*

MnO ₂ in original sample.	Time of reduction.	Temperature of reduction.	Loss in weight after reduction.	MnO ₂ after reduction, calculated on original weight.	Manganous-manganite compound obtained through reduction.	
					MnO.	MnO ₂ .
<i>Per cent.</i>	<i>Hours.</i>	<i>° C.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
16.064.....	2	73-75	0.40	16.10	None.	100.00
16.064.....	2	95-97	.66	15.50	3.75	96.25
16.064.....	2	118-121	.80	14.70	8.49	91.51
16.064.....	2½	137-139	1.19	13.88	13.60	86.40
16.064.....	2	147-150	1.40	12.96	19.32	80.68
16.064.....	2	168-170	3.00	7.64	52.44	47.56
16.064.....	2	193-195	3.52	5.235	67.41	32.59
16.064.....	2	255	4.15	2.76	82.82	17.18
16.064.....	15	255	4.40	2.33	85.50	14.50
16.064.....	2	300	4.75	1.38	91.41	8.59
16.064.....	2	350	4.93	1.30	91.91	8.09
16.064.....	2	420	5.51	.71	95.58	4.42
16.064.....	2	450	5.60	.60	96.43	3.57
16.064.....	2	465	5.97	None.	100.00	None.

NOTE.—The MnO₂ in this ore occurs as "wad," an earthy form of MnO₂. The ore sample used in these experiments was ground to 200 mesh and was thoroughly mixed. Temperatures below 255° were measured with a mercury thermometer, while those above were measured with a Le Chatelier platinum-rhodium thermocouple. Heating was accomplished in a Hoskins electric combustion furnace. The samples of ore were placed in a small porcelain boat, which was pushed into the center of the ¾-inch porcelain tube of the furnace. All samples were cooled to room temperature in a stream of dry hydrogen.

Figure 2 gives a graphic comparison of H and CO as reducing agents at various temperatures.

Bell ⁴⁰ states that at a heat short of redness, MnO₂ is converted by CO into MnO in 4½ hours; furthermore, that MnO₂ and manganomanganic oxide (Mn₃O₄) readily lose their oxygen at the temperature of the melting point of zinc, 419° C. (786° F.), both being reduced to MnO in an atmosphere of CO. In no instance was there a trace of carbon formed. It would therefore appear that oxides of manganese are incapable of acting on CO as do the oxides of iron with the formation of C and CO₂.

It will be noted that at 465° C. (1,049° F.), at which temperature complete reduction to MnO had taken place, amorphous carbon was deposited in the ore. This reaction might appear to be at variance with Bell's statement that no deposition of carbon results when the higher oxides of manganese are reduced to MnO, but in this connection it should be remembered that these reductions were not made with pure MnO₂, but with a sample of Gedang Ilir ore, which is known to contain a small percentage of limonite (2Fe₂O₃·3H₂O). While we did not verify Bell's experiments, we believed that the presence of limonite in the ore accounts for the appearance of the carbon. Under certain conditions, deposition of carbon with formation of carbon monoxide was further confirmed by the appearance of lampblack in one of the large-scale reduction tests of Buffalo-Hunter concentrate in the

⁴⁰ Bell, I. Lowthian, The effect of certain metallic substances besides iron on carbonic oxide, including silicon: Chem. News, vol. 23, June 2, 1871, pp. 258-260.

externally heated kiln. Riché gas, containing a high percentage of CO, probably 50 per cent, was used in this test. No lampblack was observed during reduction until part of the ore which had been previously reduced, but still contained a little higher oxide, was again passed through the kiln. As soon as the partly reduced ore passed the reduction zone, lampblack appeared; however, when raw ore was again added the lampblack disappeared. Deposition of carbon seems very likely to occur when the ratio of CO in the reducing

FIGURE 2.—Curves showing comparison between hydrogen and carbon monoxide as reducing agents at various temperatures.

gases rises above a certain point; thus in reduction by pure CO the ratio of CO to other gases would be very high, particularly in the later stages of reduction. In the externally fired kiln, when Riché gas was used on partly reduced concentrate which contained very little of the higher oxides, the ratio of CO was undoubtedly high, therefore carbon was deposited.

However, it is well to state that in the many working-scale tests which have been made no difficulty was experienced in avoiding the deposition of carbon in the reducing zone. Even in the

externally heated kiln, when a high-grade gas such as Riché gas was employed, carbon appeared only on the one occasion previously cited. With lower grade gases, such as producer gas, employed in the internally fired kiln we do not believe that it would be possible to form carbon, even though it were desired to do so.

REDUCTION OF PYROLUSITE.

Wright and Luff⁴¹ state that the reduction of pyrolusite (MnO_2) by CO begins at 87°C . (188°F). It will be noted from Table 14 that we have ascertained that at 100°C . (212°F .) 11.6 per cent of the total MnO_2 content is reduced in two hours.

Moissan⁴² states that MnO_2 heated to 230°C . (446°F .) in hydrogen becomes manganic oxide (Mn_2O_3); at a somewhat higher temperature the Mn_2O_3 is converted into manganomanganic oxide, (Mn_3O_4); and at 260°C . (500°F .), MnO is formed.

It is also stated⁴³ that reduction of MnO_2 to Mn_3O_4 begins at 190°C . (374°F .) and is complete at 202°C . (395°F .), and that further reduction proceeds at a temperature above 360°C . (680°F .).

The temperature of reduction of MnO_2 depends on whether it is a natural or artificial product, also on its purity. The figures given above, therefore, do not cover all conditions.

Meyer and Röttgers⁴⁴ state that when artificial MnO_2 is heated to 530°C . (986°F .) at a pressure of one-fifth atmosphere (2.94 pounds) it is converted into manganic oxide (Mn_2O_3), while at atmospheric pressure (14.7 pounds) the same dissociation takes place at 565°C . ($1,049^\circ \text{F}$.).

Manganic oxide is further dissociated into manganomanganic oxide (Mn_3O_4) when heated to 940°C . ($1,724^\circ \text{F}$.) at one-fifth atmospheric pressure, while at atmospheric pressure the same dissociation occurs at $1,090^\circ \text{C}$. ($1,994^\circ \text{F}$.).

A sample of Gedang Ilir ore containing 23.6 per cent MnO_2 when heated to 650°C . ($1,202^\circ \text{F}$.) at atmospheric pressure had 84 per cent of the MnO_2 transformed into Mn_2O_3 . The same sample heated to 810°C . ($1,490^\circ \text{F}$.) had 93.3 per cent of the MnO_2 transformed into Mn_2O_3 . Another sample of the same ore containing 21.75 per cent MnO_2 was heated to $1,030^\circ \text{C}$. ($1,886^\circ \text{F}$.) at atmospheric pressure, and the analysis indicated that the residual compound was a mixture of Mn_2O_3 and Mn_3O_4 in about equal proportions.

It has been stated⁴⁵ that natural pyrolusite begins to dissociate in the air at 390°C . (754°F .). In ordinary practice, when an ore

⁴¹ Gmelin-Kraut, *Handbuch der Chemie*, Bd. 3, 1859, p. 249.

⁴² Moissan, H., *Sur les oxydes métalliques de la famille du fer*: *Ann. chim. phys.*, sér 5, t. 21, 1889, p. 231.

⁴³ Gmelin-Kraut, *Handbuch der Chemie*, Bd. 3, 1859, p. 249.

⁴⁴ Meyer, R. J., und Röttgers, Kurt, *Die Dissoziationstemperaturen der Manganoxyside MnO_2 und Mn_2O_3 in Luft und Sauerstoff*: *Ztschr. anorg. Chem.*, Bd. 57, 1908, pp. 104-112.

⁴⁵ Gmelin-Kraut, *Handbuch der Chemie*, Bd. 3, 1859, p. 249.

containing MnO_2 is heated above 400°C . (752°F .) it begins to lose oxygen rapidly, as is clearly indicated by the gas analyses recorded in Tables 16 and 17. In these analyses it will be noted that above this temperature there is a noticeable amount of oxygen in the gases.

TABLE 16.—*Gas analyses at rising temperatures.*

	Analysis of original gas.	Consumed gases at temperature (degrees centigrade) of—						
		250	350	450	550	650	750	850
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
CO_2	9.0	79.6	88.2	92.6	89.7	92.6	71.4	25.1
O_2	.1	.1	.4	5.5	8.7	.2	Absent.	Absent.
CO	34.6	8.6	4.2	Absent.	.2	2.2	12.4	32.3
H_2	55.1	9.3	5.4	Absent.	Absent.	3.3	13.9	40.2
N_2	1.2	2.4	1.8	1.9	1.4	1.7	2.3	2.4

TABLE 17.—*Gas analyses at rising temperatures.*

	Analysis of original gas.	Consumed gases at temperature (degrees centigrade) of—						
		250	370	470	570	650	750	850
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
CO_2	10.3	69.6	86.0	71.2	80.5	84.4	81.1	69.5
O_2	.2	.3	1.1	25.9	13.7	1.5	.4	.3
CO	47.6	16.4	7.1	Absent.	2.9	9.1	11.4	18.1
H_2	39.3	10.7	2.8	Absent.	.3	1.4	4.0	8.5
N_2	1.6	3.0	3.0	2.9	2.6	3.6	3.1	3.6

Total disappearance of the reducing gases coincident with the gain in oxygen indicates the very active reactions which take place at this temperature. In practice, when the ore in the preheating zone has reached a temperature of 400°C ., similar reactions will take place. When reduction is carried on with excess of reducing gas, and all the MnO_2 has been reduced to Mn_3O_4 at a temperature of 390°C ., it is evident that no dissociation will take place, as Mn_3O_4 is the final product of dissociation.

OPERATING RESULTS IN M'DOUGALL FURNACE.

In the operation of a McDougall furnace in the earlier experiments, before the ore cooler had been constructed, it was necessary to collect the hot ore in water as it was discharged from the furnace. Reoxidation by this method could be prevented, but it was observed that the rapidly cooled ore reoxidized more quickly than the same ore slowly cooled in reducing gases, as shown in Table 18.

TABLE 18.—Conditions for reoxidation of MnO after reduction, and influence on silver extraction.

How cooled.	MnO_2 after reduction.	MnO_2 after drying.	MnO_2 after.	Assay.				Milling.	Silver recovery.	
				Au, per metric ton.	Au, per short ton.	Ag, per metric ton.	Ag, per short ton.		After milling.	After agitation.
				Grams.	Ounces.	Grams.	Ounces.		Ag.	Time.
In gas.	Per cent.	Per cent.	Treated direct.	32.6	0.94	6,808	198.1	20	Per cent.	Hours.
Do.	None.		1½ years later, none.	36.0	1.04	7,060	205.4	20	97.6	
Do.	None.		Treated direct.	31.2	.90	3,491	101.3	2	97.3	
Do.	None.		After wet treatment, ^a none.	31.2	.90	3,491	101.3	2	89.4	72
Do.	None.		Treated direct.	30.2	.87	3,737	110.2	2	88.1	
Do.	None.		do.	30.0	.87	3,737	110.2	2	86.8	
Water.	None.	Not dried.	do.	18.4	.53	3,240	94.3	2	86.5	
Do.	2.5	2.5	2 months later, 4.3 per cent.	18.4	.53	3,240	94.3	2	84.7	24
Do.	.0087	2.02	Treated direct.	18.0	.52	3,230	94.0	2	70.5	
Do.	.49	2.02	1 month later, 3.45 per cent.	18.0	.52	3,230	94.0	2	85.2	24
Do.	.50	2.30	Treated direct.	28.4	.82	3,888	113.1	2	79.8	
Do.	.50	2.30	2 months later, 5.80 per cent.	28.4	.82	3,888	113.1	2	85.6	
Do.									73.2	
Do.									88.6	
Do.									77.9	

^a Sample kept wet in contact with air for 1½ hours at a temperature of 85° C.

An illustration of the stability of the MnO when the ore had been reduced at a temperature of 850° C. (1,562° F.) and slowly cooled in gas, is the fact that ore so heated during the earlier experiments at Delft, Holland, and since exposed to the air for 1½ years, showed no higher oxides of manganese. The extraction of silver from this ore by cyanide, made directly after reduction, was 97.6 per cent; and a similar test made 1½ years later gave 97.3 per cent. This clearly shows the stability of the reduced MnO under these conditions, and the retention of the silver in a form amenable to cyanidation.

RESULTS AT LOW REDUCTION TEMPERATURES.

At lower temperatures of reduction—for example, 500 to 600° C. (932 to 1,112° F.)—even when the reduced ore is cooled in gas, slow oxidation of the MnO begins on exposure to the air. A sample of Gedang Ilir ore, containing approximately 16 per cent MnO₂, gave the following results under the conditions set forth below (Table 19):

TABLE 19.—*Effect of exposure to air on reduced ore.*

Reduction temperature, °C.	How cooled.	Any higher oxides after reduction?	Ag extracted by KCN, per cent.	First exposure to air, hours.	Any higher oxides after exposure? Per cent MnO ₂ .	Ag extracted by KCN, per cent.	Second exposure to air, hours.	Any increase in MnO ₂ ? Per cent.	Ag extracted by KCN, per cent.
500.....	In gas...	None.	95.8	195	0.87	92.7			
600.....	do.....			69	None.	98.15	427	0.863	96.6
700.....	do.....			70	None.	97.4	426	None.	95.5
800.....	do.....			72	None.	96.9	414	None.	95.9
900.....	do.....			87	None.	95.5	429	None.	95.6

RESULTS AT HIGH REDUCTION TEMPERATURES.

Consideration of these results indicates that at the higher temperatures of reduction, the initial recovery of silver is somewhat lower, but the MnO formed is more stable, and therefore recovery of silver is affected less by exposure to the air. These results also indicate that the best recovery is obtained when the ore is reduced at 600° C. (1,112° F.) and cyanided at once without undue exposure to the air. In actual practice, therefore, it is clearly evident that with regard to fuel economy and silver recovery it is desirable to carry on the reduction at a temperature of 600 to 700° C. (1,112 to 1,292° F.), and grind and cyanide the ore as rapidly as possible. For results of experiments on these points see Table 20.

TABLE 20.—Effect of temperature of reduction, reoxidation, and period between reduction and cyanidation on silver extraction.

Sample No.	Tem- per- ature of reduc- tion, °C.	Period of reduc- tion, min- utes.	Total Mn content in ore, per cent.	Reoxi- dation to Mn ₂ O ₄ should give an amount of MnO ₂ equal to, per cent—	Time between reduc- tion and treat- ment, hours.	Assay of ore.			Silver recovered, per cent.			MnO ₂ in man- ganite com- pound after 2 hours' milling and 72 hours' agita- tion, per cent.	Remarks.		
						Au.		Ag.	After 2 hours' milling.	Followed by agitation for—					
						Ounces per short metric ton.	Grams per metric ton.			Ounces per short metric ton.	24 hours.			48 hours.	72 hours.
37-a	900	50	10.32	5.44	87	16.8	0.49	3,419	99.5	95.1	95.0	95.3	0.9	After treatment no trace of MnO ₂ could be found by the Bunsen method, while the oxalic acid method showed 0.175 per cent.	
38-a	800	55	10.00	5.27	70	16.8	.49	3,154	91.8	94.9	96.6	96.9	1.01		
39-a	700	50	10.00	5.27	72	14.4	.42	3,130	91.1	94.4	97.0	97.25	1.05		
40-a	600	45	10.18	5.37	69	14.4	.42	3,123	90.8	94.95	97.5	98.0	3.11		
41-a	900	50	10.85	5.72	85	18.0	.53	3,322	96.7	92.7	93.9	94.1	.8		
48-a	500	70	10.44	5.51	0.5	19.2	.56	3,250	94.5	81.3	92.4	95.5	5.10	MnO ₂ in reduced sample before milling, 0.866 per cent.	
37-b	800	35	10.00	5.27	241	16.8	.49	3,154	91.8	(c)	95.8	95.9	.43		
39-b	700	50	10.00	5.27	241	14.4	.42	3,130	91.1	(c)	95.5	96.0	.72		
40-b	600	45	10.18	5.37	255	14.4	.42	3,123	90.8	(c)	96.3	96.8	1.50		
41-b	900	50	10.85	5.72	255	18.0	.53	3,322	96.7	(c)	93.8	93.8	.264		
48-b	500	70	10.44	5.51	195	19.2	.56	3,250	94.5	89.0	90.7	91	92.7	3.1	MnO ₂ in reduced sample before milling, 0.866 per cent.
37-c	900	50	10.32	5.44	429	16.8	.49	3,419	99.5	94.5	95.1	(c)	95.6	.256	
38-c	800	35	10.00	5.27	414	16.8	.49	3,154	91.8	93.6	95.4	(c)	95.9	.51	
39-c	700	50	10.00	5.27	426	14.4	.42	3,130	91.1	93.2	94.5	95.2	95.5	.62	
40-c	600	45	10.18	5.37	427	14.4	.42	3,123	90.8	93.3	95.3	96.4	96.6	1.49	
41-c	900	50	10.85	5.72	427	18.0	.53	3,322	96.7	92.9	95.7	(c)	93.9	.425	MnO ₂ in reduced sample before milling, 0.863 per cent.

^a The ore used was between 2 and 48 mesh in size, the fines having been screened out. All "a" samples agitated in laboratory containing more or less acid fumes. All "b" and "c" samples agitated in outside air.

^b Reduction was started at 500° C. for all samples except No. 41, which was heated to 900° C., cooled to 700°, and reduced at that temperature. Samples reduced at and above 700° C. did not show reoxidation of MnO in the air; the samples reduced at 600° C. and below, however, showed reoxidation even in dry air. All MnO₂ reduced to MnO by the reduction.

^c Not taken.

After treatment no trace of MnO₂ could be found by the Bunsen method, while the oxalic acid method showed 0.175 per cent.

MnO₂ in reduced sample before milling, 0.866 per cent.

MnO₂ in reduced sample before milling, 0.863 per cent.

OXIDATION AT DIFFERENT TEMPERATURES.

During the cyanidation of the finely ground ore pulp, more or less oxidation of the MnO to the higher oxides may take place, depending upon the temperature of reduction, alkalinity of the solution, etc. As illustrating the effect of temperature of reduction on the oxidation of MnO during cyanidation, the following figures are instructive:

After 72 hours agitation with air, the ore reduced at 500° C. (930° F.) contained 3.1 per cent MnO₂; at 600° C. (1,112° F.), 1.49 per cent; at 700° C. (1,472° F.), 0.62 per cent; at 800° C. (1,292° F.), 0.51 per cent; while at 900° C. (1,652° F.) it contained no higher oxides.

CYANIDE TREATMENT.

In dissolving the silver from the reduced ore by cyanide solution, it has been found that much the same conditions as regards cyanide concentration are required as in the treatment of simple silver ores of like grade.

The alkalinity should in general be sufficient to protect the cyanide, but an unduly high alkalinity should be avoided on account of the more rapid oxidation of MnO in the presence of high alkalinity. The reaction involved here appears to be somewhat similar to that involving the formation of "Weldon mud." It will be recalled that in this method of manganese recovery, used in conjunction with earlier processes of making chlorine, the manganese was precipitated from the chloride solution by means of lime in the presence of an excess of air, the air serving to oxidize the manganese to higher oxides, which in turn formed rather loosely linked compounds known as "manganites" with the lime, and possibly part of the manganese. In most of the ores investigated, if the alkalinity of the solution is permitted to rise above 50 points, there is an undue consumption of lime with a corresponding formation of higher oxides of manganese. This may also lead to lower silver recovery, possibly through silver being precipitated as a manganite. It was also observed with one ore that high alkalinity increased the consumption of cyanide. On the other hand, if the alkalinity is permitted to drop much below 20 points, there is an undue loss of cyanide. We found considerable difference in this respect in the various ores with which we experimented, some of them permitting a much higher alkalinity than others.

INTRODUCTION OF AIR.

The importance of an excess of air during the treatment can not be emphasized too strongly. Introduction of air must begin with the grinding and be continued throughout the agitation period. Sufficient oxygen must be supplied to dissolve the metallic silver formed during reduction. On the other hand, as has been pointed

out in connection with the alkalinity, reoxidation of MnO must be avoided as far as possible. In this case, MnO acts as a reducing agent, and the function of the air is to overcome any interference through this cause with the dissolution of the silver. Accordingly, adjustment of alkalinity and air must be made so as to supply the necessary oxygen for dissolution of the silver, without creating the unfavorable conditions that arise when a large proportion of the MnO is oxidized to higher oxides during cyanidation. With reference to the quenched product, it has been found that this, under the same conditions, oxidizes much more rapidly than the slowly cooled and more stable gas-cooled product.

Throughout the tests it has been our experience that the highest ultimate recovery is obtained when the conditions during milling are such, as regards aeration, etc., that the maximum dissolution of silver takes place as soon as possible during treatment.

EFFECT OF THE PRESENCE OF BASE METALS.

When base metals such as copper and zinc are present in manganese-silver ores they generally cause increased consumption of cyanide: and with copper especially it is not unusual for the consumption of cyanide to be increased after reduction. Copper and certain other base metals have been shown to occur as manganites. These are decomposed, like the silver manganite, by reduction which liberates metallic copper, a substance soluble in cyanide solutions, whereas copper in the original form is not soluble to any great extent. In fact, copper in the form of manganite is not soluble in dilute nitric acid.

