~~UNCLASSIFIED~~ ~~SECRET~~

This document consists of 50 pages
No. 56 of 65 copies, series A

Battelle Memorial Institute

~~CONFIDENTIAL~~

5 0 5 K I N G A V E N U E C O L U M B U S I , O H I O

February 9, 1955

BMI-279

CLASSIFICATION CHANGED TO CONFIDENTIAL
DATE <u>11-2-56</u>
<u>H. F. Canale</u> Chief, Declassification Branch

Classification cancelled (or changed to)

~~CONFIDENTIAL~~

by authority

by

TLCA, date

Dr. George G. Marvin
Assistant Director
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Dr. Marvin:

Attached to this letter is our final report, BMI-279, dated January 31, 1955, on "Nonaqueous Extractive Methods for Western Uranium Ores". A separate report (BMI-280) is being submitted on the pilot-plant phase of the project.

Very truly yours,

A. E. Bearse

A. E. Bearse
Division Chief
Chemical Research

This document contains Confidential-
restricted data relating to civilian
application of atomic energy.

AEB/NLC

Classification cancelled (or changed to) UNCLASSIFIED

by authority

by

Reith H. Kerr

11-16-56

AEC RESEARCH REPORT

~~RESTRICTED DATA~~

~~UNCLASSIFIED~~

This document contains restricted data as defined in the Atomic Energy Act of 1954. Its transmittal or disclosure of its contents in any manner to an unauthorized person is prohibited.

059 001

~~CONFIDENTIAL~~

1 8:54

1 8:54

R E S E A R C H F O R I N D U S T R Y

~~SECRET~~

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

UNCLASSIFIED

SECRET

Report No. BMI-279
Metallurgy — Raw Materials

3 and 4

3

CONFIDENTIAL

FINAL REPORT

on

NONAQUEOUS EXTRACTIVE METHODS FOR
WESTERN URANIUM ORES

to

U. S. ATOMIC ENERGY COMMISSION

by

R. A. Ewing, S. J. Kiehl, Jr., and A. E. Bearse

January 31, 1955

Contract No. AT-(49-1)-635

BATTELLE MEMORIAL INSTITUTE

505 King Avenue
Columbus 1, Ohio

059 2
UNCLASSIFIED

SECRET

CONFIDENTIAL

~~SECRET~~

5 and 6

~~UNCLASSIFIED~~

Report No. BMI-277

Metallurgy — Raw Materials

~~CONFIDENTIAL~~

Distribution — Series A

Copy No.

Allied Chemical and Dye Corporation	1
Arthur D. Little, Inc.	2
Argonne National Laboratory	3 - 4
Atomic Energy Commission, Washington	5 - 6
Battelle Memorial Institute	7 - 12
Bureau of Mines, Salt Lake City	13
Carbide and Carbon Chemicals Company (K-25 Plant)	14
Carbide and Carbon Chemicals Company (ORNL)	15 - 18
Chicago Patent Group	19
Columbia University (Hassialis)	20 - 21
Division of Raw Materials, Washington	22 - 28
Dow Chemical Company, Pittsburg	29
General Electric Company, Richland	30 - 33
Grand Junction Operations Office	34 - 37
Hanford Operations Office	38
International Minerals and Chemical Corporation	39
Iowa State College	40
Los Alamos Scientific Laboratory	41
Mallinckrodt Chemical Works	42
National Lead Company, Inc. (Winchester)	43 - 44
National Lead Company of Ohio	45
New Brunswick Laboratory	46
New York Operations Office	47
Patent Branch, Washington	48
Rohm and Haas Company, Philadelphia	49
Tennessee Valley Authority (Walthall)	50
Texas City Chemicals, Inc.	51
U. S. Geological Survey	52 - 53
University of California Radiation Laboratory, Berkeley	54
Virginia-Carolina Chemical Corporation	55
Technical Information Service, Oak Ridge	56 - 65

~~UNCLASSIFIED~~

~~CONFIDENTIAL~~

~~SECRET~~

~~SECRET~~

7 and 8

7

~~UNCLASSIFIED~~

~~CONFIDENTIAL~~

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION.	9
SUMMARY	11
EXPERIMENTAL DETAILS AND DISCUSSION OF RESULTS . . .	15
HCl-Acetone Process	15
Extraction of Uranium From the Ore.	15
Recovery of Uranium From Leach Liquors.	35
Nonaqueous Extraction With Other Solvents.	41
High-Temperature Chlorination	44
RECOMMENDATIONS FOR FUTURE WORK	46

APPENDIX

Analyses of Ores	47
List of Related Reports	47

~~UNCLASSIFIED~~

059 003

~~SECRET~~

~~CONFIDENTIAL~~

~~SECRET~~

9

UNCLASSIFIED
Report No. BMI-279
Metallurgy - Raw Materials

NONAQUEOUS EXTRACTIVE METHODS FOR WESTERN URANIUM ORES

by

R. A. Ewing, S. J. Kiehl, Jr., and A. E. Bearse

~~CONFIDENTIAL~~

Outstanding settling rates and high extractions of uranium have been obtained with Western ores in hydrochloric acid-acetone systems; no sliming problems exist in such systems. Sulfuric acid can be partially substituted for hydrochloric acid, up to equivalency with the limestone present, without seriously affecting uranium extraction or settling rates.