The presence of antimony may give rise to serious complications. Tests of several ores containing antimony indicate that the extraction of silver and gold may not be improved by reduction and sometimes indeed the extraction has been less than for the original ore, leading to the conclusion that under the influence of heat the antimony contained in the antimonial mineral combines with the silver to form insoluble compounds.

METHOD OF MAKING SMALL-SCALE TESTS.

SPECIAL APPARATUS REQUIRED.

Preliminary reduction of small samples may be accomplished in iron tubes externally heated and arranged so that a reducing gas may be passed through them and over the ore, but we have found the apparatus shown in Plate I to be more satisfactory.

The laboratory gas producer employed for supplying gas for reduction is largely constructed from standard pipe and fittings. The 5-inch pipe body of the producer is surrounded by a thin sheet-iron jacket. The annular space between the pipe and jacket is filled with sand to prevent undue radiation of heat, thereby maintaining the

interior of the producer at a temperature high enough for proper functioning. The fuel is supported on a removable grate, and air under moderate pressure is introduced at the bottom of the producer, at the point indicated, through a suitable connecting pipe. Charcoal, the fuel used, contains enough moisture so that it is not necessary to provide for the introduction of steam, as is the general practice in commercial producers.

The gas holder is made of thin galvanized iron with riveted and soldered joints. It is of the telescopic type and is mounted in a wooden framework.

The reducing drum shown in detail in Plate I is made of cast iron, and is provided with a removable cover. The surfaces of both the drum and cover where they come together are machined in order to make a tight joint. The cover is held in position by bolts which may be tightened with nuts if they are threaded, or if plain bolts are used slots may be cut in the ends into which wedges can be driven to draw the cover down tight on the surface of the drum. Both the trunnions are hollow, and it has been found more satisfactory to make them larger than shown in the drawing and cast them integral with the heads. One hollow trunnion serves to admit the reducing gas, while through the other the thermocouple is passed. The drum may be heated either by a gas or gasoline burner. A 2-inch Carey hydrocarbon burner, employing gasoline as fuel, has been found effective for this purpose. Attention is called to the fact that the gas producer and gas holder are only intended to supply the gas which is used within the reducing drum, the equipment being entirely inadequate to heat the drum.

A pyrometer should be provided for accurately measuring the temperature within the drum. In general, the Leeds and Northrup potentiometer instrument in conjunction with their iron-pipe constantan-wire couple, which requires no protecting tube, has been found to be most satisfactory for this purpose.

The opening in the trunnion through which the couple extends should be large enough to leave a free space of at least one-eighth inch between it and the protecting tube of the pyrometer. When the drum is in operation, the protecting tube of the pyrometer or the pipe of the pipe couple is clamped in a stationary position. The object of the clearance suggested is to permit the drum to rotate freely about the tube without binding, even though the supporting trunnions become somewhat distorted after continued heating, and further to permit the free passage of gases from the interior of the drum. It is advisable to use pyrometric equipment having automatic compensation for cold-junction temperature, thereby avoiding the necessity of making correction for the temperature of the cold junction. The arrangement shown in Plate I is of the millivoltmeter type, but the compensating potentiometer type is more satisfactory.

OPERATING THE EXPERIMENTAL EQUIPMENT.**OPERATING THE GAS PRODUCER.**

This laboratory gas producer works most satisfactorily when charcoal is employed as fuel, as it is readily ignited and kept burning and there are no troublesome by-products to pass over with the gas. The charcoal used should not be too fine nor too coarse; if too fine, it prevents the regular upward flow of the air and gases through the fuel bed, while if too coarse, low-grade gas may result through imperfect contact of the air and partly formed gas with the hot carbon. In general, we have found that charcoal crushed to $1\frac{1}{2}$ inches, with the fines removed by shaking on a one-fourth inch screen, gives good results. Either hard or soft wood charcoal may be used.

In starting the producer, a small amount of charcoal is placed on the grate and is ignited most conveniently by means of a blowtorch introduced through the opening provided for this purpose just above the grate in the side of the producer. After the charcoal is alight the blowtorch is removed, and the opening is closed with a screw plug. The air is then turned on gradually, and more charcoal is added until finally the producer is filled within 12 or 14 inches of the top.

During starting, the valve connected with the gas holder is kept closed, and the valve in a pipe leading to the outside of the room is kept open. The quality of the gas may be judged by the way it burns, a valve and burner being provided for this purpose in the plug at the top of the producer. After the producer appears to be working smoothly, the second valve may be closed, the valve at the test burner opened, and the gas ignited at the burner. If it burns freely with a strong blue flame, it may be regarded as all right. If apparatus for gas analysis is available, the conditions for making a gas corresponding to a good grade of producer gas may be readily ascertained. After the producer is operating properly and making gas of the desired grade, the valve connected with the reducing drum should be closed. The valve in the pipe leading from the room should be closed and the valve connected with the gas holder opened. As soon as the holder is filled with gas, this valve is closed and the air is shut off from the producer. A gas holder of the dimensions shown will contain enough gas for two or three tests in the reducing drum. During the filling of the gas holder it is necessary to add enough weight to the counterweights to let the holder rise freely against a moderate gas pressure. When gas is being drawn from the holder, this weight is removed and placed on top, so as to give the desired pressure. Once the gas producer is filled with charcoal it may be operated a number of times, without being cleaned out, by adding charcoal through the plug opening at the top. After the producer has been used several times it is advisable to remove the plug that supports the grate at the bottom of the producer and allow the producer to empty, thereby removing any clinker or ash that may have formed.

OPERATING THE REDUCING DRUM.

A 2-pound sample (1 kilogram, if the metric system is employed) of the ore which has previously been crushed dry to the desired size is introduced into the drum. The cover is tightly clamped in place and the drum placed within the furnace structure with the trunnions resting on the supporting bearings. The drive chain, which is an ordinary bicycle chain having a removable link, is connected. The stationary pipe through which the gas is introduced, and which passes through a stuffing gland at the end of one of the trunnions, is connected to the gas holder by means of rubber tubing. The thermocouple is passed in through the other hollow trunnion so that the end is at the center of the drum. The thermocouple is connected with a galvanometer, which indicates the temperature. Plate I shows the cold junction in a bottle of water fitted with a mercury thermometer for determining cold-junction temperature.

The removable cover of the furnace is closed and the heating burner started. After the drum and contents have reached a temperature of 200 or 300° C. (392 to 572° F.), the valve at the hose cock (Pl. I) is opened to allow a slow stream of gas to pass through the drum. The flow of gas is continued during the heating and as long thereafter as may be necessary to obtain complete reduction. During the earlier stages of reduction the whole of the gas is consumed, but after reduction is complete the gas may be ignited where it issues around the thermocouple protecting tube.

The completion of reduction is judged by the appearance of this flame. The size of flame, when no gas is being utilized for reduction, may be readily ascertained by turning the valve at the hose cock at the beginning of the test to the desired point (this same valve setting being used throughout the test), igniting the gas, and observing the size of the flame. The general practice is to continue the passage of the gas through the reducing drum 5 or 10 minutes after it burns readily with a full flame.

When reduction is complete, the heating flame is turned off, and after it has cooled a short time the top of the furnace is removed and the drum lifted out of the furnace structure and permitted to rest on top of the furnace in free contact with the air in order to hasten cooling. Before the drum is removed the pyrometer is disconnected and the end of the trunnion through which it was introduced is closed by means of a cork or screw cap. The gas is left turned on during the removal and cooling of the drum to insure a reducing atmosphere, also to give a slight outward pressure which prevents any tendency for air to be drawn into the drum through minute cracks. Little gas is consumed in this way. The drum is not opened until the temperature has fallen to a point where the drum can be handled readily—say below 100° C. (212° F.). As soon as the temperature reaches this point the gas may be shut off, the drum opened, and the reduced ore removed.

IMPORTANT FACTORS TO BE DETERMINED BY REDUCING TESTS.**SIZE OF ORE.**

The size of ore varies greatly with different types of ore. With very dense ores, 10 mesh or even finer may be advantageous; while with less dense ores, particles having a maximum size of 2 to 3 inches may be completely reduced. In general, we have found that the most satisfactory size for the reduction of most ores is 1 to 2 inches; but in order to determine the most suitable size of any particular ore it is necessary to run a series of tests on a wide range of sizes.

TEMPERATURE OF REDUCTION.

The reduction temperature is of the greatest importance, as with every ore there is a reduction temperature at which the best extraction of the precious metals results during cyanidation. In general, a temperature of 500 to 700° C. (932 to 1,292° F.) gives the best results, with an average of about 600° C. (1,112° F.). With certain ores a somewhat higher temperature can be used to advantage. In order to determine the best temperature it is necessary to run a series of tests, beginning at, say, 600° C., and working above and below that point.

PERIOD OF REDUCTION.

After a little experience an operator can judge fairly accurately when reduction is finished by the flame test previously described. All possible data should be obtained on this point during the tests covering size and temperature, since the approximate period of reduction is necessary in designing large-scale equipment. Under normal conditions, and with ores which are not too dense, and, further, which are not extremely high in manganese, the time required for reduction will vary from 20 to 45 minutes.

METHOD OF DETERMINING HIGHER OXIDES OF MANGANESE.

In general, it has been found necessary, in order to attain the highest recovery of silver by cyanidation, to reduce completely the higher oxides of manganese to manganous oxide; therefore methods for determining both qualitatively and quantitatively the higher oxides of manganese are desirable for the control of the reducing operation.

In the absence of sulphides in the ore we have found that the Bunsen method is satisfactory both as a qualitative and quantitative method. It is based upon the principle that when a sample is heated with concentrated hydrochloric acid (c. p.) chlorine is evolved in direct proportion to the amount of higher oxides of manganese present. Manganous oxide does not evolve chlorine under these conditions. The apparatus used for this test is simple, and consists of a flat-bottom flask fitted with a two-hole rubber stopper. Through

one opening of the stopper is passed the stem of a separatory funnel, through which the hydrochloric acid is introduced, and through the other opening a small glass tube bent at right angles is introduced; and connected to this is a short piece of rubber tubing, which in turn connects with a piece of glass tubing.

A 5 to 10 gram sample is introduced into the flask, and the glass stopcock of the separatory funnel is opened and 40 to 50 c. c. of the acid is allowed to flow into the flask. After the stopcock is closed the flask is placed over a burner and the contents heated until all action ceases. Chlorine is evolved if there are higher oxides present. Since it is difficult to distinguish between HCl vapor and Cl by the odor, especially where the two are together, the glass tube is introduced into a beaker containing a 10 per cent solution of KI through which the gases are caused to bubble. The qualitative test is generally used. The presence of higher oxides, even in small quantities, is indicated by the colorless KI solution becoming brown through liberated iodine, the depth of tint increasing with greater proportion of higher oxides. If the solution remains perfectly clear, or nearly so, it may be safely assumed that there are no higher oxides remaining. This test is very delicate.

When this test is used as a quantitative method, a weighed quantity of ore is taken and the amount of iodine liberated is determined by titration with a standard solution of sodium thiosulphate, and from the amount of iodine so found the percentage of higher oxides of manganese may be readily calculated.

APPARATUS FOR CYANIDE TESTS.

In addition to the special equipment previously described for conducting the reducing tests, apparatus is required for making small-scale cyanide tests of the reduced ore. Standard laboratory grinding equipment is all that is required for preliminary preparation of the ore.

We recommend that the fine grinding be done in cyanide solution with a porcelain pebble mill.

In the treatment of reduced ores it has been found advantageous to use rather more air during agitation than is required for ores which have not been reduced. Small Pachuca agitators meet this requirement; or if mechanical stirring is used, a small jet of air should be introduced through a glass tube extending down into the ore pulp. The principal difficulty in using small agitators is the tendency for the heavier particles of the ore to stick to the tank bottom, thereby introducing an error. The interior of the small agitators should be smooth and easily cleaned, and for this reason glass is preferable. We have found that a convenient form of agitator can be made from a large glass separatory funnel fitted

with a two-hole rubber stopper, a glass tube passing through one hole to the bottom of the bowl of the funnel. Through the other hole is a short glass tube which is just flush with the bottom of the stopper. The tube is connected to an ordinary laboratory filter pump, or other source of exhaust. If suction is not available, this same agitator can be operated with compressed air by reversing the connections—that is, connecting the tube which extends to the bottom of the bowl with the compressed air, using the other tube as a vent. Ordinary bottle tests have proved satisfactory with ores low in manganese. If closed bottles are used, it is advisable to open them several times during the agitation. In addition to the agitators, large Buchner funnels are required; also filtering flasks and exhausting apparatus for filtering and washing the ore pulp after treatment. Equipment for assaying gold and silver in the various samples is also necessary.

MAKING CYANIDE TESTS.

If a 2-pound sample is used for reduction, enough material will remain after the head sample is separated from the reduced ore to allow a 1½-pound sample to be used for the cyanide tests. This is ground dry to 50 mesh, either with a disk pulverizer or on the bucking board.

The 50-mesh sample is placed in the porcelain jar mill with the estimated quantity of lime, cyanide, and water required for a dilution of about 1½ to 1. The lime should be adjusted to approximately 20 points of alkalinity in the solution. (In the system which we use for recording alkalinity, 100 points corresponds to a saturated solution of lime in water at ordinary temperatures.)

The strength of the cyanide solution is one of the variables to be determined; but generally speaking, in making preliminary tests we have found that a solution containing about 0.2 per cent of NaCN gives good results on most silver ores. We also generally use, as indicated above, a 1½ to 1 dilution during grinding. Periods of 24, 48, and 72 hours indicate the time required for agitation. It is not necessary to run separate samples for each of these periods of agitation, as with a 1½-pound ore sample there is sufficient pulp to permit small samples being taken for assay at the end of 24 and 48 hours, the 72-hour sample being the whole of the remaining pulp and the final sample.

Titration should be made of the cyanide and alkalinity during the period of agitation. With ores consuming much cyanide, it will probably be necessary to add cyanide during agitation. Lime should be added when the alkalinity falls below the limit.

A sizing test of the final sample should be made to determine the proper degree of comminution.

It is our general practice to run the pebble mill on separate samples and for different periods to determine the degree of comminution which each period will give. With most ores, from 1 to 1½ hours is sufficient, provided the mill is not too small.

After grinding is finished the mill is opened and the contents are poured on a granite-ware colander to separate the pebbles from the pulp. The pebbles are then rinsed with a little cyanide solution, the solution thus used being carefully measured in order to give the desired final dilution of 3 to 1 in the agitators. The pulp is then transferred to the agitator for further treatment.

Generally speaking, fine grinding is required for efficient recovery of silver, and manganese-silver ores rendered amenable to treatment by reduction are no exception to this rule.

Cyanide tests carried out as recommended above will check closely with the results obtained in large-scale tests, though both the extraction and cyanide consumption are generally slightly higher. In the earlier stages of an investigation it is desirable to devote most of the effort to ascertaining the conditions of reduction, and after these data are secured refinements of cyanide treatment, which may mean somewhat greater economy in cyanidation, may be studied. The principal factors to be determined concerning cyanidation are: 1, Degree of comminution necessary; 2, time of agitation; 3, strength of cyanide solution; and 4, alkalinity.

These notes, in so far as they apply to cyanide tests, are merely intended to be suggestive, since it is assumed that most operators are thoroughly familiar with this feature of the work.

DEVELOPMENT OF WORKING-SCALE EQUIPMENT FOR OPERATING THE CARON PROCESS.

All of the original experiments carried out at Batavia, Java, Dutch East Indies, in August and September, 1914, and at Delft, Holland, in August to December, 1916, were made either in graphite crucibles or in iron tubes. Twenty tests also were made in iron tubes at Golden, Colo., reducing the ore mostly at 900° C. (1,652° F.), and treating in cyanide solution. Eliminating three special tests, the average recoveries were 92.6 per cent of the gold and 90.5 per cent of the silver. The general procedure was to place the ore in the container, heat to the desired temperature, and then pass through the reducing gas, always taking the precaution to cool the hot ore in a stream of the reducing gas or quench it in water. It was clearly evident that this method could not be elaborated into an efficient large-scale operation; therefore, one of the principal problems of the later investigation was to develop suitable equipment for carrying on reduction and cooling under proper conditions.

As laboratory experiments had shown that carbon dioxide would not oxidize the reduced ore and, furthermore, that a small amount of oxygen in the reducing gases could be tolerated, it seemed probable that reduction could be accomplished in a multiple-hearth furnace of the McDougall type, modified for the purpose. Accordingly, a

small furnace of this type was assembled in the power house of the School of Mines at Golden, Colo., near a gas producer of the West-inghouse type. This producer had a double combustion zone and was equipped with scrubbers for washing the gas. The roasting furnace had only two hearths, and was therefore not particularly well suited for the work contemplated.

The lower hearth of the furnace was connected with the gas producer by means of 4-inch pipe, while the upper hearth was so arranged that additional heat could be supplied if necessary through the medium of an oil burner. Later, two burners were installed on opposite sides of the furnace so that the flame from them came in tangentially to the inner lining. Although it had previously been clearly established that gas was the most desirable fuel—in fact, the only fuel which could be used effectively in the reducing zone—the oil burners on the upper hearth in this experimental unit were necessary on account of the small gas supply available.

Two general methods of operation suggested themselves:

In one method complete combustion of the gas would take place on the upper hearth which would function as a preheating zone, the ore at reaction temperature being passed to the lower hearth where it would meet the incoming stream of reducing gas.

The difficulty with this method was that in order to obtain complete reduction the ore had to be heated in the upper hearth at a temperature far above that giving the best results in order that it would retain enough heat to be completely reduced in passing through the lower hearth. On the whole, this method did not prove satisfactory on account of the time required for reduction and the strong cooling effects of the incoming gas, which required scrubbing to remove tar and other interfering elements. Preheating the gas gave better results but introduced another complication, and furthermore did not prove entirely efficient.

In the second method the multiple-hearth furnace is operated on the principle of progressive combustion with the two-hearth experimental unit, only enough air being admitted to the lower hearth to maintain the required temperature and still keep the gases of the lower hearth strongly reducing. As sufficient air is admitted to the upper hearth to burn the gas completely, this hearth therefore functions as a preheating zone, while the lower hearth would be the reducing zone.

With this method of operation in actual practice, a multiple-hearth furnace would be used in which the ore would be fed counter-current to the ascending gases. The descending ore would first meet the waste gases on the upper hearth and absorb the sensible heat contained therein, and finally be heated to reaction temperature on perhaps the next two hearths. From this point downward

INTERNALLY FIRED REDUCING FURNACE WITH FEEDER ABOVE AT LEFT, AND COOLER AT RIGHT. EXTERNALLY FIRED REDUCING FURNACE, USED FOR EXPERIMENTAL PURPOSES, IN FOREGROUND

in the furnace a more or less constant temperature would be maintained through the properly regulated admission of air to the various hearths; and as the ore passed downward it would meet constantly stronger reducing conditions, finally being discharged from the lower hearth in an atmosphere of producer gas, and from thence into the cooler, where gas would be introduced to prevent reoxidation.

A number of tests were made, as noted elsewhere, operating the two-hearth furnace on this principle; however, it was not as satisfactory as a working furnace having a number of hearths. It was clearly demonstrated that even under these adverse conditions complete reduction of the higher oxides of manganese could be accomplished, provided the ore was heated to a sufficiently high temperature in the upper hearth.

After further investigation it was decided that this new general principle of reduction—namely, passage of the ore through a furnace countercurrent to a stream of gas which might vary from neutral or slightly oxidizing to highly reducing—could be more effectively and efficiently carried out in a special type of rotary furnace. This was proved later by extensive experiments.

Briquetting the ore and reducing the briquets in a large muffle was also tried, but was found to be impracticable on a working scale.

ROTARY FURNACE.

A rotary-kiln type of furnace 32 feet long, having an internal diameter of 10 inches, as shown in Plates II and III, A and B, was designed for operation on the principle of progressive combustion of the gases. In this unit the preheating, reducing, and cooling zones were all made integral. The reducing zone was provided with a bustle pipe for admission of air, to which short connections were made leading into the center of the kiln. Each of these connections was fitted with a valve for close regulation of the air. The lower end of the bustle pipe was connected by means of an elbow to a short length of pipe which extended through the shell of the kiln at the lower part of the reducing zone. This in turn was connected with an air-supply pipe, placed centrally to the cooling zone, which extended through a stuffing box in the side of the discharge hopper. (See Fig. 3.) Connection with this pipe was made through the medium of a rotating sleeve in the form of a stuffing box to a stationary air-supply pipe outside of the kiln. The lower end of the kiln passed into a stationary hopper, the connection with which was made gas-tight by means of a large stuffing box. This hopper was provided at the bottom with a slide for intermittent removal of the reduced ore. The gas supply was connected with the top of the hopper by means of a 4-inch pipe running to the gas producer. The preheating and reducing zones of the kiln were

lined with 3 inches of a mixture of Portland cement and crushed fire brick. The cooling end of the kiln was made from an unlined 10-inch water pipe. A water spray was arranged to play on this part of the kiln if necessary. The outside of the kiln, throughout the pre-heating and reducing zones, was insulated by a 2-inch layer of asbestos boiler covering to prevent heat losses. The whole kiln was mounted on two large steel channels and set at an inclination of three-fourths inch per foot. Provision was made for varying the speed of the kiln by a number of pulley changes on the driving shaft. The drive end of the kiln and ore bin and feeder are shown in Plate IV, A.

FIGURE 3.—Details of discharge end of cooler.

In the earlier experiments with this kiln a single-unit Riché gas producer was used. It was found that this was not sufficiently large to raise the temperature of the kiln to the desired point. This producer is not recommended for regular practice, but was constructed to ascertain its probable value for use in Sumatra, where wood only is available as fuel. After investigation it was abandoned as not being suited even to the peculiar conditions existing in that country. A small coal gas-producer, shown in Plate IV, B, was improvised from such equipment as was at hand, and this proved very satisfactory throughout all the tests. The use of coke in this producer instead of coal proved advantageous because the producer was of the up-draft type, and satisfactory scrubbing arrangements were not available for cleaning the gas when coal was used.

4. PLAN OF INTERNALLY FIRED REDUCING FURNACE AND ACCESSORIES

B. ELEVATION OF INTERNALLY FIRED REDUCING FURNACE, FEEDER, AND COOLER

During the first trial of the furnace with producer gas it was found that the temperature at the first air inlet was not high enough to keep the gases ignited. The Riché gas, high in hydrogen and carbon monoxide and containing little nitrogen, did not occasion this trouble but with the lean producer gas it was found necessary to equip the first air inlet of the kiln with a burner. The complication of an external gas supply to the burner was overcome by so constructing it that the gas was drawn into the mixing tube from the body of the kiln by the air current which was controlled from the outside of the kiln by a valve. The preheating and reducing zones of the kiln were provided with base-metal thermocouples placed 43 inches apart for the proper control of the temperature. These couples extended into the kiln beyond the inner lining for a distance of $1\frac{1}{2}$ inches. The reducing zone of the kiln was also provided with $1\frac{1}{2}$ -inch openings, closed with pipe caps at intervals of 43 inches, which were used for inspection and for withdrawing samples of ore at various points in the zone of reduction.

OPERATION OF FURNACE.

In operating the experimental furnace the producer is first started and the gas is discharged into the atmosphere until the producer is working smoothly and making high-grade gas. The gas is then turned into the furnace, and after all the air has been displaced it is ignited at the upper end of the furnace. After proper regulation of the air the burner is lighted through one of the inspection openings. When the burner is first lighted a slight explosion may take place, but this is not dangerous, because the whole upper end of the furnace is open. After the burner is working properly air is admitted through the other valves in carefully regulated quantities to give the desired temperature throughout the reducing zone. As soon as this zone has reached a uniform temperature the ore feeder is started. During the earlier stages it is necessary to measure the temperature frequently until the gas and air supply has been properly adjusted to the rate of ore feed. After this little attention is required, but it has been our general practice to make temperature measurements at intervals of about one hour. As the ore passes forward in the kiln, and until all adjustments have been made, frequent samples are taken to ascertain the completeness of reduction. After proper regulation it is only necessary to take occasional samples from the discharge end of the kiln in order to be sure that reduction is complete.

EXTERNALLY HEATED FURNACE.

For the purpose of comparison, an externally heated rotary-kiln type of furnace was constructed. It consisted of a length of 10-inch pipe mounted on suitable rollers, and connected with a cooler. The

furnace, throughout its length, with exception of the cooler, was surrounded by a fire-brick arch, which in turn was connected to two fire boxes. (See Pl. II, p. 56.) Lignite was used for heating the furnace. The ore was fed at the head end and discharged from the cooler, as in the internally fired furnace. Producer gas was introduced at the lower end of the kiln through an arrangement similar to that used with the internally heated furnace. A number of tests were made both on the Sumatra and Buffalo-Hunter (Colorado) ores,

FIGURE 4.—Flow sheet of experimental plant at Colorado Springs, Colo.

employing Riché gas, since the other producer was not completed at the time these experiments were made. On the whole, good results were obtained, but it is obvious that a furnace of this type can not be operated as efficiently on a large scale as an internally heated furnace; and, furthermore, in large sizes it would present rather difficult problems of construction. However, it proved satisfactory for making comparisons with the performance of the other unit. Figure 4 shows the flow sheet of the experimental plant at Colorado Springs, while Plate V shows the cyanide plant.

A. UPPER END OF INTERNALLY FIRED REDUCING KILN, SHOWING DISK FEEDER

B. GAS PRODUCER AND BLOWER

EXPERIMENTAL CYANIDE PLANT

APPLICATION OF THE CARON PROCESS TO ORE FROM THE GEDANG ILIR MINE, SUMATRA.

The Gedang Ilir mine, owned and operated by the Netherlands East Indies Government, is situated in the Province of Benkoelen, Island of Sumatra. The vein mined has a known length of approximately 1 mile, and varies in width from a few inches to 45 feet. The silver content is from a few grams up to 20,000 grams per metric ton. The ratio of silver to gold ranges from 30 to 1 up to 200 to 1. The manganese content of the ore body so far opened is chiefly present as dioxide and the content ranges from 2 to 25 per cent MnO_2 . The ratio of manganese dioxide to silver is in general the same in all the products resulting from screening or concentration of the same sample, but this ratio varies widely in samples from different parts of the mine.

Direct cyanidation of ore containing 2 to 10 per cent MnO_2 recovered approximately 50 per cent of the silver, whereas with ore containing a higher percentage, up to 25 per cent of MnO_2 , the recovery was only about 25 per cent. It will be noted that this is a typical manganese-silver ore, and is therefore not only refractory to cyanide treatment but to all other forms of treatment generally applied to silver ores. The refractory ore is known to extend to a depth of at least 300 feet. Three typical analyses of the ores are shown in Table 21.

TABLE 21.—*Analyses of ores from the Gedang Ilir mine.*

Moisture.....	per cent..	2. 01	1. 80	1. 56
Fe_2O_3	do....	1. 49	1. 04	0. 62
MnO_2	do....	18. 93	15. 55	4. 47
MnO	do....	1. 40	1. 43	0. 25
SiO_2	do....	67. 60	73. 75	87. 50
S.....	do....	0. 0011	0. 00098	0. 000068
Al_2O_3	do....	2. 60	2. 92	1. 90
CaO.....	do....	0. 20	0. 68	0. 69
Insoluble.....	do....	3. 15	2. 0	2. 4
Au.....	grams per ton..	8. 4	22. 80	11. 20
Au.....	ounces per ton..	0. 24	0. 66	0. 32
Ag.....	grams per ton..	311. 0	3, 177. 0	350. 0
Ag.....	ounces per ton..	9. 1	92. 4	10. 2

The characteristic vein minerals are quartz—which is frequently pseudomorphic after calcite—limonite, wad, and kaolin.

When the large oxidized ore body was developed a few pockets of unoxidized ore were found, in which the silver is present chiefly as argentite, carrying some copper. Small-scale experiments indicate that the argentite is amenable to direct cyanidation. It is, therefore, to be expected that when the oxidized part has been mined all the ore below the zone of oxidation will be amenable to direct treatment. Adular (potassium-aluminum silicate) and richterite (sodium-magnesium-manganese amphibole) with quartz are the characteristic vein minerals of the unoxidized ore.

Metric weights are used in Tables 22 to 29, inclusive, covering tests of Gedang Ilir ore from Sumatra, and in Table 30, covering tests of El Favor ore from Mexico. English weights are used in Table 31, covering tests of Elkoro ore from Nevada, and in Tables 32 to 37, covering tests of Buffalo-Hunter ore from Colorado.

TABLE 22.—Data on reduction test No. 9 of low-grade silver and manganese ore in externally heated rotary furnace.
Milling.

Run.	Time, hours.	Ore, kilograms.	Mill charge.				Tail solution.		Heads.		Tails.				Extraction.		Remarks.					
			Dry ore, kilograms.	Water, kilograms.	NaCN, grams.	Lime, grams.	NaCN, per cent.	Alkalinity, points.	Grams.	Ounces.	Grams.	Ounces.	Au.	Grams.	Ounces.	Ag.		Ounces.	Au, per cent.	Ag, per cent.		
1	2	First 35.6...	35.6	36	42	70	0.014		7.8	0.23	325	9.47	1.6	0.046	77	2.3	No MnO ₂ in ore before milling. Mixed charge, degree of comminution, (Tyler standard screens used): +100, 0.25 per cent; +150, 3.30 per cent; +200, 6.40 per cent; -200, 90.05 per cent.	76.3				
2	2	Next 37.1....	37.1	33	42	70	.052		7.8	.23	325	9.47	.8	.023	84	2.5		74.2				
Pilot Test.																						
1	4		Gms. C.c. P. at. Gms.				200	800	0.104	1	0.092	26	7.8	0.23	325	9.47	1.2	0.035	106	3.1	84.6	67.4

Agitation.

Day.	Hour.	Sample num-ber.	Agita-tion, hours.	Solution.		Tails.				Extraction.		Remarks.
				NaCN, per cent.	Alka-linity, points.	Au.		Ag.		Au, per cent.	Ag, per cent.	
						Grams.	Ounces.	Grams.	Ounces.			
July	6 p. m.	1	Started.	0.106	10	0.4	0.012	76	2.3	94.9	76.6	Added 170 grams NaCN and 99 grams lime at 5.30 p. m. Added 113 grams lime at 7.45 p. m.
	7 p. m.	2	1	.100	9	0.2	.006	64	1.8	97.4	80.3	
	8 p. m.	3	2	.096	22	Trace.	Trace.	66	1.9	99.0	79.7	
	9 p. m.	4	3	.096	20	Trace.	Trace.	62	1.8	99.0	80.9	
	10 p. m.	5	4	.095	20	Trace.	Trace.	56	1.6	99.0	82.8	
	11 p. m.	6	5	.094	18	Trace.	Trace.	53	1.5	99.0	83.7	
	12 p. m.	7	6	.092	17	Trace.	Trace.	52	1.4	99.0	84.0	
	6 a. m.	8	12	.124	7	Trace.	Trace.	44	1.2	99.0	86.5	
	9 a. m.	9	15	.122	30	Trace.	Trace.	40	1.1	99.0	87.7	
	12 m.	10	18	.121	26	Trace.	Trace.	38	1.1	99.0	87.7	
	3 p. m.	11	21	.118	9	Trace.	Trace.	36	1.05	99.0	88.3	
	9 p. m.	12	27	.118	10	Trace.	Trace.	35	1.02	99.0	88.9	
	13 p. m.	13	39	.118	13	Trace.	Trace.	34	1.00	99.0	89.2	
	9 a. m.	14	45	.118	12	Trace.	Trace.	33	0.96	99.0	89.5	
	3 p. m.	15	63	.118	12	Trace.	Trace.	32	0.93	99.0	89.8	
5 p. m.	16	71	.118	18	Trace.	Trace.	31		99.0	90.2		
9 a. m.	17	84	.118	8	Trace.	Trace.	37	1.08	99.0	90.5		
3 p. m.	18	48	.040	2	Trace.	Trace.	37	1.08	99.0	88.6		
.....do.		2	72	.012	28	Trace.	Trace.	37	1.08	99.0	88.6	

Samples from Large Agitator. Treated in Small Pilot Agitator.

July	12	6 p. m.		1	24	0.06	4	Trace.	Trace.	53	1.5	99.0	83.7	Without lead acetate.
	13	4 p. m.		46	.074	5	Trace.	Trace.	47	1.4	99.0	85.5		
	13	6 p. m.		72	.02	14	Trace.	Trace.	46	1.3	99.0	85.8		
	12	do.	2	24	.072	1	Trace.	Trace.	39	1.1	99.0	88.0	Added 0.125 kg. of lead acetate per ton of solution.	
	13	4 p. m.		46	.048	5	Trace.	Trace.	36	1.05	99.0	88.9	Do.	
	14	6 p. m.		72	.02	16	Trace.	Trace.	36	1.05	99.0	88.9	Do.	

NOTE.—Riché gas was used for reduction in this test. Total consumption of NaCN on big scale test was 0.98 kg. per metric ton, and lime consumption was 4.15 kg. per ton.

TABLE 23.—Data on reduction test No. 10 in externally heated rotary furnace (27 kilograms per hour).

Milling.

Run.	Time, hours.	Mill charge.				Tail solution.	Heads.				Tails.				Extraction.		Remarks.	
		Dry ore, kilograms.	Water, kilograms.	NaCN, grams.	Lime, grams.		NaCN, per cent.	Alkalinity, points.	Au.	Ag.	Grams.	Ounces.	Au.	Ag.	Grams.	Ounces.		Au, per cent.
1	3	43.7	45	42	255	0.028	2	11.6	0.34	362	10.5	2.0	0.06	101	2.9	82.8	72.1	No MnO ₂ in ore before milling. 28 grams NaCN and 57 grams lime added after milling. Degrees of comminution of mixed charge (Tyler standard screen used): +200, 0.02 per cent; +150, 0.40 per cent; +200, 2.30 per cent; —200, 97.28 per cent.
2	3	38.1	45	42	255	.036	2	11.6	.34	362	10.5	2.0	.06	88	2.6	82.8	75.7	

Agitation.^a

Date.	Hour.	Sample number.	Agitation hours.	Solution.		Tails.		Extraction.		Remarks.
				NaCN, per cent.	Alkalinity, points.	Au.	Ag.	Au, per cent.	Ag, per cent.	
Aug.	5 9 p. m.	1	Start.	0.026	4	0.6	0.018	80	2.3	111 grams NaCN and 113 grams lime added. 28 grams lime added. Do. 42 grams lime added. MnO ₂ , 0.45 per cent.
	5 10 p. m.	2	1	.084	14	.6	.018	71	2.1	
	6 9 a. m.	3	12	.084	6	.4	.012	57	1.7	
	6 3 p. m.	4	18	.082	6	.2	.006	51	1.5	
	6 7.30 p. m.	5	22.5	.082	6	.2	.006	48	1.4	
	7 8.30 a. m.	6	35.5	.076	5	.2	.006	44	1.3	
	7 4 p. m.	7	43.0	.074	9	.2	.006	42	1.3	
	8 8.30 a. m.	8	59.5	.068	4	.2	.006	44	1.2	

^a 245 kilograms of water added to dry charge for agitation, which gives a dilution of ± 1.3 .

TABLE 24.—Data on reduction test No. 10 (a) in externally heated rotary furnace (41 kilograms per hour.)

Milling.

Run.	Time, hours.	Mill charge.			Tail solution.		Heads.		Tails.			Extraction.		Remarks.
		Dry ore, kilo-grams.	Water, kilo-grams.	NaCN, kilo-grams.	Lime, grams.	NaCN, per cent.	Alkali, points.	Au.	Ag.	Au.	Ag.	Au, per cent.	Ag, per cent.	
								Grams.	Ounces.	Grams.	Ounces.			
1	3	27.8	34	28	84	0.025		9.4	0.27	331.0	9.6	2.0	96.0	71.0
2	3	27.4	34	28	84	.028		9.4	.27	331.0	9.6	1.6	77.0	76.7

No MnO₂ in ore before milling. 112 grams lead acetate added.
Do. a

Agitation.

Day.	Hour.	Sample number.	Agitation, hours.	Solution.		Tails.		Extraction.		Remarks.
				NaCN, per cent.	Alkali, points.	Au.	Ag.	Au, per cent.	Ag, per cent.	
						Grams.	Ounces.	Grams.	Ounces.	
July 31	4 p. m.	1	Start.	0.028		1.2	0.035	87.0	2.5	73.7
31	5 p. m.	2	1	.09	2	.8	.024	73.0	2.1	91.5
31	6 p. m.	3	2	.086	2	.2	.006	72.0	2.1	97.9
31	7 p. m.	4	3	.088	3	.1	.003	65.0	1.9	98.9
31	8 p. m.	5	4	.084	5	.1	.003	60.0	1.8	98.9
31	9 p. m.	6	5	.086	14	.1	.003	58.0	1.7	98.9
Aug. 31	7 a. m.	7	15.5	.084	8	Trace.	Trace.	41.0	1.2	99.0
1	9 a. m.	8	17	.086	8	Trace.	Trace.	41.0	1.2	99.0
1	3 p. m.	9	23	.084	6	Trace.	Trace.	39.0	1.1	99.0
1	8 p. m.	10	28	.084	6	Trace.	Trace.	36.0	1.02	99.0
2	9 a. m.	11	41	.074	5	Trace.	Trace.	33.0	.96	99.0
2	3 p. m.	12	47	.070	5	Trace.	Trace.	33.0	.96	99.0
3	8 a. m.	13	64			Trace.	Trace.	30.0	.88	99.0

42 grams lime added and 3 ounces NaCN.
Do.
Do.
Do.
Do.

0.5 per cent MnO₂.

a Degree of comminution of mixed charge (Tyler standard screens used): +100, 0.1 per cent; +150, 0.2 per cent; +200, 1.5 per cent; —200, 98.2 per cent.
b 350 pounds of water added to dry charge for agitation, which gives a dilution of $\pm 1:3$.

TABLE 25.—Data on reduction test No. 11.

[Sample A, Sumatra ore. Passed through 2 mesh. Externally heated furnace and Riché gas used. Furnace speed, 0.64 r. p. m. Temperature was maintained between 580 and 650° C. Feed of 21, 36, and 64 kilograms per hour. The ore was perfectly reduced throughout the test, and after reduction it was crushed to about 6 mesh and then milled in cyanide solution.]

Milling.

Period.			Mill charge.				Tail solution.		Heads.		Tails.		Ex-trac-tion.	Remarks.
Day.	Hour.	Dura-tion, hours.	Ore, kilo-grams.	Water, kilo-grams.	NaCN, grams.	Lime, grams.	NaCN, per cent.	CaO, points.	NaCN.	CaO.	Ag, grams.	Ag, ounces.		
Aug. 23	10 a. m.	2½	68	68	113	652	0.092	9	1.17	1.08	273	7.95	72.0	Diluted 3:1. 142 grams NaCN+113 grams lime added. Do. Do. Do.
23	1 p. m.	2	68	68	113	652	.090	7	1.18	1.11	255	7.43	71.2	
23	3.20 p. m.	2	68	68	113	652	.098	12	1.11	1.04	255	7.43	69.0	
23	5.30 p. m.	2	63.5	63.5	113	652	Lost.				Lost.			
											a 239.5	a 7.5		

Agitation.

Sam-ple No.	Period.		Solution.		Chemicals added.		Consumption, kilograms per metric ton.		Tails.		Ex-trac-tion.	Remarks.
	Day.	Hour.	NaCN, per cent.	CaO, points.	NaCN, grams.	CaO, grams.	NaCN.	CaO.	Ag, grams.	Ag, ounces.		
1	Aug. 23	8 p. m.					1.18	2.04	66.0	1.83	74.6	Sizing test (I. M. M. screens): +100, 2 per cent; -100+150, 4.5 per cent; -150+200, 2.5 per cent; -200, 91.0 per cent. Agitation stopped 8.30 a. m. August 27, 1918. 2.15 per cent MnO ₂ . Sample taken from settled pulp. 2.30 per cent MnO. Sample taken from discharge pulp.
2	Aug. 24	8 a. m.	0.086	10	142	226	1.58	2.89	40.0	1.17	84.6	
3	do.	12 m.	.090	4	113	226	1.64	3.19	38.8	1.13	85.0	
4	do.	4 p. m.	.102	12			1.64	3.31	43.0	1.25	85.4	
5	Aug. 25	8 a. m.	.100	9			1.70	3.99	34.4	1.00	86.7	
6	do.	5 p. m.	.100	7			1.70	4.47	26.5(?)	.77	89.8	
7	Aug. 26	4 p. m.	.099	10			1.73	5.10	27.2	.79	89.5	
8	do.	8 a. m.	.100	11			1.70	5.07	28.0	.82	89.2	
9	Aug. 27	8.30 a. m.	.098	30			1.76		24.0	.70	90.7	
10	do.	4 p. m.							22.6	.65	91.3	
11	do.	do.							20.8	.62	92.0	

a Average.

NOTE.—Mill leaked during fourth run.

Lime used contained 72 per cent available CaO.

TABLE 26.—Data on reduction test No. 12.

[Sample "A," Sumatra ore. Passed through 2-mesh screen before reduction. Internally heated furnace and producer gas used. Furnace speed, 0.52 r. p. m. Temperature, between 540 and 600° C. Feed 21 and 29 kilograms per hour. The ore was completely reduced throughout the test.]

Milling.