The uranium may be recovered from the acetone leach liquor by neutralization with anhydrous ammonia to produce a primary precipitate containing from 3 to 7 per cent uranium. After removal of the bulk of the chlorides by washing or calcination, and removal of the vanadium by a ferric vanadate precipitation, a uranium concentrate containing 60 per cent U_3O_8 or over may be produced.

Uranium and vanadium have been volatilized from Western ores by high-temperature vapor-phase chlorination, using either Cl_2 at about $1000^{\circ}C$., or CCl_4 at $600^{\circ}C$. Removals of from 95 to 98 per cent have been attained.

Dissolution of carnotite in several readily liquefiable gases, including ammonia, sulfur dioxide and trioxide, nitrogen dioxide, and chlorine, was found to be negligible, even in the presence of uranium complexing agents. No low-boiling liquids were found which would dissolve carnotite directly.

INTRODUCTION

The Western uranium-bearing ores contain a variety of uranium minerals, of which the predominating one is carnotite (potassium uranyl vanadate). These ores are currently processed by hydrometallurgical methods to recover both uranium and vanadium. An important complicating factor in this processing is the tendency of the ores to slime, which results in serious thickening and filtration problems.

At the request of the Division of Raw Materials, the possibilities of overcoming the sliming problem by nonaqueous extractive methods were investigated at Battelle Memorial Institute. In view of the importance of solvent recovery, the range of solvents tested was limited to readily liquefiable gases and low-boiling liquids, either of which could be recovered

UNCLASSIFIED ~~SECRET~~

~~CONFIDENTIAL~~

SECRET

10

readily by volatilization. The original objective was to discover a solvent of this type which would extract uranium directly from Western ores. This goal was never realized, and it was soon apparent that a more drastic attack, such as with a mineral acid, was needed to first solubilize the uranium, after which it could be readily extracted by a number of low-boiling solvents. Extension of this approach culminated in the development of the hydrochloric acid-acetone process. Because of the outstanding settling rates which can be realized in acetone systems, the sliming problem is eliminated.

Simple solid-liquid separation devices, such as classifiers, are therefore applicable, and filtration is unnecessary. Another feature of the process is the low retention time, which makes possible high throughputs in moderate-sized equipment. The process can utilize equipment generally similar to types now in use. Except for the intensified corrosion problem, the process resembles current aqueous methods. Uranium extractions as good or better than those obtained with current methods are attainable. Recovery of the uranium from acetone leach liquors can be accomplished by straightforward chemical procedures, yielding a high-grade concentrate suitable for a refinery feed.

The other nonaqueous extractive method investigated comprises volatilization of the desired metal values by a high-temperature vapor-phase chlorination, employing either Cl_2 or CCl_4 vapors. This method produces uranium extractions comparable to those from the HCl -acetone leaching process, and substantially better vanadium extractions. Temperature requirements are high, 600 to 1000°C. Consumption of chlorinating agent is also high, since no possibilities exist for the substitution of a cheap radical, such as sulfate, for the more expensive chloride radical, as in the leaching process. Equipment needs for the process would be unlike those of any plant now operating on Western ores. The indications are that this would be the higher cost process. Both vapor-phase chlorination and HCl -acetone leaching are essentially acid processes, and are not applicable to limestone ores.

After the complete HCl -acetone process had been blocked out in the laboratory, a pilot plant of about 100 lbs./hour capacity was erected, to demonstrate the proposed ore-processing cycle in continuous operation. This summary report covers only the laboratory phases of the investigation. The construction and operation of the pilot plant is described in a separate report*. A series of progress reports, the most recent of which was BMI-278, covers the earlier work on this project in greater detail.

*BMI-280.

SECRET

SECRET

11

SUMMARY

Through laboratory work at Battelle, a simple process involving hydrochloric-sulfuric acid treatment, followed by acetone extraction, has been developed for the recovery of uranium from Western ores. Since considerable processing capacity for materials of high uranium content exists at the present time, the emphasis in this work was placed on developing a method for efficiently concentrating, by chemical means, ores that might be available in relatively small quantities and at remote locations. Subsequent work may demonstrate the feasibility of applying the acetone leaching process on a larger scale.

The extractive solvent selected was acetone, partly because it has a high solubility for uranium and vanadium chlorides, but primarily because with its use, remarkable agglomeration and settling behavior can be obtained in the presence of calcium chloride; under the proper conditions any fine ore particles agglomerate, and the resulting aggregates settle equally as rapidly as do coarse ore particles. The over-all settling rate is very high, nearly instantaneous in some instances, and the supernate is clear and free of suspended fines.

The evidence suggests that the settling phenomenon is the result of a preferential wetting of the ore particles by a small amount of water, and is dependent on the presence of a concentrated solution of CaCl_2 resulting from the reaction between HCl and the limestone content of the ore. The mechanism is largely independent of particle size, and very rapid settling rates are attainable even with minus 325-mesh ore. The dissolved metal values are readily extracted by acetone, in which the CaCl_2 is relatively insoluble. Countercurrent washing of the acidulated ore should yield high recoveries, and filtration does not appear to be necessary. With the rapid settling rates attainable, the separation of liquid and solid phases is feasible in a continuous system in rather compact equipment at high throughput rates. In-process inventory would be at a minimum with this process.

Since the agglomeration and rapid settling appear to depend on the presence of CaCl_2 , the presence of some lime in the ore is necessary. However, not all of the CaCO_3 in an ore need be reacted with HCl ; the test data indicate that no more than perhaps 0.4 to 0.6 per cent CaCO_3 is needed to provide the CaCl_2 for satisfactory settling. All lime above this approximate level can be reacted with the cheaper sulfuric acid, without significantly affecting either settling rates or uranium extraction. Substitution of sulfuric for portions of the more expensive hydrochloric acid can reduce acid costs materially, especially for the higher lime ores. Complete substitution is not possible, since the desired agglomeration is absent, and since uranyl sulfate is only very slightly soluble in acetone.

SECRET

SECRET

12

The initial step in the process, that of solubilization of the uranium, is readily accomplished by attack with an aqueous mineral acid, either HCl, or HCl + H₂SO₄. Owing to the importance of the water content of the acetone leach solution with respect to agglomeration of the solid phase, the acidulation is preferably done with concentrated acid, so that the acidulated ore is just damp. Most of the Western ores are quite amenable to acid attack, and treatment conditions required are quite mild. For many ores a short (15 minutes or less) contact at ambient temperature is adequate to provide excellent uranium extractions. Other ores may require the addition of small quantities of oxidizing agent, or a short bake at a temperature not exceeding 100°C., for maximum solubilization of the uranium. Heating would otherwise be required only for the occasional case in which acid demand was such that excessive amounts of water were introduced, and then only to evaporate excess moisture. Solubilization of uranium appears to be good quite generally on coarse (minus 12-mesh) ore and fine grinding should not be necessary.

Because HCl is required, acid cost is one of the major cost items of the process. With maximum H₂SO₄ substitution, this cost can be brought down to a level, which, though higher than for current acid processes, appears to be within reasonable limits when the process as a whole is considered. For example, with A-51 ore, a low-lime normal carnotite containing 0.27 per cent uranium, 95 to 97 per cent extraction is attainable with 70 lbs. HCl/ton* and 35 lbs. H₂SO₄/ton*, which corresponds to an acid cost of about \$5.57/ton or approximately \$1.09/lb. of uranium. A uranium extraction of 98 per cent is similarly possible with Lukachukai ore, a high-lime ore containing 0.46 per cent uranium, with 61 lbs. HCl/ton and 247 lbs. H₂SO₄/ton, which represents an acid cost of \$7.85/ton or \$0.87/lb. of uranium.

Other attempts to reduce acid costs included the preparation of HCl, in situ, by the reaction of H₂SO₄ and a chloride, and an HCl-acidified acetone leach of H₂SO₄-solubilized ore. Neither of these approaches appeared to be applicable on the basis of the limited work done.

Vanadium recoveries by the HCl-acetone process are extremely variable. That vanadium which is readily reacted is recovered, essentially completely; but in many ores much of the vanadium is apparently present in a refractory form, which is virtually untouched by normal treatment procedures. Recovery of vanadium was a distinctly secondary problem, and was not thoroughly studied during this investigation.

*Acid utilization is expressed as pounds of 100 per cent acid throughout this report.

SECRET

SECRET

13

Several methods of recovering uranium from nonaqueous leach solutions are possible. The most attractive one appears to be neutralization, which provides a medium-grade primary precipitate that can be further refined in subsequent steps. For acetone solutions the alkali should be anhydrous, to avoid dilution of the solvent with water, and anhydrous NH_3 is the logical choice here. Ammonia consumption for precipitation is moderate, of the order of 3 to 5 lbs./lb. of uranium. The precipitate settles and filters quite rapidly. Depending on the composition of the ore this primary precipitate may contain from 3 to 7 per cent uranium, 1 to 5 per cent vanadium, 10 to 20 per cent iron, 0.5 to 3 per cent calcium, and 60 per cent or more ammonium chloride. If the uranium content of the ore is high in relation to the iron and other acid-consuming constituents, the precipitate will analyze higher in uranium. After removal of the acetone for recovery and recycle, the precipitate is repulped in water or calcined to eliminate the bulk of the ammonium chloride. The washed or calcined precipitate, which might constitute the final product of the mill, would contain from 10 to 15 per cent uranium, with proportionally increased vanadium and iron contents.