Period.		Mill charge.					Tail solution.		Consumption, kilo-grams per ton.		Heads.		Tails.				Extraction.	Remarks.
		Ore, kilo-grams.	Water, kilo-grams.	NaCN, grams.	Lime, grams.	NaCN, per cent.	CaO, points.	NaCN.	CaO.	Au.		Ag.		Au.		Ag.		
Day.	Hour.									Duration, hours.	Grams.	Ounces.	Grams.	Ounces.	Grams.	Ounces.	Grams.	Ounces.
Sept. 20	8.30 a. m....	3	68	113	113	0.055	None.	1.16	1.16	7.2	0.210	300	8.74	118	3.44	72.2	60.6	Diluted 3 to 1; added 142 grams NaCN and 113 grams lime.
20	12 m.	3	72.5	113	113	0.030	3	1.34	1.05	4.8	.140	250	7.28	185	5.39	41.6	26.0	
								a 6.0	a 0.175	a 276	a 8.1	a 2.4	a 0.070	a 153	a 4.5	a 60.0	a 44.6	

Diluted 3 to 1; added 142 grams NaCN and 113 grams lime.

Agitation.

Sam- ple No.	Period.		Solution.		Chemicals added.		Consumption, kilograms per ton.		Tails.			Extraction.		Remarks.		
									Au.	Ag.		Au, per cent.	Ag, per cent.			
	Grams.	Ounces.	Grams.	Ounces.												
					NaCN.	CaO.										
.....	Sept. 20	3.30 p. m.	2	0.028	4	283	113	2.79	1.46	2.4	0.070	134.0	3.90	60.0	51.4	Agitation stopped Sample for detailed pulp. Staining test (M. M. screens) +150, 1.6 per cent; -150+200, 1.8 per cent; -200, 96.6 per cent.
.....	Sept. 21	9 a. m.	10½	.060	13	113	226	3.84	2.14	.6	.018	58.0	1.67	90.0	79.0	
.....	do	3.30 p. m.	26	.080	12	113	113	4.05	2.98	.8	.004	54.8	1.59	86.7	80.1	
.....	Sept. 22	9 a. m.	43½	.070	2	142	113	4.80	3.59	.2	Trace.	40.5	1.17	96.7	85.2	
.....	Sept. 23	8 a. m.	66½	.092	2		113	4.80	3.57	.2	Trace.	21.2	.79	99.1	90.1	
.....	do	2.30 p. m.	73	.088	8			4.82	3.19	Trace.	Trace.	31.4	.91	99.1	88.6	
.....	Sept. 24	10 a. m.	92½	.069	4		113	5.38	4.35	Trace.	Trace.	20.6	.77	99.1	88.6	
.....	do	3.30 p. m.	98	.065	9			5.50	4.72	Trace.	Trace.	27.6	.81	99.1	90.0	
.....	Sept. 25	1.30 p. m.								Trace.	Trace.	26.0	.76	99.1	90.6	

Agitation stopped.
Sample from settled pulp. Sizing test
(1. M. screens) +150, 1.6 per cent;
-150+200, 1.8 per cent; -200, 96.6 per cent.

^a Average.

^b Lime used contained about 70 per cent available CaO.

TABLE 27.—Data on reduction test No. 19.

[Sample "C," Sumatra ore. Passed through $\frac{3}{4}$ -inch screen before reduction. Internally heated furnace and producer gas used. Temperature maintained, between 550 and 590° C. A furnace speed of 0.52 r. p. m. and a feed of 45 kilograms per hour were employed during the first 8 hours of the test, then increased to 0.86 r. p. m. and 63 pounds, respectively, for the following 4 hours. The ore was completely reduced throughout the test, and the reduced ore was crushed to about 4 mesh before milling.]

Milling.

Period.		Mill charge.				Tail solution.		Consump- tion, kilo- grams per ton.		Heads.				Tails.				Extraction.		Remarks.
Day.	Hour.	Dur- ation, hours.	Ore, kilo- grams.	Water, kilo- grams.	NaCN, grams.	Lime, grams.	NaCN, per cent.	CaO, points.	NaCN.	CaO.	Grams.	Ounces.	Ag.	Grams.	Ounces.	Ag.	Grams.	Au, per cent.	Ag, per cent.	
1918. Oct.	8 8.30 a. m....	2	68.0	68.0	113	452	0.098	48	0.68	4.03	7.6	0.22	359	10.5	3.0	0.09	132	60.5	63.2	Diluted 3 to 1, 142 grams NaCN added.
8	11 a. m....	2	79.3	79.3	142	452	.092	41	.87	3.46	7.2	.21	364	10.6	1.2	.04	119	83.3	67.3	Do.
8	1.15 p. m....	2	79.3	79.3	142	452	.084	49	.95	3.34	7.2	.21	364	10.6	2.2	.06	108	69.4	67.3	Do.
8	3.40 p. m....	2	79.3	79.3	142	452	.082	51	.97	3.32	7.2	.21	364	10.6	1.4	.04	107	80.5	70.6	Do.
8	6 p. m.....	2	84.0	84.0	170	452	.114	46	.88	3.17	7.2	.21	364	10.6	1.4	.04	117	80.5	67.8	Do.
									a. 87	a 3.45	a 7.28	a 0.21	a 363	a 10.6	a 1.81	a 0.05	a 114	a 75.1	a 68.6	

Agitation.

Sam- ple No.	Period.		Solution.		Chemicals added, kilo- grams per ton.		Consumption, kilograms per ton.		Tails.				Extraction.		Remarks.
									NaCN, per cent.	CaO, points.	NaCN.	CaO.	Au.		
	Agita- tion, hours.	Day.	Hour.	Grams.	Ounces.	Grams.	Ounces.								
1	Oct. 8	8.25 p. m.	5	0.086	20	169	1.06	3.27	1.0	0.029	91	2.7	86.3	74.9	Sizing test (I. M. M. screens) +100, 1.9 per cent; -100+150, 7.0 per cent; -150+200, 7.3 per cent; -200, 83.8 per cent.
2	Oct. 9	8 a. m.	17	.091	16	85	1.35	3.42	.4	.012	72	2.1	94.5	80.1	
3	do.	12 m.	21	.098	14		1.36	3.50	.4	.012	66	1.9	94.5	81.8	
4	do.	4 p. m.	25	.098	14		1.36	3.50	.6	.013	57	1.7	91.8	84.3	
5	Oct. 10	8 a. m.	41	.095	11		1.44	3.63	.6	.013	51	1.4	91.8	85.9	
6	do.	12 m.	45	.095	9		1.44	3.70	.4	.012	57	1.7	94.5	84.3	
7	do.	4 p. m.	49	.095	9		1.44	3.70	.4	.012	57	1.7	94.5	84.3	
8	Oct. 11	8 a. m.	65	.095	11		1.44	4.03	.4	.012	52	1.5	94.5	85.7	
9	do.	12 m.	69	.095	9		1.44	4.11	.4	.012	49	1.4	94.5	86.5	
10	do.	4 p. m.	73	.094	16		1.47	4.25	.4	.012	46	1.3	94.5	87.3	Agitation stopped. Sample from settled pulp.
11	do.	8 a. m.	89	.094	12		1.47	4.40	.4	.012	43	1.2	94.5	88.1	
12	Oct. 12	11 a. m.	92	.094	11		1.47	4.45	.4	.012	43	1.2	94.5	88.1	
13	do.	4 p. m.	97	.092	10		1.53	4.48	.4	.012	43	1.2	94.5	88.1	
14	Oct. 13	10 a. m.		.089	8		1.72	4.56	.4	.012	41	1.19	94.5	88.7	

^a Average.

NOTE.— Lime used contained about 70 per cent available CaO.

TABLE 28.—Data on reduction test No. 14.^a

[Sample "B", Sumatra ore. Passed through 4-inch screen before reduction. Internally heated furnace and producer gas used. Temperature maintained between 550 and 630° C. Furnace speed, 0.52 r. p. m. Feed, 41 kilograms per hour. A furnace speed of 0.86 r. p. m. was tried, but was found too high, as the ore was incompletely reduced. The ore was completely reduced at the lower speed, and was crushed to about 10 mesh before milling.]

Milling.

Day.	Period.	Mill charge.				Tail solution.		Consump- tion, kilo- grams per ton.		Heads.				Tails.				Extraction.		Remarks.
		Ore, kilo- grams.	Water, kilo- grams.	NaCN, grams.	CaO, grams.	NaCN, per cent.	CaO, points.	NaCN.	CaO.	Grams.	Ounces.	Grams.	Ounces.	Grams.	Ounces.	Grams.	Ounces.	Au, per cent.	Ag, per cent.	
Oct. 13	9 a. m.	68	68	567	679	0.178	100	6.55	(?)	28.6	0.83	6,178	180.0	12.4	0.36	1,371	40.0	56.7	77.8	Diluted 3.5 to 1; 85 grams NaCN added.
13	11.30 a. m.	68	68	567	679	.172	110	6.63	(?)	28.6	.83	6,178	180.0	13.6	.40	1,502	43.8	52.5	75.6	Do.
13	2 p. m.	45	45	340	226	.084	42	6.71	4.73	26.1	.76	5,255	182.2	13.0	.38	1,362	39.8	50.2	78.2	Diluted 3.5 to 1.
										628.0	60.82	66,197	6180.7	613.0	60.38	61,418	641.4	653.5	677.2	

Agitation.

Sample No.	Period.		Solution.		Chemicals added.		Consumption.		Tails.				Extraction.		Remarks.	
	Day.	Hour.	Agitation, hours.	NaCN, per cent.	CaO, pounds.	NaCN, grams.	Lime, grams.	NaCN, grams.	Lime, grams.	Au.		Ag.		Au, per cent.		Ag, per cent.
										Grams.	Ounces.	Grams.	Ounces.			
1	Oct. 13	5 p. m.	4	0.062	25	340		6.90	4.98	0.6	0.018	1, 015	29.5	65.7	83.6	MnO ₂ , 3.56 per cent. Agitation stopped. Sample from discharge pulp. Sizing test (1. M. M. screens), +100, 0.3 per cent; -100+150, 1.8 per cent; -150 +200, 2.7 per cent; -200, 95.2 per cent.
2	Oct. 14	8 a. m.	19	.106	19		7.24	5.26	2.8	.08	438	13.3	90.0	92.6		
3	do.....	12 m.	23	.096	16		7.58	5.40	2.0	.06	429	12.5	92.9	93.1		
4	do.....	4 p. m.	27	.086	15		7.94	5.44	2.0	.06	409	11.9	92.9	93.4		
5(4a)	do.....	4.30 p. m.	27½	.086	21		7.94	6.04	1.4	.04	313	9.1	95.0	94.9		
5	Oct. 15	8 a. m.	43	.084	28		453	8.00	7.47							
6	do.....	12 m.	47	.084	41			8.00	8.62	1.2	.035	330	9.6	95.7	94.7	
7	do.....	4 p. m.	51	.080	39	113	453	8.14	8.71	1.0	.029	324	9.4	96.4	94.8	
8	Oct. 16	8 a. m.	67	.102	47			8.00	10.12	8	.024	292	8.5	97.1	95.3	
9	do.....	12 m.	71	.102	45			8.00	10.18	8	.024	300	8.7	97.1	95.2	
10	do.....	4 p. m.	75	.102	43			8.00	10.28	8	.024	282	8.2	97.1	95.5	
11	Oct. 17	8 a. m.	91	.101	37			8.03	10.57	8	.024	238	6.9	97.1	96.2	
12	do.....	12 m.	95	.101	37			8.03	10.57	8	.024	271	7.9	97.1	95.6	
13	do.....	4 p. m.	99	.101	35			8.03	10.65	4	.012	264	7.6	98.6	95.7	
14	do.....									4	.012	247	7.2	98.6	96.0	

^a MnO₂ in head sample, 20.9 per cent; Mn, 13.2 per cent. Lime used contained about 70 per cent available CaO.

^b Average.

TABLE 29.—Data on reduction test No. 15.

Sample "A", Sumatra ore. Passed through $\frac{3}{4}$ -inch mesh before reduction. Internally heated furnace and producer gas used. Temperature maintained between 640 and 680° C. Furnace speed, 0.52 r. p. m. Feed, 45 kilograms per hour. The ore was completely reduced throughout the test, and was crushed to about 10 mesh before milling.]

Milling.

Day.	Period.	Mill charge.				Tail solution.		Consumption, kilograms per ton.		Heads.				Tails.				Extraction.		Remarks.
		Ore, kilograms.	Solution, kilograms.	NaCN, grams.	CaO, grams.	NaCN, per cent.	CaO, points.	NaCN.	CaO.	Au.	Grams.	Ounces.	Ag.	Grams.	Ounces.	Au.	Grams.	Ag.	Ounces.	
Oct. 23	8 a. m.	68	68	85	679	0.062	97	1.41		9.2	0.27	1,167	34.0	5.0	0.15	332	9.7	34.8	71.5	Diluted 3 to 1; 56 grams NaCN added.
23	10.15 a. m.	68	68	85	679	.072	91	1.31		9.2	.27	1,167	34.0	5.0	.15	259	7.6	45.7	77.8	Do.
23	12.25 p. m.	68	68	113	679	.091	111	1.53		10.7	.31	1,174	34.2	5.6	.16	260	7.6	47.6	77.9	Do.
23	2.35 p. m. ...	68	68	113	679	.094	115	1.50		10.7	.31	1,174	34.2	4.4	.14	258	7.5	58.8	78.0	Do.
								a1.44		a10.0	a0.29	a1,170	a34.1	a5.3	a0.15	a277	a8.1	a47.0	76.3	

Agitation.

Sam- ple No.	Period.			Solution.		Chemicals added.		Consumption, kilograms per ton.		Tails.			Extraction.		Remarks.
	Day.	Hour.	Agita- tion, hours.	NaCN, per cent.	CaO, points.	NaCN, grams.	Lime, grams.	NaCN.	CaO.	Au.		Ag. Ounces.	Au, per cent.	Ag, per cent.	
										Grams.	Ounces.				
1	Oct. 23	5 p. m.	4	0.107	42	168	340			3.6	0.105	192	5.6	83.6	Agitation stopped. Sample from settled pulp. Sample after barren solution wash. ^b Sizing test: (Tyler standard screens). +100, 0.5 per cent; -100+150, 5.77 per cent; -150+200, 2.5 per cent; -200, 91.2 per cent.
2	Oct. 24	8 a. m.	19	.127	47					1.8	.054	111	3.2	82.0	
3	do.	12 m.	23	.125	44					1.6	.047	103	3.0	91.2	
4	do.	4 p. m.	27	.125	37		340			1.6	.047	96	2.8	82.0	
5	Oct. 25	8 a. m.	43	.124	38					1.6	.047	89	2.6	92.4	
6	do.	12 m.	47	.124	38					1.6	.047	92	2.7	82.0	
7	do.	4 p. m.	51	.123	34		340			1.2	.035	91	2.7	88.0	
8	Oct. 26	8 a. m.	67	.120	40					1.2	.035	85	2.5	92.2	
9	do.	12 m.	71	.120	38					1.2	.035	74	2.2	88.0	
10	do.	4 p. m.	75	.120	37		340			0.6	.018	73	2.1	94.0	
11	Oct. 27	8 a. m.	91	.115	38					0.6	.018	70	2.04	94.0	
12	do.	5 p. m.	100	.115	30					0.6	.018	80	2.3	93.2	
13	Oct. 28	4 p. m.	27	.112	27		340			0.6	.018	78	2.27	94.0	
14	Oct. 30	9 a. m.		.105	18					0.6	.018	96	2.8	91.8	

^a Average.^b Barren solution free from previous millings used contained 0.31 gram of zinc per liter, 0.078 per cent NaCN (free), and 7 points alkalinity.

MISCELLANEOUS TESTS OF ORES FROM THE UNITED STATES AND MEXICO.

Following the experiments made on ore from Sumatra were those on ores from the Buffalo-Hunter mine at Silver Cliff, Colo.; from Butte, Mont.; the Elkoro gold mine at Jarbidge, Nev.; and the El Favor mine in Jalisco, Mexico. Results may be summarized as follows:

ORE FROM BUTTE, MONT.

An ore containing 29 per cent manganese and 4.1 ounces of silver per ton was milled, without preliminary treatment, in a 0.198 per cent solution of NaCN for 30 minutes, during which period 12.9 per cent of the silver was recovered and 8.8 pounds of cyanide was consumed. At the end of 24 hours agitation the extraction was 80 per cent and consumption 13.1 pounds. After 72 hours the total recovery increased to 87.1 per cent.

A sample was then given an oxidizing roast between 400 and 600° C. for 42 minutes, followed by a reduction for 65 minutes at 620° C. The silver content was 5.2 ounces per ton. After milling for 30 minutes in a 0.206 per cent solution of NaCN the recovery was 8.7 per cent and the consumption 1.44 pounds. After 24 hours agitation the recovery was 86.2 per cent and the consumption 5.6 pounds, while at the end of 72 hours the total recovery was 94.2 per cent.

Magnetic separation of rhodochrosite (MnCO_3) from the gangue of some of this ore was tried with a Wetherill machine. The product passing the 8-mesh and remaining on the 28-mesh screen, constituting 76.3 per cent of the total sample, yielded a concentrate carrying 40.0 per cent Mn, 9.8 per cent SiO_2 , and 3.4 ounces Ag; a middling with 22.0 per cent Mn and 3.55 ounces Ag; and a tailing with 2.41 per cent Mn and 1.98 ounces Ag. From the minus 28-mesh product, equal to 23.7 per cent of the total, there was obtained a concentrate assaying 42.4 per cent Mn, 4.5 per cent SiO_2 , and 1.65 ounces Ag; a middling carrying 25.6 per cent Mn and 4.89 ounces Ag; and a tailing with 3.08 per cent Mn and 10.85 ounces Ag. The tailings from both products contained 21.8 per cent of the original Ag, but only 1.5 per cent of the Mn.

Concentrates were obtained by using 2 amperes, field strength, and middlings and tailings by using 4 amperes. The manganese was chiefly carbonate (MnCO_3), and no higher oxides of manganese were present. The silver probably was in fahlore (gray copper ore) associated with antimony. A qualitative test of the minus 28-mesh tailing proved the presence of copper.

This is an example of somewhat improved recovery from an unoxidized ore.

ORE FROM EL FAVOR MINE.

The treatment applied to this ore and the results obtained are shown in Table 30:

TABLE 30.—*Reduction tests with El Favor ore.*

Sample. ^a	MnO ₂ per cent.	Dilution.	NaCN added, per cent.	CaO added, per cent.	200 grams of ore milled, in NaCN solution, hours.	NaCN after milling, per cent.	Protective alkali in quantity after milling, per cent.	Heads.		Tails.			Extraction.										
								Au.	Ag.	After milling 2 hours.	Followed by agi- tation for—			After milling 2 hours, per cent.	Followed by agi- tation for—								
											24 hours.	48 hours.	72 hours.		24 hours.	48 hours.	72 hours.						
																		Gms.	Gms.	Gms.	Gms.	Gms.	Gms.
Original, without any preparatory treatment.....	7.20	1 to 4	0.202	0.5	2	0.177	0.013	Gms. 1.0	Gms. 0.029	Gms. 293	Gms. 273	Gms. 268	Gms. 263	29.4	34.2	35.4	36.6						
A: 1 to 3 mesh produced after reduction.....	5.56	1 to 4	.202	.5	2	.170	.034	1.2	.04	10.7	55	45	43	85.1	87.8	88.4	88.7						
B: 3 to 4 mesh produced after reduction.....	6.28	1 to 4	.202	.5	2	.166	.034	1.3	.04	512	48	40	39	90.6	92.2	92.5	92.5						
C: Mixed product, coarse material after reduction.....	6.00	1 to 4	.202	.5	2	.160	.036	1.2	.04	411	11.9	63	46	84.7	88.5	89.5	89.8						
D: Mixed product, fine material after reduction.....	6.90	1 to 4	.202	.5	2	.158	.042	1.2	.04	513	14.8	82	61	84.0	87.7	88.1	88.9						

Degree of comminution before reduction (Tyler standard screens):

Sample C.	Per cent.	Sample D.	Per cent.
+ 1 to 3 mesh.....	55.6	+ 10 mesh.....	4.6
— 3+ 4 mesh.....	12.4	— 30+ 30 mesh.....	55.0
— 4+ 6 mesh.....	10.9	— 30+ 60 mesh.....	19.5
— 6+ 8 mesh.....	8.4	— 60+ 90 mesh.....	3.5
— 8+ 10 mesh.....	4.5	— 90+ 120 mesh.....	5.1
— 10+ 20 mesh.....	4.3	— 120+ 150 mesh.....	1.2
— 20 mesh.....	3.9	— 150+ 200 mesh.....	2.3
	100.0	— 200 mesh.....	8.8
			100.0

Degree of comminution before milling in cyanide (Tyler standard screens):

	Per cent.
+ 60 mesh.....	21.0
— 60+ 90 mesh.....	12.1
— 90+ 120 mesh.....	23.3
— 120+ 150 mesh.....	3.0
— 150+ 200 mesh.....	9.1
— 200 mesh.....	31.5
	100.0

^a All samples were ground approximately to the above degree of comminution preparatory to milling in cyanide solution, grinding was done in a small Trojan laboratory porcelain ball-mill (19 centimeters inside diameter), containing a charge of flint pebbles of nearly 3 kilograms (6 pounds), and running about 60 revolutions per minute. Analysis of the producer gas used for reduction is as follows: CO₂, 5 per cent; O₂, 0.6 per cent; CO, 21.4 per cent. The temperature of reduction was nearly 900° C. The consumption of cyanide per ton of untreated ore was 2 pounds, and was 3.36 pounds after reduction, plus 1.36 pounds added later. The consumption of lime with the raw ore was 8.86 pounds per ton.