The washed precipitate may be redissolved in sulfuric acid, and neutralized with ammonia to a pH of about 2, precipitating most of the vanadium and some of the iron, as ferric vanadate. The large excess of iron present insures a high degree of elimination of the vanadium. Further neutralization of the filtrate precipitates ammonium diuranate, which is washed and calcined to the oxide. The analysis of one oxide product prepared via this procedure was as follows:

<u>Constituent</u>	<u>Per Cent</u>
U_3O_8	64.9
V_2O_5	0.71
Fe_2O_3	28.6
SiO_2	2.1
MnO_2	1.4
CaO	0.4
NH_4	<0.001
Cl	<0.1

Vanadium content was 0.7 per cent on a uranium basis, well within refinery feed specifications. Both ammonia and chloride contents were also

SECRET

SECRET

14

satisfactory. Test data indicate that the normal loss of uranium to the ferric vanadate precipitate would be of the order of 0.25 per cent.

Calcination is not a satisfactory method of chloride removal from the primary precipitate when the vanadium separation is to be made by stepwise neutralization. Acid-insoluble residues are high, and losses of uranium to this residue are excessive.

When the vanadium separation is to be made by the conventional soda ash-sawdust fusion method, calcination of the primary precipitate is an acceptable method of chloride removal. Although satisfactory vanadium elimination is also obtained by the fusion procedure, the grade of the final product does not approach that from stepwise neutralization, since elimination of iron is negligible. Typically, a water-leached fusion residue may contain from 14 to 18 per cent U_3O_8 , 0.2 to 0.6 per cent V_2O_5 , 70 to 75 per cent Fe_2O_3 , and 6 to 7 per cent CaO . Based on laboratory observations, the physical difficulties in a soda ash-sawdust fusion would be greater than for a high-grade concentrate such as yellow cake.

Satisfactory elimination of vanadium (and iron) is also obtained by carbonate leaching of primary precipitates. However, uranium losses of between 5 and 10 per cent to the insoluble residue were indicated in preliminary tests.

Other methods examined for recovering and concentrating the uranium from leach solutions included distillation, fractional precipitation with NH_3 , and precipitation with sulfates. None of these appeared promising. Ion exchange is one possible method of recovering a high-grade uranium product, either directly from an acetone leach solution, or from the aqueous sulfuric acid solution of a primary precipitate. Uranium distribution coefficients in nonaqueous solvents are high, but adsorption rates are quite low. Excellent vanadium separation is possible.

Early in the investigation, extraction of uranium directly from Western ores by readily liquefiable gases or low-boiling solvents was studied. None of the readily liquefiable gases tested, which included ammonia, sulfur dioxide and trioxide, nitrogen dioxide, and chlorine, were found to be effective solvents for carnotite, at pressures up to 1000 psi.

No low-boiling liquid capable of dissolving carnotite was found. Sulfur chloride, thionyl chloride or thiophosphoryl chloride converted carnotite into uranium and vanadium chlorides which were then readily soluble in water or certain organic solvents such as methyl alcohol, ethyl alcohol, and acetone. The mechanism appeared to be essentially a simple acid dissolution, the HCl arising from partial hydrolysis of the solvent by the water of hydration of the carnotite.

SECRET

SECRET

15

Another nonaqueous extractive method studied involved the volatilization of uranium by high-temperature vapor-phase chlorination, using Cl_2 or CCl_4 . This method produced uranium extractions as good as (but not significantly better than) the simpler HCl -acetone process. Temperatures of around 600°C . are required with CCl_4 , and 900 to 1000°C . with Cl_2 . Consumption of these reagents was high, and the over-all economics appear to favor considerably the leaching process.

EXPERIMENTAL DETAILS AND DISCUSSION OF RESULTS*

The HCl -acetone process evolved from an extended research program, during which a number of other alternative methods were investigated. It is described in more detail than the work on alternative methods, although many of the preliminary data have been omitted for the sake of brevity. This report deals primarily with the process at its present stage of development. A description of the earlier work, in considerable detail, may be found in the seven progress reports issued during the course of the investigation, which are listed at the end of this report. Similarly, the alternative methods, which include volatilization and leaching with readily liquefiable gases, are described only briefly in this report; the details of these studies are contained in the progress reports.

HCl -Acetone Process

Extraction of Uranium From the Ore

The initial solubilization of the uranium present in Western ores is accomplished by attack with a mineral acid. The solubilized uranium may then be extractively leached by a suitable solvent. Water may be used, but has the disadvantage that sliming may be a serious problem, greatly hampering thickening and filtration. A number of low-boiling organic solvents, among which are acetone, methanol, and ethanol, are also suitable.

The use of acetone as a nonaqueous solvent for extraction of uranium was investigated during an earlier phase of the program, primarily in connection with studies of direct leaching with acidified solvents. It had been observed then that settling and filtration rates were similar but more rapid than those with methanol, approximately in proportion to the relative viscosities of the two solvents. However, the reactivity of acetone appeared to be unsatisfactorily high at the acid concentrations required for satisfactory uranium extraction. When the process was later modified so that the

*Some of the experimental work described was carried out by R. B. Kimball and M. Pobereskin.

SECRET

10

solubilization of uranium was accomplished by an aqueous acid cure preceding the leaching step, it appeared that residual acidity could be sufficiently reduced to permit the use of acetone for leaching. In an effort to further increase the settling and filtration rates above those obtainable with methanol, the use of acetone was therefore re-examined on Temple Mountain ore which had been HCl-cured.

Rapid Settling in Acetone. In one of the first of these tests it was observed that the settling behavior was unlike that of any previous sample. Normally the fine ore particles were dispersed throughout the solvent and exhibited the classical graded settling according to particle size and density. In this test, the fine ore particles appeared to agglomerate, and the resulting aggregates settled out extremely rapidly, almost instantaneously, along with the coarse particles. The supernate was clear and free of suspended fines.

This unusual settling behavior has been verified on other Western ore samples. Settling rates so rapid as to be difficult to measure appear to be attainable on most ores. These data indicated that, under suitable conditions, there would be no thickening problems with an HCl-acetone system, a conclusion confirmed by the subsequent pilot-plant investigation.

The present hypothesis is that the phenomenon is based on the preferential wetting of the ore particles by a small amount of water. This preferential wetting appears to be dependent on the presence of a concentrated solution of CaCl_2 (the result of the reaction of HCl with the limestone naturally present in the ore). The concentrated CaCl_2 solution is not appreciably soluble in acetone; in addition, the high viscosity of the concentrated CaCl_2 solution may assist in agglomerating the ore particles. Some water is necessary, although not enough for a discrete water phase to be visible. When excessive amounts are present the ore particles again become dispersed and settling rates are poor.

Settling behavior appears to be nearly independent of particle size; test data have indicated that minus 325-mesh ore agglomerates equally as well as coarser ore and also settles very rapidly. Slightly larger quantities of water are required to moisten very fine ore.

The agglomeration and rapid settling are not inherent characteristics peculiar to the Western ores. Comparable results have been obtained with acetone slurries of Chattanooga shale and pure silica sand upon the addition of a slight quantity of concentrated CaCl_2 solution.

Not all of the CaCO_3 content of an ore need be reacted with HCl in order to provide the CaCl_2 for rapid settling. Satisfactory settling may be obtained if from approximately 0.4 to 0.6 per cent CaCO_3 is reacted with HCl . The acid demand of all CaCO_3 above this can be satisfied with H_2SO_4 . High-lime ores almost demand substantial substitution of H_2SO_4 for HCl , partly from cost considerations and partly because excessive CaCl_2 tends to make the ore mass so gummy that extraction of the metal values by the acetone is hampered.

The water content of the acetone in contact with the ore mass is important. In a near-anhydrous system there is no agglomeration and graded settling occurs. With excessive moisture present the fine particles are no longer bound into agglomerates and graded settling is again observed. However, these limits are well separated and control of moisture levels offers no problems. The optimum water content is a function of the amount of CaCl_2 formed, the pulp density, and of the characteristics of a particular ore. As an example, for normal carnotite ore using one volume of acetone per unit weight of ore, and with H_2SO_4 added equivalent to all CaCO_3 above 0.3 per cent, good settling may be obtained when the acetone contains 100 to 150 ml. of water/liter. Decreasing the extent of H_2SO_4 substitution, which increases the CaCl_2 content, broadens these limits still further.

Uranium Solubilization in Amenable Ores. The ease of initial solubilization of uranium, by a mineral acid attack, is to a large extent a function of the characteristics and mineralization of a given ore. A normal carnotite ore, examples of which are A-50 and A-51 (both from Stockpile 29), is quite readily attacked under moderate conditions of time and temperature, with from 88 to 123 lbs. HCl /ton. The results summarized in Table 1 are illustrative of the results which may be expected with an amenable ore such as A-51. The sample designated A-51 was one taken of the 5-ton lot of Stockpile 29 ore used for the pilot-plant investigation and is considered to be reasonably representative of this lot of ore.