This ore is comparatively low grade, both in manganese and silver; when treated raw it gave low recoveries of the silver, but after reduction and grinding it gave a very satisfactory recovery. It will be noted that during the milling for two hours most of the silver (up to 90.6 per cent) is dissolved, but at the end of 72 hours agitation the extraction is only a little better than after 24 hours. The consumption of chemicals is not abnormal for this class of ore. The ore is more or less typical of many manganese ores.

ELKORO ORE.

As it was known that the silver in the Elkoro ore was refractory to cyanidation, it was considered instructive to ascertain to what extent, if at all, it was similar in its behavior to the refractory minerals occurring in typical manganese-silver ores.

The management of the property, in compliance with our request, sent a sample of the ore as it came from the mine in a tightly sealed container, which prevented evaporation of moisture from the ore during transit and the subsequent tests.

The ore was roughly crushed to pass a one-half-inch screen, and portions were rapidly separated for each test. The plan was to make tests of this ore similar to those which had been made with manganese-silver ores. At that time it was not known that the Elkoro ore contained manganese, but an analysis indicated that a small percentage was present. For a basis of comparison, a cyanide test was made with a sample of the ore as received. The effect of drying the ore was also observed in two tests, and in certain samples the recovery of both gold and silver was improved by drying. However, the gain in silver recovery by drying on a steam plate is small, and there is a positive loss in recovery by drying at 300°. The preliminary treatment in each test prior to cyanidation was as below:

Preliminary treatment prior to cyanidation.

1. Original ore as received.
2. Ore dried on steam hot plate below 100° C.
3. Ore dried at 300° C., with exclusion of most of the air.
4. Ore given preliminary reduction at 400° C.
5. Ore given preliminary reduction at 500° C.
6. Ore given preliminary reduction at 600° C.

The cyanide tests were all made under as nearly similar conditions as possible, as detailed below:

Details of cyanide tests.

Assay of ore:	
Silver, ounces per ton.....	4.37
Gold, ounces per ton.....	1.06
Zinc, per cent.....	0.25
Manganese dioxide, per cent.....	0.23
Weight of ore used, grams.....	250
Weight of solution used (dilution 3 to 1), grams.....	750
Size of ore prior to milling in cyanide solution, mesh.....	40
Time of milling in cyanide solution with small jar mill, hours.....	2
Size of each pulp after milling, mesh.....	-200
Strength of solution used, per cent NaCN.....	0.101
Weight of lime ^a used, gram.....	1
Temperature of air during period of tests, °C.....	15 to 20

No. 1 sample was ground as rapidly as possible to pass a 40-mesh screen, every precaution being taken to minimize loss of moisture by evaporation. The moisture was determined, and sufficient ore to equal 250 grams of dry ore was placed at once in the jar mill, and treated under the conditions outlined above. After milling was completed the pulp was transferred to a glass air agitator. Nos. 1 and 2 samples were dried as indicated, but after drying were ground to pass 40 mesh. From this product quantities of 250 grams were weighed into the jar mill and milled. Nos. 4, 5, and 6 samples received the preliminary reduction treatment without further grinding (one-half inch). After treatment in the reducing drum these samples were ground dry to 40-mesh size prior to being milled in the jar mill.

CYANIDE TESTS.

Recoveries of the gold and silver, together with consumption of chemicals, are shown in Table 31.

^a Sodium cyanide and lime were added as was found necessary to maintain the solution strength.

TABLE 31.—Cyanide tests with raw, dried, and reduced Elkoro ore.

Preliminary treatment.	Extraction during milling.		Total extraction after agitation.						Consumption of chemicals.	
	Au.	Ag.	Au.			Ag.			NaCN, pounds per ton.	CaO, pounds per ton.
			24 hours.	48 hours.	72 hours.	24 hours.	48 hours.	72 hours.		
None.....	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	0.90	7.2
Dried on steam plate.....	92.5	13.5	96.2	98.1	99.1	17.8	19.0	19.2	0.90	7.2
Dried at 300° C.....	92.5	21.7	98.1	98.1	99.1	22.4	23.6	26.3	1.60	7.2
Reduced at 400° C ^a	85.9	8.5	92.5	96.2	96.2	11.4	12.6	20.8	1.66	9.9
Reduced at 500° C.....	47.2	81.7	99.1	99.1	99.1	75.7	75.5	73.7	.54	11.2
Reduced at 500° C.....	35.8	81.7	99.1	99.1	99.1	78.5	79.0	81.9	.78	10.1
Reduced at 600° C ^a	90.5	77.1	99.1	99.1	99.1	77.3	77.3	80.8	.68	10.8

^a All the MnO₂ was reduced to MnO.

DISCUSSION OF RESULTS.

The recovery of gold from this ore in the tests is generally satisfactory. This is confirmed by the uniformly high recoveries obtained in the regular milling operations (100 tons daily at the mine). It is, however, noteworthy that drying at 300° C. appreciably lowers the ultimate gold recovery after 72 hours. This test showed a recovery of 96.2 per cent as against 99.1 per cent for all the other tests.

Recovery of the silver at the mine plant has been uniformly unsatisfactory. The efficiency is shown by a period of 9 days, when only 18.3 per cent of the silver was saved, whereas the recovery of gold for the same period was 98.4 per cent. The results of the small-scale tests given herein confirm the mill work. For example, the silver recovery from the sample as received, after 72 hours agitation, was 19.2 per cent; after drying at a low temperature, 22.4 per cent was recovered, which indicates a small improvement over the original ore, while drying at 300° C. reduced the recovery to 11.4 per cent.

Preliminary reduction gives results that are quite satisfactory for ore of this silver content. Similar ore with a higher silver content would undoubtedly yield a higher percentage of recovery. The maximum recovery of 81.9 per cent is obtained when reduction is carried on at 500° C.

It is of interest to note that the cyanide consumption is greatly increased by drying the ore, whereas it is considerably lowered when preliminary reduction is employed. The consumption of lime is higher with the reduced ore. Although not proved, it is thought that the zinc present in the ore may influence the cyanide consumption as indicated in the various modes of preliminary treatment.

In general, this ore behaves similarly to the typical manganese-silver ores, and although the percentage of MnO_2 present is small (0.23 per cent), it evidently has a most marked effect on the silver recovery. Intimate association of some of the silver with the zinc may also render a part of the silver refractory.

These tests, while only preliminary, indicate that the extraction of silver from Elkoro ore can be materially improved by reduction prior to cyanidation. The silver content of the ore is too low, however, to make preliminary treatment profitable.

BUFFALO-HUNTER CONCENTRATE.

A number of small and large scale experiments were made with concentrate from the Buffalo-Hunter property, and the results are set forth in the following tables (Nos. 32 to 37). The concentrate carried 6.68 to 7.03 per cent Fe, 28.60 to 35.90 per cent Mn, 1.14 to 1.25 per cent CaO, 29.10 to 41.55 per cent SiO₂, and 0.153 to 0.391 per cent K₂O.

This concentrate is an example of a product that requires finer grinding for satisfactory reduction than typical manganese-silver ores.

TABLE 32.—*Reduction test with Buffalo-Hunter concentrate.***Extraction from Untreated High-Manganese Concentrate.**

Sample.	Heads.		Strength of NaCN added, per cent.	Cyanide consumption after milling, pounds.	Ag extraction.				Remarks.
	Ag, ounces per short ton.	MnO ₂ , per cent.			After 2 hours milling, per cent.	Followed by agitation of —			
						24 hours, per cent.	48 hours, per cent.	72 hours, per cent.	
Concentrate from tables 1 and 2.	33.13	48.6	0.200	1.36	10.2	8.1	9.8	12.4	Sample contains small amount of lead and between 0.025 and 0.020 per cent phosphorus.
Concentrate from table 3.	41.78	58.1	.200	Lost.	Lost.	8.7	9.8	Not taken.	
Middlings from tables 4 and 5.	23.90	33.3	.200	2.00	12.6	10.3	9.4	11.6	

Extraction after Reduction at 900° C. with Producer Gas.^a

Concentrate from tables 1 and 2.	39.67	None.	0.200	4.48	89.9	91.5	91.3	91.4	No MnO ₂ present in tailings after agitation.
Concentrate from table 3.	49.15	None.	.200	5.60	94.5	96.4	96.3	96.5	
Middlings from tables 4 and 5.	24.80	None.	.200	3.04	93.7	93.9	93.4	93.7	

^a After reduction, all MnO₂ was converted into MnO. As the psilomelane was very dense, the sample had to be crushed to 14 mesh before reduction to obtain fairly rapid reduction.

TABLE 33.—*Data on reduction test No. 2 with Buffalo-Hunter concentrate.*

[Screened table concentrate, 20 to 48 mesh, 42 per cent MnO₂. Externally heated furnace and Riché gas used. Temperature maintained between 600 and 650° C. Furnace speed, 0.73 r. p. m. Feed, 34 pounds per hour. The reduced ore was caught in gas-filled cans, which were soldered air-tight when full, and shipped to Golden for cyanidation.]

Milling.

Milling, hours.	Mill charge.				Tail solution.		Consumption, pounds per ton.		Heads.	Tails.	Extraction.	Remarks.
	Ore, pounds.	Water, pounds.	NaCN, ounces.	Lime, ounces.	NaCN, per cent.	CaO, points.	NaCN.	CaO.	Ag, ounces.	Ag, ounces.	Ag, per cent.	
2	87	90	2.0	4	0.028	250	2.29		15.08	14.90	1.2	Diluted 3 to 1. No air during milling. Do.
2	58	75	1.5	3	.052	250	1.89		14.96	13.77	8.0	
							a 2.13		a 15.03	a 14.48	a 3.98	
	45	80	.198	.178	.176	19			15.08	1.75	88.3	Pilot test milling.

a Average.

TABLE 33.—Data on reduction test No. 2 with Buffalo-Hunter concentrate—Continued.

Agitation.

Sam- ple No.	Period.		Solution.		Chemicals added.		Consumption, pounds per ton.		Tails.		Extraction.	Remarks.
	Day.	Hour.	Agitation, hours.	NaCN, per cent.	CaO, points.	NaCN, ounces.	Lime, ounces. ^b	NaCN.	CaO.	Ag, ounces.	Ag, per cent.	
1	July 24	8 p. m.		0.016	84	7.5	7	5.06		14.10	6.0	$\frac{1}{2}$ ounce lead acetate added. 0.63 ounce lead acetate added.
2	do.	9 p. m.		.072	88	2		8.20		12.23	18.5	
3	do.	10 p. m.		.100	96			8.21		10.55	29.7	
4	do.	11 p. m.		.084	84			9.17		10.12	32.5	
5	do.	12 m.		.084	88	3		9.17		9.32	37.9	
6	July 25	6.30 a. m.	10 $\frac{1}{2}$	.124	80			9.38		7.82	47.9	
7	do.	9 a. m.	13	.116	74			9.85		7.52	49.9	
8	do.	12 m.		.120	66			9.62		6.74	55.1	
9	do.	3 p. m.		.120	60			9.62		6.40	57.3	
10	do.	9 p. m.		.118	56			9.62		5.25	65.0	
11	July 26	8 a. m.		.114	50			9.73		4.84	67.7	
12	do.	12 m.		.112	48			9.98		4.22	71.9	
13	do.	3 p. m.		.116	44			10.10		4.16	72.3	
14	do.	9 p. m.		.118	36			9.85		3.85	74.5	
15	July 27	8 a. m.		.114	36			9.74		2.89	80.7	
16	do.	3 p. m.		.112	36			9.98		2.68	82.1	
17	do.	7 p. m.		.116	36			10.10		2.19	85.4	
18	July 28	9 a. m.		.108	36			9.85		2.12	85.9	
19	July 29	8 a. m.		.108	36			10.33		1.77	88.2	
20	July 30	do.		.098	34			10.95		1.64	89.1	

3.55 per cent MnO₂.

Pilot Agitation.

Sam- ple No.	Period.		Solution.		Chemicals added.		Consumption, pounds per ton.		Tails.		Extraction.	Remarks.
	Day.	Hour.	Agitation, hours.	NaCN, per cent.	CaO, points.	NaCN, ounces.	Lime, ounces. ^b	NaCN.	CaO.	Ag, ounces.	Ag, per cent.	
1	July 27	9 a. m.		0.136	36					1.20	92.0	Sample from pilot test milling. { Sample taken from large agitator at 3 p. m., July 29, and finished in small agitator.
2	do.	7 p. m.		.108	38					1.15	92.4	
3	July 29	7 a. m.		.064	44					1.07	92.9	
1	do.	29		.092	38					1.67	88.9	
2	July 30	6 a. m.		.074	46					1.54	89.7	Sample from pilot test milling. { Sample taken from large agitator at 3 p. m., July 29, and finished in small agitator.
3	do.	7 p. m.		.108	38					1.15	92.4	
4	do.	7 a. m.		.064	44					1.07	92.9	
5	do.	29		.092	38					1.67	88.9	

^b Lime used contained about 70 per cent available CaO.

TABLE 34.—Data on reduction test No. 3 with *Buffalo-Hunter concentrates*.

[140 pounds of screened concentrate and 420 pounds of straight table concentrate. Externally heated furnace and Riché gas used. Temperature maintained between 600 and 650° C. Furnace speed, 0.64 r. p. m. Feed, 47 pounds per hour. The ore was completely reduced throughout the test. It was caught in gas-filled cans, which were kept sealed until a mill charge was obtained.]

Milling.

Period of milling.			Mill charge.				Tail solution.		Consumption, pounds per ton.		Tails.	Extraction.	Remarks.
Day.	Hour.	Duration, hours.	Ore, pounds.	Water, pounds.	NaCN, ounces.	Lime, ounces.	NaCN, per cent.	CaO, points.	NaCN.	CaO.	Ag, ounces.	Ag, per cent.	
Aug. 12	5 p. m.	2	150	150	4	None.	0.095	115	1.43	None.	3.99	71.9	Milled 5 to 5.30 p. m. without air.
12	9 p. m.	2	134	134	4	None.	.085	111	2.03	None.	2.88	78.6	Stood in mill till 7.15 p. m.
12	11.15 p. m.	2	150	150	4	None.	.095	73	1.43	None.	3.29	74.2	Milled with air. Discharged into agitator. Diluted 3 to 1; 5 ounces NaCN added.
									a 1.62		a 3.40	a 74.7	

Agitation.^b

Sample No.	Period.		Agitation, hours.	Solution.		Chemicals added.		Consumption, pounds per ton.		Tails.		Extraction.		Remarks.
	Day.	Hour.		NaCN, per cent.	CaO, per cent.	NaCN, ounces.	Lime, ounces. ^c	NaCN.	CaO.	Ag, ounces.	Ag, per cent.			
1	Aug. 14	8.10 a. m.	9	0.107	23	1.35				2.50	81.4	Agitation with air until about 4 a. m., then air off. Off from 1 to 4 p. m. Air from 4 p. m. until finish.		
2	do.	12.30 p. m.	13	.100	23	1.78				2.30	82.9			
3	do.	8.30 p. m.	18							1.81	86.5			
4	Aug. 15	8.30 a. m.	30	.095	23	2.06				1.70	87.4			
5	do.	1 p. m.	34	.090	23	2.38				1.63	87.9			
6	do.	5 p. m.	38	.090	20	2.38				1.57	88.3			
7	do.	9 p. m.	42							1.64	87.8			
8	Aug. 16	8 a. m.	53	.085	19	3	3	2.67		1.54	88.5			
9	do.	1 p. m.	58	.100	21			2.64		1.41	89.5			
10	do.	4.30 p. m.	62	.095	19			2.95		1.49	88.9			
11	Aug. 17	8 a. m.	77	.087	19	3		3.41		1.44	89.3			
12	do.	3.30 p. m.	85	.105	31			3.24		1.41	89.5			
13	Aug. 18	8 a. m.	101	.095	23			3.82		1.35	90.0			
14	Aug. 19	8.30 a. m.	125	.073	27			5.10		1.23	90.9			
													2.23 per cent MnO ₂ .	

^a Average.^b Sizing test of grab sample (Tyler standard screens): +100, 0.7 per cent; -100+150, 1.1 per cent; -150+200, 1.8 per cent; -200, 96.4 per cent.^c Lime contained about 70 per cent available CaO.2.23 per cent MnO₂.

TABLE 35.—Data on reduction test No. 4 with *Buffulo-Hunter concentrate*.

[Screened table concentrate. Externally heated furnace and Riché gas used. Temperature maintained between 600 and 650° C. Furnace speed, 0.64 r. p. m. Feed, 28 and 38 pounds per hour. The smaller particles of ore were completely reduced throughout the test, but the larger particles contained a small core of higher oxides, showing that the time of reduction was too short. The discharge ore was caught in gas-filled cans which were sealed until a mill charge was obtained.]

Milling.

Period of milling.		Mill charge.				Tail solution.		Consumption, pounds per ton.		Heads.	Tails.	Extraction.	MnO ₂ before milling, per cent.	Remarks.
Day.	Hour.	Duration, hours.	Ore, pounds.	Water, pounds.	NaCN, ounces.	Lime, ounces.	NaCN, per cent.	Lime, points.	NaCN.	CaO.	Ag, ounces.	Ag, per cent.	Ag, per cent.	
Aug. 28	4 p. m.	2	152	150	4	16	0.05	0.24	2.30		33.70	13.21	60.8	1.7
28	6.15 p. m.	2	156	150	4	16	.08	1.47	1.67		31.30	12.21	61.0	3.4
28	8.25 p. m.	2	150	150	4	16	.083	1.50	1.57		27.32	9.82	64.0	Do.
28	10.25 p. m.	2	150	150	4	16	.100	1.77	1.33		30.52	12.13	60.2	Do.
									<i>a</i> 1.72		<i>a</i> 30.89	<i>a</i> 11.85	<i>a</i> 61.6	Diluted 3 to 1; and 6 ounces NaCN added.

Sam- ple No.	Period.			Solution.		Chemicals added.		Consumption, pounds per ton.		Tails.	Extraction.	MnO ₂ per cent.	Remarks.
	Day.	Hour.	Agitation, hours.	NaCN, per cent.	CaO, points.	NaCN, ounces.	Lime, ^c ounces.	NaCN.	CaO	Ag. ounces.	Ag. per cent.		
1	Aug. 29	1 a. m.	4	0.078	52	6		3.02		10.59	65.7		
2	do.	8.30 a. m.	11½	.092	45	3		3.24		8.45	72.6		
3	do.	3.30 p. m.	18½	.100	40			3.53		8.08	73.8		
4	Aug. 30	8.30 a. m.	35½	.097	39			3.74		6.82	79.6		
5	do.	3.30 p. m.	42½	.093	35	2		4.00		6.10	80.3		
6	Aug. 31	8 a. m.	59	.095	42	2		4.30		5.34	82.7		
7	do.	3.30 p. m.	66½	.105	35			4.16		5.01	83.8	6.7	
8	Sept. 1	8.30 a. m.	83½	.104	37			4.16		3.92	87.3		
9	do.	4 p. m.	91	.098	36			4.54		3.92	87.3		
10	Sept. 2	8 a. m.	107	.092	36			4.89		4.19	86.4	7.8	Agitation stopped.
Pilot Agitation.													
Milling No. 1.													
1	Aug. 28	6 p. m.				Per cent.				13.21	60.8		
2	Aug. 30	8 a. m.	38	0.037	40	0.027				4.14	87.7		
3	Sept. 1	do.	86	.028	50	.011				4.00	88.1		
Milling No. 2.													
1	Aug. 28	8.15 p. m.				0.027				12.21	61.0		
2	Aug. 30	10.15 a. m.	38	0.070	40	.007				5.08	81.9		
3	Sept. 1	do.	86	.050	74					5.26	83.2		
Milling No. 3.													
1	Aug. 28	10.30 p. m.				0.027				9.82	64.0		
2	Aug. 30	do.	38	0.100	39					3.75	86.2		
3	Sept. 1	12.30 p. m.	86	.068	48					3.53	87.1		

^a Average.

^b Sizing test on No. 10 agitation (Tyler standard screens): +100, 1.5 per cent; -100+150, 5.5 per cent; -150+200, 5.1 per cent; -200, 87.9 per cent.

^c Lime used contained about 70 per cent CaO.

TABLE 36.—Data on reduction test No. 5 with *Buffalo-Hunter concentrate*.

[Screened table concentrate, crushed to 30 mesh before reduction. Average head contained 30.44 per cent Mn. Internally heated kiln used. Rate of feed at first, 60 pounds per hour, increased to ward the last to 90 pounds per hour. The higher oxides of manganese in the concentrate were completely reduced at both rates of feed. The concentrate was milled at once to avoid oxidation.]

Milling.