The first nine tests shown comprised a limited series of time-temperature tests. Like other amenable ores, curing at 75°C . produced no significant increase in uranium extraction above that realized with a cure at ambient temperature. Essentially the same uranium extraction was obtained with from 105 to 122.5 lbs. HCl /ton. Five minutes of contact appeared to be almost enough; after 15 minutes of contact at ambient temperature uranium extraction appeared to be at its practical maximum. Increasing HCl input to 140 to 175 lbs./ton and contact time to 60 minutes increased uranium extraction only a few tenths per cent. Going in the other direction, when HCl input was reduced to 87.5 lbs./ton, uranium extraction was still 97 per cent.

SECRET

18

TABLE 1. EXTRACTION OF URANIUM FROM A-51 ORE^(a) AFTER AN HCl CURE

Procedure: 50 g. of minus 12-mesh Stockpile 29 ore was mixed with the indicated quantity of HCl (added as 37 per cent HCl), cured under the conditions shown, leached in 50 ml. of acetone at room temperature, filtered, and the washed residue analyzed.

HCl, lbs./ton ^(b)		Curing Conditions		Leach-Liquor Acidity, N	Uranium, per cent	
Added	Consumed ^(c)	Time, min.	Temp., °C.		Residue Assay	Extraction ^(d)
122.5	111.5	60	R. T.	0.15	0.006	98
122.5	111	30	R. T.	0.16	0.006	98
122.5	110	15	R. T.	0.17	0.006	98
122.5	108	5	R. T.	0.20	0.008	97
114	105	5	R. T.	0.20	0.008	97
105	100	5	R. T.	0.15	0.011	96
114	114	30	75	0	0.006	98
114	111	15	75	0.04	0.005	98
114	107	5	75	0.10	0.008	97
105	105	30	75	0	0.011	96
122.5	122.5	30	75	0	0.006	98
140	110	60	R. T.	0.21	0.005	98
175	110	60	R. T.	0.45	0.005	98
105	99	15	R. T.	0.08	0.006	98
96	90	15	R. T.	0.08	0.010	96
87.5	87.5	15	R. T.	0	0.008	97

(a) Normal carnotite ore, Stockpile 29 (0.27 per cent uranium, 0.94 per cent vanadium, 2.98 per cent CaCO₃).

(b) 100 per cent HCl basis.

(c) Difference between acid added and acid found in leach liquor by oxalate titration method.

(d) Based on residue and head assays.

SECRET

SECRET

19

Steen Ore. Normal carnotite ores are among the most amenable to the HCl-acetone process, and treatment conditions required are mild. Other ores may require more drastic conditions in the acid-curing step. Ores from the Steen claims are one example of this. The principal sample in this group was the ore designated A-71. This sample appeared, like those from the Temple Mountain area, to be a carbonaceous type of ore. The content of organic carbon was lower than in Temple Mountain ore, and was about 1 per cent. However, as illustrated by the summarized results presented in Table 2, satisfactory uranium extractions were never obtained from raw A-71 ore by the use of HCl alone. The mesh size of the ore did not seem to be a significant factor; uranium extraction did not exceed 85 per cent at a minus 200-mesh grind. The data indicated that hindrance by the associated carbonaceous material, or possibly the presence of reduced uranium, were more likely causes of the low extractions. Either roasting of the ore, or moderate additions of an oxidizing agent to the acid cure, increased uranium extraction to high levels (Table 2). With 10 lbs. KClO_3 /ton, uranium extraction was high with either minus 50-mesh ore or minus 200-mesh ore. Sodium silicofluoride additions of from 5 to 40 lbs./ton were tested, with negligible effect. Uniformly low vanadium extractions, less than 10 per cent, were found in the several tests in which vanadium extraction was determined. Even with 40 lbs. Na_2SiF_6 /ton vanadium extraction was negligible.

In view of the small quantity of oxidizing agent required for excellent uranium extractions from Steen ore, the addition of an oxidizing agent appears to be more economical than roasting.

Temple Mountain Ore. Another of the less amenable types of ore is that from the Temple Mountain area. Two samples of raw Temple Mountain ore were received (A-10 and A-11). These had, respectively, about 6.2 and 3.8 per cent organic carbon. Earlier investigation had shown that when this ore was completely roasted at a moderate temperature (450 to 500°C.) the uranium was readily extracted after an acid cure with moderate quantities of HCl, without any oxidizing agent. The previous work had also indicated that a residue of 0.03 per cent uranium (89 per cent extraction in the case of A-11) was about the minimum which could be expected from minus 50-mesh raw Temple Mountain ore following an HCl cure with reasonable quantities of acid. As indicated by the results summarized in Table 3 this residue was not decreased significantly even when large excesses of HCl were used.

Lack of liberation of the uranium at a minus 50-mesh grind seemed to be one of the factors reducing uranium extraction from raw Temple Mountain ore. Grinding to minus 200 mesh produced uranium extractions comparable to those obtained with roasted ore. Grinding to minus 100 mesh gave results only slightly better than those from minus 50-mesh ore. The information available suggests that the costs of grinding to minus 200 mesh probably

SECRET

SECRET

20

TABLE 2. EXTRACTION OF URANIUM FROM A-71 ORE^(a) AFTER AN HCl CURE

Procedure: Same as outlined in Table 1 except data is for 25 g. of ore sample per 50 ml. of acetone.

Mesh Size of Ore	HCl, lbs./ton ^(b)		Curing Conditions			Leach-Liquor Acidity, N	Uranium, per cent	
	Added	Consumed	Time, hrs.	Temp., °C.	KClO ₃ Added, lbs./ton		Residue Assay	Extraction ^(c)
Raw Ore								
-50	245	245	15	R. T.		0	0.098	69
-50	280	270	15	R. T.		0.06	0.065	80
-50	315	272	15	R. T.		0.17	0.052	78
-50	350	325	15	R. T.		0.30	0.066	84
-200	210	210	2	R. T.		0	0.14	57
-200	245	242	2	R. T.		0.02	0.12	63
-200	210	210	0.25	75		0	0.16	51
-200	245	245	0.25	75		0	0.077	76
-200	280	280	0.25	75		0	0.052	84
-50	245	245	0.50	75		0	0.078	76
-200	245	245	0.50	75		0	0.047	85
-200	280	280	0.25	75	40	0	0.007	98
-200	280	280	4	R. T.	40	0	0.007	98
-50	280	280	0.50	75	10	0	0.017	95
-200	280	280	0.50	75	10	0	0.014	96
-50	280	280	0.50	75	5	0	0.030	91
-200	280	280	0.50	75	5	0	0.020	94
Roasted Ore ^(d)								
-50	280	275	15	R. T.		0.04	0.016	95
-50	350	330	15	R. T.		0.15	0.009	97

(a) Steen ore; head assays were:

	U	V	CaCO ₃
Raw, %	0.32	0.48	12.5
Roasted, %	0.33	0.49	12.7

(b) 100 per cent HCl basis.

(c) Based on residue and head assays.

(d) Roasted at 450°C.

SECRET

SECRET

21

TABLE 3. EXTRACTION OF URANIUM FROM A-11 ORE^(a) AFTER AN HCl CURE

Procedure: Same as outlined in Table 1 except data is for 25 g. of ore sample per 50 ml. of acetone.

Mesh Size of Ore	HCl, lbs./ton ^(b)		Curing Conditions			Leach-Liquor Acidity, N	Uranium, per cent	
	Added	Consumed	Time, hrs.	Temp., °C.	KClO ₃ Added, lbs./ton		Residue Assay	Extraction ^(c)
<u>Raw Ore</u>								
-50	70	70	0.5	75		0	0.041	84
-50	105	90	0.5	75		0.10	0.029	89
-50	140	100	0.5	75		0.29	0.025	90
-50	175	125	0.5	75		0.33	0.025	90
-50	210	140	0.5	75		0.47	0.025	90
-50	105	83	15	R. T.		0.15	0.034	86
-50	140	97	15	R. T.		0.30	0.028	88
-200	105	90	15	R. T.		0.10	0.016	94
-200	140	105	15	R. T.		0.25	0.016	94
-200	70	70	0.25	75		0	0.030	88
-200	105	87	0.25	75		0.12	0.021	92
-50	105	105	0.50	75	20	0	0.027	90
-200	105	105	0.50	75	20	0	0.017	94
-50	105	102	0.50	75	10	0.02	0.032	88
-200	105	104	0.50	75	10	0.01	0.019	93
<u>Roasted Ore^(d)</u>								
-50	70	70	0.50	75		0	0.032	89
-50	105	102	0.50	75		0.02	0.025	91
-50	140	95	15	R. T.		0.24	0.019	93
-50	105	85	4	R. T.		0.13	0.026	91
-50	105	80	1	R. T.		0.17	0.027	91
-50	70	70	1	R. T.		0	0.035	87

(a) Temple Mountain ore; head assays were:

	U	V	CaCO ₃	CO ₂	Total C
Raw, %	0.26	0.60	1.6	1.0	4.1
Roasted, %	0.28	0.65	~1.7	~1	~0.3

(b) 100 per cent HCl basis.

(c) Based on residue and head assays.

(d) Roasted at approximately 450°C.

SECRET

SECRET

22

approximate those of roasting, indicating no economic advantage for grinding. Also, elimination of the organic material by roasting may simplify the subsequent acetone leaching.

The addition of an oxidizing agent such as KClO_3 to the acid cure of raw ore appeared somewhat unattractive, in view of the amount of oxidizable organic matter present. The results of a few tests in which 10 and 20 lbs. KClO_3 /ton were added (Table 3) showed that uranium extraction from minus 50-mesh ore could be slightly increased. However, roasting of the ore again seemed to be a more effective, and probably less costly, method of obtaining maximum uranium extractions.