Period of milling.			Mill charge.				Tail solution.		Consumption, pounds per ton.		Heads.	Tails.	Extraction.	Remarks.
Day.	Hour.	Dura- tion, hours.	Ore, pounds.	H ₂ O, pounds.	NaCN, ounces.	Lime, ounces.	NaCN, per cent.	CaO, points.	NaCN	CaO.	Ag, ounces.	Ag, per cent.	Ag, per cent.	
Nov. 14	1.05 p. m.	2	150	150	5	16	0.046	45	3.24		34.01	15.34	54.89	Diluted 3 to 1; 6 ounces NaCN added. Do. Do. Diluted 3 to 1; 4 ounces NaCN added.
14	5 p. m.	2	150	150	6	16	.085	61	3.30		34.32	15.66	54.37	
14	9.40 p. m.	2	150	150	7	16	.110	90	3.65		34.36	18.95	44.84	
15	1 a. m.	2	150	150	7	16	.110	86	3.65		34.12	13.65	60.00	

Agitation.

Sam- ple No.	Time taken.		Tail solution.		Chemicals added.		Consumption.		Extraction. ^b
	Day.	Hour.	NaCN, per cent.	CaO, pounds.	NaCN, ounces.	Lime, ^a ounces.	NaCN, pounds.	CaO, pounds.	
1	Nov. 15	8 a. m.	0.106	25		4	3.10		71.78
2	do.	4 p. m.	.004	24		10	4.12		9.075
3	Nov. 16	8 a. m.	.102	27			4.09		8.24
4	do.	4 p. m.	.100	22		12	4.21		75.90
5	Nov. 17	8 a. m.	.110	25			4.02		77.60
6	do.	4 p. m.	.100	24			4.62		78.94
7	Nov. 18	8 a. m.	.080	18		8			7.05
8	do.	4 p. m.	.080	29					6.78
9	Nov. 19	8 a. m.	.112	17		10			80.00
10	do.	4 p. m.	.106	29					6.575
11	Nov. 20	8 a. m.	.100	30		10			6.15
12	do.	4 p. m.	.170	33		2			5.77
13	Nov. 21	8 a. m.	.142	18			5.78		6.23
14	do.	4 p. m.	.140	20			5.99		6.16
									6.06
									5.44

^a Lime used contained about 70 per cent CaO.

^b During the cyanide treatment the weather unexpectedly turned very cold, and as no provision for heating the solutions had been made, the silver recovery was not as high as it would have been otherwise. Under favorable conditions a 90 per cent recovery would probably have been realized.

TABLE 37.—Data on reduction test No. 6 with Buffalo-Hunter concentrate.

A mixture of table concentrate was ground to 20 mesh and reduced in the internally heated furnace. Producer gas made from coke was used. It was intended to run this test at a temperature of 700° C., but through an error in reading the calibration curve of the pyrometer it was found later that it was actually run at a temperature of 820° C. The feed was at the rate of 60 pounds per hour. No difficulty was experienced in getting the manganese completely reduced at all stages of the operation. The reduced concentrate was held until the following day in air-tight cans, when it was milled and cyanided.]

Milling.

Period of milling.			Mill charge.			Tail solution.		Consumption, pounds per ton.		Heads.	Tails.	Extraction.	Remarks.
Day.	Hour.	Duration, hours.	Ore, pounds.	Water, pounds.	NaCN, ounces.	Lime, ounces.	NaCN, per cent.	CaO, points.	NaCN.	CaO.	Ag, ounces.	Ag, per cent.	
1918.													
Mar. 12	1:30 p. m.	1½	150	150	5	None.	0.075	25	2.66	None.	32.0	10.67	66.6
12	3:50 p. m.	1½	150	150	5	None.	.074	28	2.69	None.	32.0	9.00	71.9
12	5:45 p. m.	1½	150	150	5	None.	.070	28	2.76	None.	32.0	9.87	69.1
12	7:35 p. m.	1½	100	100	4		.075	28	3.50	None.	32.0	8.80	72.4
Dilution 3.27 to 1. Air throughout milling.													

Agitation.

Sample No.	Period.		Solution.		Chemicals added.		Consumption, pounds per ton.		Tails.	Extraction.		Remarks.
	Day.	Hour.	Agitation, hours.	NaCN, per cent.	CaO, points.	NaCN, ounces.	Lime, ^a ounces.	NaCN.	CaO.	Ag, ounces.	Ag, per cent.	
1	1918.											
1	Dec. 12	9:30 p. m.		0.088	11	20	15	3.01	2.04	7.32	77.2	Weather cold, solution heated to 60° F.
2	Dec. 13	8 a. m.	10½	.086	14	30	5	3.22	3.2	5.82	81.0	
3	do.	3:30 p. m.	18	.101	14		5	2.92	3.9	6.05	81.2	
4	Dec. 14	8 a. m.	34½	.101	16		3	2.92	4.5	5.65	82.3	
5	do.	3:30 p. m.	42	.101	12			2.92		5.57	82.6	
6	Dec. 15	8 a. m.	58½	.088	16			3.77		5.27	83.5	If alkalinity had been kept up at end of test, cyanide consumption would have been less.
7	do.	3:30 p. m.	66	.088	14			3.77		5.10	84.0	
8	Dec. 16	8 a. m.	82½	.071	14							

^a Lime used contained 70 per cent available CaO.

WORKING-SCALE TESTS AT PACHUCA, MEXICO.

The development of the Clevenger furnace and its trial upon a large scale culminated in large-scale tests at Pachuca, Mexico, during 1921. Through the courtesy of Cia de Real Del Monte y Pachuca we are able to give a brief account of some of these tests and the general conclusions reached. The furnace used had a daily capacity of 50 metric tons. Direct oil firing was employed in the preheating unit and an improvised charcoal gas-producer supplied gas of about 150 B. t. u. to the reducing unit. Complete details of this equipment are shown in Plate VI. The motors used were those available and were larger than was necessary. The actual power requirement for treating 50 metric tons daily is given below:

	Kw.
Preheating unit and feeder.....	1. 27
Reducing unit and cooler.....	2. 31
Gas and air blowers.....	3. 66

A general description of the Clevenger reducing furnace as now developed is given below, before the large-scale tests are discussed.

CLEVENGER REDUCING FURNACE.

Attention has been called elsewhere in this paper to the fact that reduction of the higher oxides of manganese to manganous oxide, which takes place at the same time the silver and gold are freed so that they are soluble in cyanide solution, can be effected with the majority of ores on a coarse rock-breaker product. The advantages of this are obvious. As is well known, the rotating-kiln type of furnace is better suited to the treatment of coarse material than are furnaces of the horizontal-hearth, mechanically rabbled type. The rotating cylinder can be readily insulated against heat losses; moreover, the fundamental idea of progressive combustion of the gas and final complete combustion of the gas with counter flow of the ore, a principle essential to high fuel economy, can be applied most conveniently to a furnace of the kiln type. In the development of this equipment standard cement-kiln construction has been followed so far as possible, thus insuring freedom from mechanical difficulties.

UNITS OF FURNACE.

The general features of the equipment as developed through extensive large-scale experimentation are shown in Plate VI and a diagram of the operation of the furnace is shown in Plate VII (p. 90). The equipment comprises a preheating unit in which the ore is brought to reaction temperature, a reducing unit in which reduction is accomplished, and a cooler in which the ore is cooled under reducing conditions. These units may be built integral but we regard it as better practice to build the reducing and cooling units integral and to interpose a stationary combustion chamber between them and a separate preheating unit.

PREHEATING UNIT.

The cold ore is fed to the head end (Pl. VIII, *A*) of the preheating unit and during the passage through it part of the sensible heat of the hot gases is transferred to the ore (see Pl. IX, *A* and *B*). The ideal condition is to discharge from the lower end of this zone into the reducing zone the ore heated to reaction temperature, and to discharge from the upper end the spent gases at or near the temperature of the outside air. In practice the ore has been heated to reaction temperature but all the heat can not be abstracted from the gases unless the preheating zone is made excessively long. The economical limit would probably be reached with a waste-gas temperature of 100 to 200° C. The length of the preheating zone is therefore governed by these two considerations. Another important function of this zone is the elimination of whatever water the ore may contain. Briefly, then, the ore is prepared for reduction in this zone by drying and preheating to reaction temperature; this is accomplished with an efficient utilization of the heat units delivered to this unit.

REDUCING UNIT.

Reduction of the higher oxides of manganese to manganous oxide, rendering the silver and gold amenable to cyanidation, is accomplished in the reducing unit. Since the reactions involved are largely endothermic and since despite heat insulation there is some loss of heat from the shell of the kiln through radiation, some heat must be supplied to the reducing unit. This is accomplished by burning enough gas progressively to hold the desired temperature. Producer gas of about 150 B. t. u. per cubic foot can generally be used to greatest advantage. The gas enters the lower end of the reducing zone after leaving the cooling zone and passes up the kiln counter-current to the oncoming ore. Plate VIII, *B*, shows the gas producer. What we term "air burners" are located along the axis of this zone at suitable intervals and are connected with a bustle pipe attached to the shell of the kiln, through which the air enters. A supply pipe runs through a stuffing gland in the discharge hopper and up through the axis of the cooling zone, passing outward through the shell of the kiln at about the point where the cooling and reducing zones join. Here it is connected to the bustle pipe on the outside of the reducing zone. This pipe rotates with the kiln and just outside the stuffing gland in the discharge hopper has a special joint which connects it with the stationary air-supply line. The air burners consist of a flaring sleeve with the air nozzle located centrally and at one end. The air issuing from the nozzle aspirates or draws in through the sleeve part of the gas which is passing upward through the reducing zone; the amount of gas so drawn is being regulated by adjustable openings. The gas-air mixture that issues from the other

end of the sleeve burns in the gas atmosphere with a flame resembling the burning of an air-gas mixture in the air. The size of the flame is governed by the amount of air passed through the burner, which is readily adjusted by an external valve. The burner is so mounted that it may be readily removed as a unit by disconnecting it from the bustle pipe and removing the nuts which hold it to the shell of the kiln. This permits the quick change of a defective burner. Plate X, A, shows the burner connections, collector, rings for thermocouples, driving gear, and riding ring.

COOLING UNIT.

The cooling unit is quite simple, as it may consist merely of an inclined steel shell, upon which a spray of water plays, attached to the lower end of the reducing zone (see Pl. XI). The other end connects with the discharge hopper by means of a suitable joint (see Pl. X, B). In smaller kilns this joint may be an ordinary stuffing gland with asbestos packing, but in general a joint similar to a marine thrust-bearing has been found to be most satisfactory. The lower end of the discharge hopper is immersed in mill solution to give a gas-tight seal. The gas line from the producer is connected to the discharge hopper, therefore the cold gas has part of the sensible heat of the reduced ore transferred to it as it passes along. The rest of it is dissipated through the shell of the cooler. There is no burner for some distance at the lower end of the reducing zone so that the sensible heat of the reduced ore is utilized so far as practicable.

An alternative is either to have no cooler or a very short section of cooler and to discharge the hot ore into mill solution. With this arrangement hot gas directly from the producer might be used without scrubbing, thereby obtaining somewhat better fuel efficiency.

There are two alternative methods of operating the kiln. (1) All of the fuel is gasified and the combustion chamber merely used for admixing the amount of air necessary to obtain complete combustion. (2) Only enough of the fuel is gasified to meet the gas requirement of the reducing zone and the balance of it is burned directly either in the combustion chamber or in special fire boxes communicating with it. Oil lends itself particularly well to this arrangement as oil burners can be introduced directly into the combustion chamber.

A reducing unit for the treatment of manganese-silver ores should meet the following requirements:

1. It should give high fuel efficiency.
2. It should be capable of close regulation.
3. It should require minimum attention; in other words, be largely automatic in action.
4. It should be capable of completely, or just about completely, reducing the higher oxides of manganese to manganous oxide.

The sensible heat of the hot reduced ore is partly transferred to the entering cold gas and air. Such additional cooling as is required to lower the temperature below the point at which the reduced ore re-oxidizes, is obtained by radiation through the bare steel wall of the kiln in this zone

The preheated unreduced ore passes from the neutral, slightly oxidizing, or slightly reducing atmosphere of the preheating zone through the steadily increasing reducing atmosphere of the reducing zone. In the reducing zone it is necessary to supply the heat lost through radiation and to satisfy endothermic reactions that take place. This is attained by progressive combustion of the combustible gases through the admission of air in carefully regulated amounts at suitable intervals. By this means the temperature is under perfect control. Reduction may take place at constant, decreasing, or increasing temperature throughout the zone

The cold incoming ore meets the hot waste gases, which give up their sensible heat to it as it advances through the zone. When the ore reaches the reducing zone, the higher oxides of manganese have lost that part of the oxygen which is expelled by direct heating and the ore should be at or near the reaction temperature. The preheating zone may have a slightly reducing, a slightly oxidizing, or a neutral atmosphere

DIAGRAM OF OPERATION OF CLEVERGER REDUCING FURNACE

a, Temperature of gas; b, temperature of ore; c, reduced ore; d, reducing gases; e, gas enters; f, air enters; g, reducing gases; h, reduced ore cooling; i, gases become less reducing as head end is approached; j, ore is reduced; k, ore is preheated; l, hot waste gases impart their heat to incoming ore; m, gases neutral or nearly so; n, unreduced ore; o, unreduced ore enters at head end; p, reduced ore is discharged at foot end

5. It should be so arranged that the ore can be brought to room temperature under reducing conditions or by quenching in water to prevent reoxidation of the manganous oxide with reversion of the silver to the refractory state.

METHOD OF MAKING TEMPERATURE MEASUREMENTS IN THE REDUCING FURNACE.

Precise temperature control is of great importance in obtaining the highest degree of efficiency in the Caron process. The temperature throughout the reducing zone of the Clevenger kiln can be adjusted closely by regulation of the valves between the air line and the burners and is measured with thermocouples located at different points. The approximate temperature, either of the gases or the ore, is determined by stopping in the kiln so that the couples are either out of the ore and surrounded by the hot gases or completely covered by the ore. Enough time, about two minutes, must be given for the couples to come to the temperature of the gases or ore.

That provision be made for obtaining a continuous record of the temperature throughout the reducing zone is highly desirable. Such a record not only indicates whether the proper temperature has been maintained, but also shows most of the irregularities which may have arisen in operation. Such a record, taken when the kiln is rotating, is a composite of gas and ore temperatures. Any particular point may be a gas or ore temperature, depending on the position of the couple when the recorder makes its imprint. After a little experience average conditions can be interpolated readily. As a matter of fact, under normal conditions of operation there is not a great deal of difference between the ore and gas temperatures.

When work with the large unit was undertaken no complete equipment was on the market for taking temperature measurements continuously in a rotating kiln. It was therefore necessary to design an installation which would meet these conditions. The standard equipment selected was manufactured by the Leeds & Northrup Co., of Philadelphia, and consisted of a six-point recorder having a temperature range of 0 to 1,000° C. and automatic cold-junction compensation. The manufacturers state that this recorder has an accuracy of 0.5 per cent of the temperature range or 5° C., and "pipe type" base-metal thermocouples consisting of special iron pipe one-half inch in diameter closed at the fire end and of proper length, with a constantan wire separated from the pipe by clay insulators through the center and welded into the solid tip of the pipe. Iron-constantan duplex lead wire was used.

Five couples were located at equidistant points along the reducing unit and one at the point where the flue gases were discharged from the preheating zone. The pipe couples in the reducing unit were

screwed into the shell of the kiln so that they projected from 1 to 2 inches beyond the fire-brick lining, thus insuring proper indication of temperature without undue strain and wear upon the couples by the sliding ore. The ends of the couples will wear off in time, but they are inexpensive and can be replaced readily. Couple 1, located at the head of the reducing unit, gives the average temperature of the ore entering and the gases leaving the unit. Couples 2, 3, and 4 show the temperature at intermediate points. Couple 5, located where the reducing unit joins the "cooler" unit, gives the temperature of the ore leaving and the gas entering the reducing unit. Provision is made for taking the temperature of the fire box and various points in the flue by means of a long pipe couple and portable galvanometer. It is generally unnecessary to make these measurements except when a special study of the performance of the kiln is being made.

A steel conduit similar to that used in electrical work is bolted to the shell of the reducing unit adjacent to the line of couples and extending from the couple at the head end of the kiln to the slip rings. Through this are passed the asbestos-covered iron and constantan leads which connect the couples to the slip rings. It is possible to use either a single or a double slip ring for each couple. If a single ring is used, the iron tubes of all the couples are grounded by connecting to the steel shell. When two rings are used for each couple, the iron tube is connected to one ring and the constantan wire to the other. Since the maker of the recorder preferred to use a pair of rings for each couple, this installation, which provided for five couples in the rotating member of the kiln, was provided with five pairs, or a total of 10 rings (see Pl. X, A).

The rings are formed by brazing together the ends of copper busbar three-fourths inch wide and one-half inch thick (see Pl. XII). These are supported on hardwood spacer blocks resting on one-half inch transite board, bolted to the shell of the kiln. The rings are attached to the wooden blocks by countersunk bronze screws. As the shell of the kiln does not get very hot, by reason of the sil-o-cel insulation, this construction, although inexpensive, has proved very satisfactory. The lead wires are brazed or soldered to the underside of the rings, thus insuring good contact at all times. Stationary contact with the rotating rings is made through the medium of copper-leaf brushes held by the standard type of brush holders. Connection between the brush holders and the recorder is made with asbestos-covered iron and constantan wire similar to that used for connecting the couples to the rings. This is in effect practically the same as if the couples were directly connected to the recorder. Since compensation for the temperature of the cold junctions is made in the recorder, the temperature of the hot end of the couples is

A. HEAD END OF PREHEATING UNIT

B. VIEW OF GAS PRODUCER

A. DISK FEEDER WHICH DISCHARGES INTO SHAKING FEEDER SHOWN IN B

B. SHAKING FEEDER INSIDE DUST CHAMBERS AT END OF PREHEATING UNIT

A BURNER CONNECTIONS, COLLECTOR RINGS FOR THERMOCOUPLES,
DRIVING GEAR, AND RIDING RING

B. LOWER END OF COOLER AND DISCHARGE HOPPER

REDUCING KILN AND COOLER, SHOWING BURNER CONNECTIONS

given directly. The temperature of the rings is immaterial if the two rings and brushes making up a pair are at the same temperature. The recorder is shown in Plate XIII, A, and opened for cleaning and oiling in Plate XIII, B (p. 96).

RESULTS OF LARGE-SCALE REDUCTION TESTS OF THREE MEXICAN ORES.

Complete tests were made of ores from three different mines, having the following composition:

TABLE 38.—*Analyses of three Mexican manganese-silver ores.*

Mineral.	Ore from Purisima mine.	Ore from Guanacevi mine.	Ore from San Juan de Pachuca mine.
	<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
SiO ₂	70.22		
Al ₂ O ₃	7.01		
Fe ₂ O ₃	2.90		
Fe.....		3.55	2.69
CaO.....	6.57	3.28	1.25
MgO.....	3.02	Fair quantity, but not determined.	
Mn.....	1.57	8.20	3.70
Mn (calculated to MnO ₂).....	2.77	12.99	5.90
Pb.....	0.15		
Cu.....	0.04		
Zn.....	0.46	1.60	0.30
S.....	0.71		
As.....	Trace.		
Insoluble.....	81.74	73.30	84.40
Loss on ignition.....	3.84		
Au.....	4.1 to 60 grams per metric ton=0.12 to 1.74 ounces per short ton.	1.3 grams per metric ton=0.038 ounce per short ton.	1.95 grams per metric ton=0.057 ounce per short ton.
Ag.....	696 to 877 grams per metric ton=20.22 to 25.52 ounces per short ton.	811 grams per metric ton=23.60 ounces per short ton.	450 grams per metric ton=13.25 ounces per short ton.

The moisture content was 2.3, 6.7, and 5.6 per cent, respectively. Three runs were made on Purisima ore and one each on the other ores. Samples were taken for small-scale cyanide tests at various periods, and the remainder of the reduced ore went into the regular circuits of a mill treating over 1,000 tons per day.

Sizing tests of the three ores as fed to the kilns gave the following:

Sizing tests.

Ore.	Size of opening, inches.	Screen mesh (Tyler standard).	Per cent.
Purisima.....	Through 2½-inch ring on 0.371-inch screen.....		60.7
	Through 0.371 on 0.0328 inch.....	0.371-inch mesh on 20 mesh.....	29.2
	Through 0.328 on 0.0029 inch.....	Through 20 mesh.....	8.0
	Through 0.0029 inch.....	Through 200 mesh.....	2.1
Guanacevi....	Through 2½-inch ring on 0.371-inch screen.....		29.4
	Through 0.371 on 0.016-inch screen.....	Over 48 mesh.....	54.2
	Through 0.016 inch.....	Through 48 mesh.....	16.4
San Juan de Pachuca....	Through 2½-inch ring on 0.371-inch screen.....		50.5
	Through 0.371 on 0.016 inch.....	0.371-inch screen on 48 mesh.....	41.0
	Through 0.016 inch.....	Through 48 mesh.....	8.5

ORE FROM PURISIMA MINE.

This ore was found to be rather low grade, and not particularly refractory. Since it was the first ore tested, the silver recovery was not so good (91.8 per cent) as had been indicated (95.1 per cent) by some of the previous small-scale tests which had been made upon higher-grade ore. However, with proper manipulation probably 93 per cent or more of the silver can be obtained with the lower-grade ore, and probably 96 per cent (indicated by the laboratory tests) could be closely approached with the higher-grade ore.

Gold recoveries were uniformly high for all the reduced samples, namely 99 per cent. Cyanidation of the raw ore recovered 85 per cent of the silver and 93 per cent of the gold.

Consumption of cyanide (3.82 kilograms per metric ton) for the reduced ore from these tests was considerably lower than that indicated (4.33 kilograms) by those made in 1918 and 1919.

The fuel consumption was the equivalent of 36 to 38 kilograms of Mexican crude oil per metric ton of dry ore, somewhat lower than was calculated, but the temperature of reduction was lower than that assumed in the calculation.

ORE FROM GUANACEVI MINE.

This ore is more or less a typical manganese-silver ore, and while not as refractory as some it is more representative of this type than is the Purisima ore. Cyanidation of the raw ore yielded 65 per cent of the silver and 77 per cent of the gold.

The recovery both of silver (90.5 per cent) and gold (99 per cent) corresponds closely with the results (91 and 99 per cent) obtained in the laboratory reduction tests made at or near the same temperatures. One small-scale test made at 700° C. showed a somewhat higher yield (92.8 per cent) of silver, but this was not checked by running the large kiln at this temperature. With this grade of ore—23.6 ounces of silver per ton—a recovery of 90 per cent or better could be expected in practice.

This ore, like that from the Purisima mine, used much less cyanide when reduced in the large than in the small kiln; however, the consumption (6.31 kilograms, or 12.63 pounds) is high both on the raw and reduced ore, largely due to the presence of zinc. It is probable that if a high alkalinity were maintained in the solutions the cyanide consumption would actually prove to be much lower than indicated here with fresh solution, because the double alkaline cyanide of zinc would be broken down to a considerable extent by the lime. There is also a possibility of working out a method of avoiding the difficulty occasioned by the zinc.

ELEVATION AND SECTION OF REDUCING KILN, SHOWING DETAILS OF PYROMETER INSTALLATION

The consumption of lime is much lower with the reduced ore than with the raw ore—namely, 4.9 kilograms (9.8 pounds) against 7.16 kilograms (14.32 pounds).

The fuel consumption, the equivalent of 60.8 kilograms of Mexican crude oil per metric ton of dry ore, was higher than with the Purisima and San Juan ores, but this increase was no doubt caused by the greater amount of higher oxides of manganese to be reduced. This corroborated the small tests.

ORE FROM SAN JUAN DE PACHUCA MINE.

Much of the ore from this mine is rather low in manganese and silver, but is a typical manganese-silver ore in that it gives a low recovery when treated raw by cyanide. The recovery from some of the reduced ore fell below the maximum (91.8 per cent) obtained in the laboratory, but this discrepancy could be overcome; in actual practice at least 89 per cent of the silver should be recovered. Cyanidation of the raw ore dissolved 60 per cent of the silver and 99 per cent of the gold.

Like the Purisima and Guanacevi ores, the San Juan also consumed less cyanide than is indicated by the small tests—namely, 0.76 kilogram (1.52 pounds) against 1.54 kilograms (3.08 pounds).

Fuel consumption, the equivalent of 41 to 42 kilograms of Mexican crude oil per metric ton of dry ore, was somewhat higher than with Purisima ore, largely owing to the higher temperatures employed, up to 675° C. (1,247° F.). The consumption of lime was 7.29 kilograms (15.58 pounds) per ton.

The strength of the cyanide solutions used, in terms of NaCN, varied from 0.1 to 0.3 per cent, but mostly 0.225 and 0.30 per cent.

HEAT REQUIREMENT.

Prior to erection of this plant the probable heat requirement was computed for reducing a typical manganese-silver ore of the Pachuca district, and its equivalent in kilograms of Mexican crude oil and cubic meters of oil producer gas per metric ton of ore treated. The known and assumed data used in making the calculation were as follows:

Water in ore, per cent.....	5
Manganese dioxide, per cent.....	3
Temperature of air, °C.....	20
Temperature of reduction, °C.....	720
Temperature of flue gas, °C.....	220
Boiling point of water at elevation of 8,500 feet, °C.....	91
Specific heat of silica.....	0.2543
Calorific value of Mexican crude oil.....	10,500
Thermal efficiency (reported) of gas producer, per cent.....	76.5

Calorific value of 1 cubic meter of oil producer gas.....	1, 272. 6
Molecular heat of formation of MnO_2	125, 300
Molecular heat of formation of MnO	90, 900
Specific heat of water.....	1. 0
Latent heat of vaporization of water, calories per kilogram	536
Specific heat of water vapor, per kilogram.....	$0.42 + (0.000185 \times t^\circ)$
Mean thermal capacity of carbon dioxide per cubic meter.....	$0.37 \times (0.00022 \times t^\circ)$
Mean thermal capacity of water vapor per cubic meter.....	$0.34 \times (0.00015 \times t^\circ)$
Mean thermal capacity of nitrogen per cubic meter.....	$0.303 \times (0.00027 \times t^\circ)$
Mean thermal capacity of air per cubic meter.....	$0.303 \times (0.00027 \times t^\circ)$
Calorific power of carbon monoxide, calories per cubic meter	3, 062

Analysis of the producer gas.

Constituent.	Per cent.	Cubic meters per 100 cubic meters of gas.
CO	15. 1	15. 1
H_2	4. 6	4. 6
CH_4	5. 4	5. 4
C_2H_2 (assumed to be ethylene, C_2H_4).....	1. 0	1. 0
CO_2	6. 2	6. 2
O_2	. 3	. 3
N_2	67. 4	67. 4

The calculated calorific power of this gas is 1,192 calories per cubic meter.

The following is a summary of the heat requirement per metric ton:

	Calories.
To heat 950 kilograms of ore from 20 to 720° C	169, 111
To heat water from 20 to 91° C	3, 500
To convert water into vapor.....	26, 800
To heat vapor to 220° C.....	2, 973
To reduce MnO_2 to MnO	11, 862
	<u>214, 296</u>
Heat loss in gas producer.....	100, 730
Heat loss in waste gases at 220° C. (CO_2).....	6, 620
Heat loss in waste gases at 220° C. (H_2O).....	3, 580
Heat loss in waste gases at 220° C. (N_2).....	26, 800
Heat loss through 20 per cent excess air at 220° C.....	3, 870
Heat loss through 1 per cent CO at 220° C.....	231
Heat loss through unburned CO.....	11, 470
Heat loss through conduction and radiation	60, 995
	<u>214, 296</u>
Total calories.....	<u>428, 592</u>

The net calories available from each cubic meter of producer gas were found to be 779; and as 214,296 calories are required for heating 1 metric ton of ore, $214,296 \div 779$, or 275.5 cubic meters of producer gas are required per metric ton of ore treated.

A. RECORDER CLOSED

B. RECORDER OPEN FOR CLEANING AND OILING

The calorific value of Mexican crude oil is 10,500 calories per kilogram, but only half of this heating value is available for heating the ore; therefore the useful calorific value becomes 5,250 calories, and $214,296 \div 5,250$, or 40.8 kilograms, of Mexican crude oil are required per metric ton. These calculations do not allow for the following factors: (1) Volume of gas required for reduction of MnO_2 to MnO ; (2) heat produced through oxidation of gas by MnO_2 ; and (3) recovery of heat in the cooling zone of the kiln. Regarding these, it is found (1) that the gas required per metric ton of ore containing 1 per cent of MnO_2 is 0.302 cubic meter; (2) that oxidation of gas by MnO_2 produces 360 calories; and (3) the recovery of heat in the cooling zone would yield 101,471 calories. This heat could be partly utilized by jacketing the cooler and passing the air through the jacket on its way to the burners. The saving effected by cooling the ore by the producer gas and air would amount to 35.6 per cent of the total heat required, 15.8 per cent of which would be taken up by the producer gas and 19.1 per cent by the air. Much steadier kiln operation would result with the air preheated than with it cold.

TREATMENT OF FLUE DUST.

The quantity of flue dust was extremely low, and the actual weight from several runs was as follows:

Quantity of flue dust recovered.

Dry weight of ore fed to kiln, metric tons.	Weight of flue dust, metric tons.	Per cent of ore fed to kiln.
29.977	0.136	0.45
33.050	.150	.45
25.338	.084	.33
27.850	.093	.33
89.216	.170	.19
98.35	.187	.21

As the recovery of both the silver and gold from raw and reduced flue dusts from Guanacevi and San Juan ores was low, a preliminary treatment with sulphur dioxide (SO_2) was tried to determine whether an improved extraction could be obtained. This treatment consisted of agitating the dust for two hours with the approximate amount of SO_2 required, followed by one-half hour with an excess of SO_2 solution. After the pulp was filtered and washed, the cyanide test (0.225 per cent NaCN) was made in the regular manner. Results are shown in the following table:

TABLE 39.—*Results of flue-dust treatment by reduction and SO₂.*

Treatment.	Extraction.		Consumption of chemicals, per ton.			
	Silver, per cent.	Gold, per cent.	Cyanide.		Lime.	
			Kilo-grams.	Pounds.	Kilo-grams.	Pounds.
Guanacevi, raw.....	50.9	60.6	7.89	15.78	9.09	18.19
Guanacevi, after reduction at 500 to 700° C....	76.8	52.6	6.27	12.54	10.51	21.01
Guanacevi, after SO ₂ treatment.....	66.7	52.7	4.12	8.23	22.47	44.94
San Juan, raw.....	41.8	72.8	.79	1.59	8.68	17.35
San Juan, after reduction at 500 to 700° C....	73.7	69.2	2.60	5.20	11.10	22.20
San Juan, after SO ₂ treatment.....	58.0	72.8	1.02	2.04	22.72	45.44

Probably the best way to handle the flue dust would be to moisten it and feed it to the furnace with the raw ore, as the extraction is much improved by reduction over what it would be if the flue dust were cyanided direct.

GENERAL CONCLUSIONS REGARDING THE MEXICAN ORES.

The tests made on a working scale proved these points:

1. The reduction process is entirely feasible, and it is probable that the results of the small tests can generally be equaled.

2. The fuel consumption is reasonable and is close to the theoretical quantity indicated by the heat balance calculated prior to the erection of the large unit.

3. The additional consumption of cyanide in actual practice will not be as great as that shown by the tests made in the laboratory equipment.

4. If a low fuel cost is assumed in plants having a capacity of 500 tons or more, the direct cost for many ores would be about 50 cents (United States currency) per metric ton and with extra cyanide consumption and amortization of plant included would fall within \$1 (United States currency) per metric ton. Costs would be correspondingly higher in small plants or in localities where fuel prices were high. But it should be remembered that these ores vary, and for certain ores that are high in manganese or have some other unfavorable property the fuel consumption might be greater, increasing the operating cost correspondingly. For example, a higher fuel consumption might be expected with the Guanacevi than with the San Juan ore.

5. It has been demonstrated that part of the fuel can be burned directly in the combustion chamber, thus directly utilizing it for preheating the ore and necessitating the conversion into gas of only that part of the fuel required for the reduction unit.

The one problem remaining unsolved is the oil-gas producer. What is required is a producer that operates continuously, making

gas of about 150 B. t. u. per cubic foot at the same or nearly the same thermal efficiency as the best types of coal-gas producers. It is important that all of the oil be converted into gas without carbon or tar by-product. An oil-gas producer of the Grine type was represented to be capable of meeting these requirements and was accordingly installed for making this large-scale demonstration, but its performance proved disappointing.

Two difficulties encountered with the gas producer used were (1) the impossibility of maintaining the coke bed at a high enough temperature and (2) the choking of this bed by finely divided carbon separating from the oil. Solution of the first difficulty seems to lie in operating the producer at a lower temperature, which would give a tar by-product but, under proper conditions, no carbon by-product. The tar could be recovered from the gas by well-known methods and burned directly in the combustion chamber between the kilns. Even at a lower operating temperature it appears necessary to supply outside heat to the producer in order to maintain the temperature of the bed, which can be done most effectively by preheating the air. If a reasonable degree of preheating proved effective, the sensible heat of the gas could be utilized, in a heat interchanger, to preheat the incoming air to the producer. This would require no extra fuel. The difficulty of fine carbon separating in the bed could probably be solved by depositing the oil directly on the coke bed without spraying with air or steam.

The Jones process of making gas from oil, as employed extensively in California, particularly by the Pacific Gas & Electric Co., could be used, but its thermal efficiency is not much above 50 per cent, its operation is intermittent, requiring a gas holder, and it gives both carbon and tar by-products. This process does not work so well with heavy residuum oil as it did with the lighter residuum oils formerly available. The fuel oil obtainable in Mexico is very heavy; therefore difficulties might arise, even with this well-established process of gas making.

The Dayton process for the manufacture of oil gas is practically continuous, and a high thermal efficiency is claimed for it. Briefly, the gas is made by injecting an intimate mixture of crude oil and air into small steel retorts. Any accumulation of carbon in the retorts is periodically removed by purging them with air; during such times the products of combustion go to the outside air, but with a large number of units the purging does not interfere with continuous gas making. A small gas holder is used to aid the control of the process and equalize inequalities of the gas flow. The air is heated by a heat interchanger in the gas line to about 175° C. (347° F.). The Dayton process can not be used with Mexican residuum oils because they are too high in free carbon. Although the development of an

oil gas-producer was not within the province of this investigation, enough data on the subject were obtained to indicate that this problem probably could be solved.

The reducing process for manganese-silver ores is firmly established for all fuels—including charcoal, coal, coke, and wood—that can be gasified in standard types of gas producers. With oil fuel, part of the oil can be burned directly in the combustion chamber to supply part of the heat needed for the preheating zone; but enough oil would have to be gasified to meet the requirements of the reducing zone.

GENERAL SUMMARY AND CONCLUSIONS.

The following general statements may be made regarding the problem of treating manganese-silver ores, and the particular application of the Caron process:

1. On account of the intimate association of the manganese and silver, all methods of concentration and direct lixiviation of the raw ore have been proved unsuitable; as are also all methods of lixiviation of ore calcined under oxidizing conditions.

2. The Caron process, in which the ore is heated in a reducing gas, the manganese dioxide changed to manganous oxide and kept from reverting by being cooled under reducing conditions or quenched in water or solution, and the silver thus freed recovered by cyanidation or other suitable method, has proved generally effective for the treatment of manganese-silver ores. Ores that contain antimony are the only exceptions that have been found so far.

3. Producer gas of 150 B. t. u. or higher, made from any fuel—coal, coke, wood, oil, or charcoal—may be used. Gas of higher grade can be used, and in some places might be found advantageous.

4. All of the fuel used can be gasified, or a part of it can be gasified to meet the requirement of the reducing zone and the remainder burned directly in a combustion chamber between the preheating and the reducing units of the kiln.

5. Although there are exceptions, most ores can be reduced in a coarse condition—that is, in sizes from 1 to 2 inches.

6. It is necessary to establish the best temperature of reduction for each ore by a series of tests. In general, this temperature is at some point between 500 and 700° C.

7. The percentage of unaltered manganese dioxide should be determined after the ore is calcined, and perhaps at a later stage in the cyanide treatment; this step might be said to be analogous to determining the sulphur and soluble sulphides in a roasted ore.

8. Proper control of alkalinity is important in cyaniding ores that have received this preliminary treatment.

9. The use of enough air during grinding and agitation is of value in neutralizing the mild reducing effect of the manganous oxide.

10. The silver extraction from ores yielding 60 per cent or lower by other methods may be increased to 88 to 96 per cent, depending on the character and grade of the ore.

11. The gold in some manganese-silver ores is amenable to direct cyanidation, and in such ores its extraction is not increased by reduction. In other ores the gold follows the silver, and is more or less refractory; in such ores the recovery of gold is increased to an even higher percentage than the silver.

12. Silver ores in general show a higher consumption of cyanide than gold ores. Manganous oxide is not a cyanicide, nor have we ever found manganese in the solution resulting from the treatment of a reduced ore. Some ores seem to consume no more cyanide after reduction than before, or no more than can be accounted for by the additional silver dissolved; other ores consume decidedly more cyanide after reduction. The increase has been found to be due to the presence of base metals in combination with manganese, like the silver. They are freed, like silver, by reduction, and are likewise dissolved by the cyanide solution.

13. The process can be most economically applied to daily tonnages of 200 or above. For lower tonnages the cost of installation and operating would be somewhat greater.

14. In a given locality the direct cost of the process would not differ greatly from the cost of dead roasting a low-sulphur ore.

BIBLIOGRAPHY OF THE TREATMENT OF MANGANESE-SILVER ORES.

1888.

1. GOODALE, CHARLES W. The occurrence of argentiferous manganese ores, Tombstone district, Arizona: Trans. Am. Inst. Min. Eng., vol. 17, 1888-89, pp. 767-778.

Describes treatment of argentiferous manganese ores of the Tombstone district by chloridization and amalgamation.

2. TRIPPEL, A. L. Manganiferous silver ores: Min. and Sci. Press, vol. 56-57, 1888, p. 238.

Discusses influence of addition of sulphur compounds such as FeSO_4 and FeS upon the chloridizing roast of argentiferous silver ores preceding amalgamation.

1890.

3. GOODALE, CHARLES W. The occurrence and treatment of argentiferous manganese ores of Tombstone district, Arizona: Trans. Am. Inst. Min. Eng., vol. 18, 1889-90, pp. 910-913.

Concludes that only the earthy manganese ores foul mercury and that their character may be changed by roasting.

1900.

- 4-6. MINING AND SCIENTIFIC PRESS. Silver manganiferous iron ore: Vol. 80, Jan. 13, 1900, p. 40.

Gives tonnages of silver-bearing manganese-iron ores shipped from Leadville, Colo., from 1890 to 1898 to lead smelters and steel mills.

7. COLLINS, H. The metallurgy of lead and silver (textbook). London, 1900.

Contains note of effect of manganese oxides on pan amalgamation of silver ores.

1902.

8. JOHNSON, E. C., and CALDECOTT, W. A. Effects of MnO_2 in refining zinc-gold slime: Proc. Chem. Met. Soc. of South Africa, vol. 3, 1902-3, p. 52.

Note on tendency of MnO to carry Ag into slag.

9. ROSE, T. K. Retention of silver by slags: Proc. Chem. Met. Soc. of South Africa, vol. 3, 1902-3, p. 60.

Retention of Ag by slags containing much Mn is probably due to the action of silicates or sesquioxides of manganese.

10. TAVENER, P. S. The lead smelting of zinc-gold slimes: Proc. Chem. Met. Soc. of South Africa, vol. 3, 1902-3, p. 125.

Calls attention to the tendency of MnO_2 to drive silver into the slag when the direct method of smelting without lead is used.

1903.

11. PEARCE, R. Discussion on "Cyaniding of some silver ores by percolation"; paper by A. P. Griffin and F. W. Oldfield: Trans. Inst. Min. and Met., vol. 12, 1902-3, pp. 449-450.

Describes experiments at a Butte mill in treating psilomelane ores. Addition of metallic sulphides aided amalgamation.

1908.

12. LINTON, ROBERT. Detrimental effect of manganese in Mexican silver ore treatment: Jour. Chem. Met. Min. Soc. of South Africa, vol. 9, 1908-9, pp. 51-52.
States the problem and calls attention to the inefficiency of ordinary methods of treatment.
13. ——— Preliminary treatment of manganiferous silver ores: Jour. Chem. Met. Min. Soc. of South Africa, vol. 9, 1908-9, pp. 307-308.
Experiments show preliminary chloridizing followed by cyanidation yielded best results.
14. GREENWOOD, H. C. Reduction temperature of manganous oxide: Trans. Chem. Soc., 1908, pp. 1491-1492.
Discusses reduction of higher oxides of manganese by hydrogen to MnO and its characteristics.

1909.

15. HAMILTON, E. M. Cyanidation of Mexican manganese-silver ores: Jour. Chem. Met. Min. Soc. of South Africa, vol. 10, 1909-10, pp. 65-67.
Discusses preliminary treatment by chloridizing alkaline sulphides and H_2S , HCl, roasting with S in absence of air and SO_2 .

1910.

16. HAMILTON, E. M. Cyanidation of manganese-silver ores: Discussion in Min. and Sci. Press, vol. 100, 1910, p. 229.
Discusses effect of presence of manganese in silver ore.

1911.

17. COGHILL, W. H. Refractory manganese ores: Min. and Sci. Press, vol. 104, 1912, pp. 754-758, 794-797.
Describes experiments on ores from Arizona and Mexico with preliminary treatment by various methods.
18. ENGINEERING AND MINING JOURNAL. Cyaniding manganiferous ore: Vol. 91, 1911, pp. 601-602.
Discusses effect of Mn upon cyanide consumption.
19. MINING AND SCIENTIFIC PRESS. Manganiferous silver ores: Vol. 102, 1911, p. 656.
Discusses occurrence and utilization of Mn-Ag ores.
20. REID, A. F. Cyaniding manganiferous ore: Eng. and Min. Jour., vol. 91, 1911, p. 995.
Describes experiments on ore from Kimberley, Utah, in which the MnO_2 did not affect KCN consumption.
21. HOLLOWAY, G. T. Notes on the valuation of ores and minerals and on metallurgical calculations, with a note on manganiferous silver ores: Trans. Inst. of Min. Met., vol. 21, 1911-12, p. 574.
Discusses occurrence and utilization of Mn-Ag ores.
22. JACKSON, BYRON. Experimental work on manganese-silver ore: Min. and Sci. Press, vol. 104, 1912, p. 732.
Discusses various methods of treatment and calls attention to the effect of organic matter.

1913.

- 23-24. JOURNAL OF THE CHEMICAL METALLURGICAL AND MINING SOCIETY OF SOUTH AFRICA. Note on some manganese-silver ores altogether untreatable by cyanide process: Vol. 14, 1913-14, p. 329.
No new information.

1916.

25. NEAL, WALTER. The manganese-silver problem: Jour. Chem. Met. Min. Soc. of South Africa, vol. 17, 1916, pp. 9-18. Reprinted in Min. and Sci. Press, vol. 114, 1917, pp. 158-159.

Thorough discussion of the problem based upon experimental results.

26. WARTENWEILER, F. Discussion of paper by Walter Neal: Jour. Chem. Met. Min. Soc. of South Africa, vol. 17, pp. 70-71.

Discusses the recovery of silver from a tailing containing pyrolusite by a chloridizing roast, followed by leaching with a brine solution charged with chlorine.

27. WHITE, H. A. Discussion of paper by Walter Neal: Jour. Chem. Met. Min. Soc. of South Africa, vol. 17, 1916, pp. 39-41.

Discusses experimental results obtained on synthetic mixtures and suggests that MnO_2 might be reduced at a low temperature by CO.

28. CALDECOTT, W. A. Discussion of paper by Walter Neal: Jour. Chem. Met. Min. Soc. of South Africa, vol. 17, 1916, p. 100.

States that the refractory silver mineral may be silver silicate formed by the oxidation by the MnO_2 of metallic silver to silver oxide, which combines with the silver, but White states that he can not confirm this.

1917.

29. CARON, M. H. Process for extracting gold and silver from ore containing gold, silver, and manganese dioxide. United States Patent 1232216, July 3, 1917.

The ore is given a reducing roast and cooled in a reducing atmosphere or by quenching in water, and the silver and gold recovered by amalgamation or cyanidation.

30. VERMAES, S. H. Treatment of refractory manganese ores containing precious metals or silver alone. United States Patent 1234426, July 24, 1917.

Mixing the ore with a reducing agent and a chlorinating agent, roasting at a comparatively low temperature or at a temperature insufficient to volatilize silver chloride out of contact with air and leaching the roasted product with a solution of alkaline cyanide.

31. VADNER, C. T. Recovering manganese and other metals from ores: United States Patent 1236236, August 17, 1917.

Preliminary treatment with SO_2 followed by brine leaching.

1918.

32. HERSAM, E. A. The possible treatment of manganese ores in California: University of California Publications in Engineering, vol. 2, No. 1, March 26, 1918, 56 pp.

Discusses possibilities of recovering manganese by chemical treatment; reviews patents.

1919.

33. CARON, M. H. Process for extracting silver from ore. United States Patent 1298454, March 25, 1919, assigned to Research Corporation, New York.

Covers details not dealt with in Caron United States patent 1232216.

1920.

34. CARPENTER, Jay A. Recovery of silver from manganese-silver ores: Eng. and Min. Jour., vol. 110, 1920, pp. 898-902.

Reviews various methods of preliminary treatment and discusses chloride volatilization.

35. AUSTIN, L. W. Treating manganese-silver ores: United States Patent 1327974, January 13, 1920.

Ore is given preliminary treatment with iron pyrite in presence of sulphuric acid, followed by recovery of precious metals by suitable methods.

1921.

36. CLEVINGER, G. H. Apparatus for treating ores or the like. Twenty claims: United States Patent 1379083, May 24, 1921.

Described in detail in this bulletin.

1922.

37. FAIRLIE, M. F., and DENNY, J. J. Process of treating manganiferous ores of the precious metals: United States Patent 1417153, May 23, 1922.

Describes process involving preliminary treatment with metallic iron and sulphuric acid, separating the treated ore, and subjecting it to cyanidation.

INDEX.

A.		Page	Caron process—Continued.		Page
Acids, solubility of silver compounds in....		12	possibilities of.....		39
Agitators, discussion of.....		53	small-scale tests of, apparatus for.....		48
Air, excess in Caron process, importance of..		47	average recoveries in.....		55
<i>See also</i> Manganous oxide, reoxidation.			success of.....		100
Alkali oxalates, as reducing agent for man- ganese oxides.....		10	<i>See also</i> Air, excess of; Gas producers; Re- duction.		
Alkali sulphides, solubility of silver sulphites in.....		12	Carpenter, J. A., acknowledgment to.....		8
Ammonia, as solvent for silver compounds..	11, 12		work cited.....		104
Antimony, interference in Caron process..	2, 48, 100		Castle, Mont., manganese-silver ores from, analysis of.....		6
Argentous oxide, solubility with different reagents.....		12	Chloride volatilization, formation of silicates in.....		20
Arizona, manganese-silver ores, shipments of.	7		Chloridized ore, calcining tests of.....		28
<i>See also</i> Hardshell ore; Pearce, Ariz.			Chloridizing roast tests, discussion of.....		26
Austin, L. W., patent cited.....	10, 105		reducing atmosphere in, discussion of....		30
B.			results of.....		29
Baeyer, Adolf, work cited.....	12		results of.....		28
Bell, I. L., work cited.....	40		wet, discussion of.....		31
Bernewitz, M. W. von, acknowledgment to..	4		Cia de Real Del Monte y Pachuca, acknowl- edgment to.....		5
Berthelot, P. M. E., work cited.....	14		Clevenger furnace, description of.....	88-91	
Bibliography on ore treatment.....	101		features of.....		2
Blower, view of.....	60		operation of, diagram of.....		90
Bouton, C. M., work cited.....	20		preheating kiln for, view of.....		92
Brunner, C., work cited.....	32		temperature measurements for.....		91
Buffalo-Hunter mine, concentrate from, analysis of.....	80		tests with.....	93-95	
reduction tests of, data on.....	80,		Clevenger, G. H., patent cited.....	3, 105	
	81, 83, 84, 86, 87		work cited.....	32	
ore from, characteristics of.....	22, 25, 37, 41, 60		Coghill, W. H., work cited.....	10, 12, 21, 26, 33, 103	
Bugbee, E. E., work cited.....	22		Collins, H., work cited.....	102	
Butte, Mont., manganese-silver ores at.....	6		Colorado, manganese-silver ore shipments from.....		7
ore from, reduction tests of, results of..	74		<i>See also</i> Colorado Springs; Leadville; Neihart; San Juan region.		
C.			Colorado School of Mines, acknowledgment to.....		4
Calcining. <i>See</i> Chloridized ore.			Colorado Springs, experimental plant at, details of.....	57-60	
Calcining plant, plan and elevation of.....	88		Comey, A. M., work cited.....	11, 12	
Caldecott, W. A., work cited.....	102, 104		Concentration tests, manganese-silver ores, discussion of.....	21, 22	
Calland, D. S., acknowledgment to.....	5		Connolly, S. J., acknowledgment to.....	4	
Candelaria district, Nev., manganese-silver ores from, analysis of.....	8		Cooler, Clevenger furnace, description of....	90	
occurrence of.....	7, 8		reducing kiln, view of.....	93	
Carbon, reduction of manganese oxides by..	39		rotary furnace, detail of.....	58	
Carbon monoxide, reduction of manganese oxides by.....	39		view of.....	56	
comparison with hydrogen, curves showing.....	41		Copper, as interference in Caron process....	48	
Caron, M. H., patent cited.....	3, 104		Croasdale, Stuart, work cited.....	32	
Caron process, basis for.....	2		Crude oil, Mexican, calorific value of.....	97	
chemistry of, discussion of.....	36		Cyanidation, chief factors in.....	55	
costs for, discussion of.....	98		temperature for, importance of.....	45	
cyanidation in, discussion of.....	47		data on.....	46	
experimental plant for, flow sheet of.....	60		tests of, apparatus for.....	53	
heat requirements, ways of meeting.....	100		description of.....	54	
interference of base metals in.....	48		<i>See also</i> Caron process.		
investigations of, patent difficulties re- tarding.....	3		Cyanidation plant, view of.....	61	
large scale tests of, conclusions from.....	98		Cyanide. <i>See</i> Gold; Potassium cyanide; Silver, ores of.		
description of.....	55-60				

D.		H.	
	Page		Page
Dayton process for making oil gas, dis- advantage of.....	99	Hamilton, E. M., work cited.....	5, 21, 26, 31, 32, 105
Delft, Holland, ore-cooling experiments at..	45	work of.....	1
Denny, J. J., patent cited.....	10, 105	Harder, E. C., work cited.....	6
Desplantes, G., work cited.....	12	Hardshell ore, preliminary crushing of.....	37
Disk feeder, views of.....	60, 93	Harris, G. W., acknowledgment to.....	5
Duschak, L. H., work cited.....	20	Harrison, E. J., acknowledgment to.....	5
Dutch East Indies. <i>See</i> Gedang Ilir mine; Netherlands.		Head, R. E., work cited.....	8
E.		Heat requirements. <i>See</i> Caron process; Pa- chuca, Mexico.	
Eagle County, Colo., manganese-silver ore in, occurrence of.....	7	Hersam, E. A., work cited.....	104
Ebell, P., work cited.....	13	Holloway, G. T., work cited.....	103
Electrostatic separator. <i>See</i> Huff separator.		Huff electrostatic separator, tests with.....	25
El Favor mine, ore from, characteristics of...	76	Hydrogen, reduction of manganese oxides by. 39, 40 comparison with carbon monoxide, curves showing.....	41
recovery from.....	22, 25	Hydrogen peroxide, reduction of manganese oxides with.....	10
reduction tests of, data on.....	75	J.	
Elkoro ore, cyanidation tests of, data on....	78	Jackson, Byron, work cited.....	103
preliminary treatment for.....	76	Jalisco, Mexico, ore from.....	21, 22
reasons for.....	76	Japan, manganese-silver ores in, occurrence of	9
results of, discussion of.....	79	Jenison, H. A. C., work cited.....	7
Embury, G. S., acknowledgment to.....	5	Johnson, C. E., work cited.....	102
Emmons, W. H., work cited.....	6	Jones process for oil gas, disadvantages of....	99
F.		K.	
Fairlie, M. F., patent cited.....	10, 105	Knopf, Adolphe, work cited.....	7
Feeder, for rotary furnace, plan of.....	58	Kuryla, M. H., acknowledgment to.....	5
view of.....	56, 60	L.	
<i>See also</i> Disk feeder; Shaking feeder.		Lake Valley, N. Mex., manganese-silver ores in, occurrence of.....	7
Ferrous sulphate, as reducing agent for manganese oxides.....	10	Leadville, Colo., district, manganese-silver ores in, occurrence of.....	6
Fischer, W. J., acknowledgment to.....	5	Lier, R. J., van, acknowledgment to.....	4, 5
Flotation tests of manganese-silver ores, dis- cussion of.....	22	Linton, Robert, work cited.....	31, 103
results of.....	23	Luff, A. P., work cited.....	39, 42
Flue dust, quantity recovered.....	97	M	
treatment of.....	98	McDougall furnace, use of.....	43, 55
Furnace. <i>See</i> Clevenger furnace; McDougall furnace.		MacLaurin, J. S., work cited.....	11
G.		Magnetic separation, disadvantages of.....	25
Gas holder for Caron process, description of..	49	tests of, discussion of.....	22
Gas producers for Caron process, discussion of.....	58	Magnetic separator. <i>See</i> Wetherill separator.	
laboratory size, operation of.....	50	Manganese, higher oxides of, solvents for.....	10
types of, discussion of.....	99	<i>See also</i> compounds named.	
view of.....	60, 92	Manganese dioxide, heated with metallic silver, data on.....	15
Gedang Ilir mine, description of.....	61	discussion of.....	16, 20
ore from, analyses of.....	61	heated with silica and metallic silver, data on.....	18
characteristics of.....	22, 23, 24, 25, 27, 29, 37, 39, 40, 42, 60, 61	discussion of.....	19, 20
reduction tests of, data on.....	62, 64, 65, 66, 67, 68, 70, 72	in silver ores, solvents for.....	11
sizing tests of.....	21	preparation of.....	14
volatilization tests of.....	30	reduction of, discussion of.....	39, 42
Gmelin-Kraut, work cited.....	42	equations showing.....	38
Gold ores, cyanide consumption by.....	101	temperatures for.....	39
Goodale, C. W., work cited.....	26, 102	stability of.....	14, 16
work of.....	1	Manganese-gold ores, occurrence of.....	6-9
Gorgen, A., work cited.....	13	Manganese ores, refractory silver in, relation of.....	10
Greenwood, H. C., work cited.....	103	Manganese oxides, determination of, appa- ratus for.....	52
Guanacevi mine, ore from, analysis of.....	93	method for.....	52
reduction tests of.....	94	silver minerals in, nature of.....	6
sizing tests of.....	93	<i>See also</i> Alkali oxalates.	

	Page		Page
Manganese-silver compounds, formation of.....	13	Potassium nitrate, solubility of metallic silver in.....	11
Manganese-silver ores, occurrence of.....	5, 6	Producer gas, analysis of.....	96
reduction methods for, discussion of.....	10	possible use of.....	100
<i>See also</i> Reduction.		<i>See also</i> Gas producers.	
tests of, summary of.....	1	Purissima mine, ore from, analysis of.....	93
solubility of silver in.....	11	reduction tests of.....	94
Manganose-manganic oxide, reduction temperatures for.....	39	sizing tests of.....	93
Manganous oxide, reduction temperatures for reoxidation of, conditions for.....	44	Pyrite, as reducing agent for manganese dioxide.....	10
exposure to air on, effect of.....	45	Pyrolusite. <i>See</i> Manganese dioxide.	
prevention of.....	43	Pyrometer used in Caron process, type of.....	49
temperature of, effect of.....	47	details of.....	94
data on.....	46		
Matignon, C., work cited.....	12	R.	
Mercury, solubility in, metallic silver.....	12	Recorder, temperature measurements, view of.....	96
silver compounds.....	11, 12	Reducing agents. <i>See</i> Alkali oxalates; Carbon; Carbon monoxide; Ferrous sulphate; Hydrogen; Hydrogen peroxide; Pyrite; Sodium oxalate.	
Metallic silver. <i>See</i> Manganese dioxide; Silica; Silver.		Reducing drum, operation of.....	51
Mexico, manganese-silver ores in, occurrence of.....	8	view of.....	48
<i>See also</i> Crude oil; Guanacevi mine; Jalisco; Minas Prietas; Pachuca; Purissima mine; San Juan de Pachuca mine.		Reducing kiln, details of, views of.....	92, 93
Meyer, R. J., work cited.....	42	Reduction, in Caron process, completeness of test for.....	51
Minas Prietas, Mexico, ore from.....	21, 32	products of.....	38
Miyazaki, Torarch, acknowledgment to.....	9	size of ore for, importance of.....	37
Moissan, Henri, work cited.....	12, 38, 42	temperatures of, importance of.....	52
Montana. <i>See</i> Butte; Castle.		effect in dry carbon monoxide of.....	39
Moore, C. F., acknowledgment to.....	5	effect in dry hydrogen of.....	40
Moore, R. B., acknowledgment to.....	4	high and low, results with.....	45, 46
Morse, H. W., work cited.....	14	initial.....	39
Mulock, F. S., acknowledgment to.....	4	tests of, weights used in.....	61
		equipment for, plan of.....	48
N.		<i>See also</i> Buffalo-Hunter concentrate; Butte, Mont.; El Favor; Elkoro; and Gedang Ilir ores.	
Neal, Walter, work cited.....	5, 25, 26, 33, 104	time required for, importance of.....	52
Neihart, Cascade County, Colo., manganese silver ores from, analyses of.....	6	Reid, A. F., work cited.....	103
Netherlands East Indies Government, cooperation with.....	2	Reoxidation. <i>See</i> Manganous oxide.	
Nevada, manganese-silver ore shipments from.....	7	Research Corporation of New York, work of.....	3, 4
<i>See also</i> Candelaria district.		Riddell, W. C., work cited.....	20
New Mexico, manganese-silver ore shipments from, statistics on.....	7	Roetgers, Kurt, work cited.....	42
<i>See also</i> Lake Valley; Silver City.		Rose, H., work cited.....	13, 102
New Zealand, manganese-silver ores in, occurrence of.....	9	Rotary furnace, externally fired, description of.....	59
Nitric acid, as solvent for silver compounds.....	11, 12	view of.....	56
		internally fired, description of.....	57
O.		operation of.....	59
Oldright, G. S., work cited.....	8	plan and elevation of.....	58
Ore, size of, importance of.....	52	view of.....	56
		<i>See also</i> Cooler; Feeder.	
P.		S.	
Pachuca, Mexico, reduction tests at, description of.....	11, 88-98	San Juan de Pachuca mine, ore from, analysis of.....	93
<i>See also</i> San Juan de Pachuca.		reduction of, heat requirements for.....	95
Pearce, Ariz., manganese-silver ores at, occurrence of.....	77	reduction tests of.....	95
Pearce, R., work cited.....	102	sizing tests of.....	93
Percy, John, work cited.....	13	San Juan region, Colo., manganese-silver ores in, occurrence of.....	7
Portland Gold Mining Co., acknowledgment to.....	4	Shaking feeder, view of.....	93
Potassium cyanide, solubility of silver and its compounds in.....	11, 12	Silica, heated with metallic silver, behavior of, data on.....	17
		discussion of.....	1, 17, 20
		<i>See also</i> Chloride volatilization; Manganese dioxide.	

	Page		Page
Silver, chemically pure, preparation of.....	14	Sulphurous acid, recovery of silver with.....	32
extraction of, temperatures during, effect		solubility of manganese oxides in.....	10
of.....	46	Sumatra. <i>See</i> Gedang Ilir mine, ore from.	
in manganese ores, solvents for.....	11		T.
metallic, solubility with different reagents			
of.....	10, 11, 12	Tavener, P. S., work cited.....	102
<i>See also</i> Manganese dioxide; Silica.		Taylor, G. M., acknowledgment to.....	4
ores of, cyanide consumption for.....	101	Temperature measurements, equipment for,	
refractory minerals of, nature of.....	20	view of.....	92
relation to manganese in ore of.....	10	method for.....	91
solubility in cyanide solutions of, curves		Temperatures. <i>See</i> Manganous oxides, reoxi-	
showing.....	19	dation; Pyrometer; Reduction.	
Silver chloride, solubility with different		Thie, A. H. J., acknowledgment to.....	4, 5
reagents of.....	11	Tippett, J. M.: acknowledgment to.....	4
Silver City, N. Mex., manganese-silver ore		Tombstone, Ariz., manganese-silver ores at,	
in, occurrence of.....	7	occurrence of.....	7
Silver manganite, formation of.....	13	Trippel, A. L., work cited.....	102
Silver oxide (Ag_2O), solubility of.....	12		U.
reaction with manganese sulphate.....	13	United States. <i>See</i> States named.	
Silver peroxide, solubility of.....	12	United States Smelting & Refining Co.,	
Silver silicate, formation of.....	13, 38	acknowledgment to.....	5
Silver sulphite, solubility of.....	12	Utah, manganese-silver ore, shipments from.....	7
Silver thiosulphate, solubility of.....	12		V.
Sizing tests, manganese-silver ores, results of.	21		
Smith, J. E., acknowledgment to.....	5	Vander, C. T., work cited.....	104
Sodium chloride, solubility of silver com-		Vermaes process, description of.....	34
pounds in.....	11, 12	Vermaes, S. H., patent cited.....	34, 104
Sodium oxalate, as reducing agent for silver		Villiger, Victor, work cited.....	12
compounds.....	10	Volatilization losses, during chloridization.....	28
solubility of manganese dioxide in.....	11	Volatilization tests, results of.....	30
Sodium thiosulphate, solubility of silver com-		<i>See also</i> Chloride volatilization.	
pounds in.....	11, 12		W.
Solvents. <i>See</i> Alkali sulphides; Ammonia;		Wad, definition of.....	5
Nitric acid; Potassium cyanide;		Wartenweiler, F., work cited.....	104
Potassium nitrate; Sodium chlo-		Water, solubility of silver compounds in.....	11, 12
ride; Sodium oxalate; Sodium thio-		Wetherill separator, tests with, results of.....	24
sulphate; Sulphur dioxide; Sul-		White, H. A., work cited.....	104
phuric acid; Sulphurous acid;		Wood alcohol, solubility of silver in.....	11
Water; Wood alcohol.		Wright, C. R. A., work cited.....	39, 42
Stas, Jean-Servais, work cited.....	13		Y.
Sulphidizing tests, wet, discussion of.....	32	Young, H. W., acknowledgment to.....	4
Sulphur dioxide, solubility of manganese			
dioxide in.....	11		
of silver compounds in.....	11		
Sulphuric acid, recovery of silver with.....	33		
solubility, of manganese oxides in.....	10, 11		
of silver in.....	11, 12