Tests on minus 50-mesh roasted Temple Mountain ore (A-11) indicated a uranium extraction of 91 per cent after a 1-hour cure at room temperature with 100 lbs. HCl /ton (Table 3). A 91 per cent extraction was also obtained after a 30-minute cure at 75°C ., and presumably shorter times would suffice with an elevated-temperature cure.

The Temple Mountain samples received were very low-lime ores. The total calcium was 1.3 and 1.6 per cent, respectively, as CaCO_3 , for A-10 and A-11 ores. However, based on the 0.75 per cent $\text{SO}_4^{=}$ analysis obtained for A-11, a substantial part of the calcium appeared to be present as gypsum. The quantity of free limestone in this ore was evidently so low as to be near marginal as a source of the CaCl_2 necessary for rapid settling. In practice, it would perhaps be preferable to blend other higher lime ores, of which there are no lack, with Temple Mountain ore for processing.

Uranium Extraction From Various Ores. Not all of the ore samples received were thoroughly investigated, and data on some are therefore scant. In the early stages of the development of the HCl -acetone process a series of settling tests was run, however, to demonstrate the applicability of the process to all of the ore samples then available. In these particular tests large excesses of HCl were used in the curing step, and the acid-consumption values are in no sense minimum values. Nevertheless, the results, summarized below, are indicative of the maximum uranium extractions which may be expected from minus 10-mesh or minus 12-mesh ore by the use of fairly drastic treatment with HCl .

SECRET

SECRET

23

Ore	HCl Consumption, lbs. /ton	Uranium, per cent		
		Head	Residue	Extraction
A-11 Temple Mountain ^(a)	115	0.28	0.023	92
A-20 Muddy River	230	0.09	0.010	89
A-30 Lukachukai	350	0.46	0.004	99
A-40 7-Mile Canyon	420	0.12	0.007	94
A-50 Normal carnotite	165	0.22	0.005	98
A-60 Copper-uranium	215	0.22	0.017	92
A-71 Steen	530	0.32	0.017	95
B-20 Bluewater No. 2	145	0.10	0.005	95
B-30 Bluewater No. 3	110	0.16	0.001	99

(a) Roasted at 450°C.

Rapid settling rates were observed on all of these ores except A-60 and B-30. Both of these are low in CaCO_3 content and apparently the quantity of CaCl_2 formed was insufficient for rapid settling. The addition of 20 lbs. CaCl_2 /ton greatly improved the settling rate of A-60, and presumably would have also for B-30. Only small percentages of a higher lime ore, blended with these ores before processing, would be required to improve these settling rates to adequate levels.

Substitutes for Hydrochloric Acid. All of the preceding discussion has dealt with the use of HCl alone in the acid cure. HCl is a relatively costly acid, the price being estimated at nearly \$0.07/lb. (100 per cent basis), delivered at Salt Lake City, Utah, on the basis of shipment from the closest present source of HCl (20° Bé), Henderson, Nevada, at a freight cost of about \$0.025/lb. Since interest in the utilization of the salt in the Great Salt Lake is currently high, the possibilities appear promising that HCl will eventually be available locally, at a more attractive price. However, even under these conditions it would still be considerably more costly than H_2SO_4 (which is probably available at Salt Lake City at about \$0.015/lb.) and the economics of the process could be substantially improved if H_2SO_4 could be substituted for the more expensive acid.

A variety of approaches aiming at attaining minimum acid costs were touched upon. The simplest and the obvious one is to use minimum quantities of HCl. Although considerable excesses were used in the earlier studies, it was later shown that satisfactory uranium extractions could be realized even when the amount of free acid in the acetone leach liquor was very slight. Besides reducing acid costs, a negligible leach-liquor acidity is advantageous from the standpoint of minimizing both NH_3 requirements for precipitation and potential degradation of the solvent.

SECRET

Complete replacement of HCl with H₂SO₄ is not feasible when acetone is the solvent. CaSO₄ does not have the agglomerating properties of CaCl₂ and graded settling occurs, much like that in aqueous systems. Also, the solubility of uranyl sulfate in acetone is quite low, whereas the solubility of uranyl chloride is high. In addition, the indications of several exploratory tests with pure uranyl sulfate in acetone were that the presence of such radicals as potassium, ammonium, iron, and aluminum resulted in the precipitation of double salts of uranium. Since several of these elements are almost invariably present in Western ores, the possibility of forming salts which are nearly insoluble in acetone appears likely. Probably because of some such mechanism, introduction of excessive amounts of sulfate must be avoided, even in acetone systems which are predominantly composed of chlorides. The use of sulfates as precipitants for recovering uranium from chloride acetone solutions was, in fact, seriously considered, and some of these are moderately effective.

Three methods by which H₂SO₄ could be utilized were investigated:

- (1) Formation of HCl, in situ, by metathesis of H₂SO₄ and such chlorides as NaCl, CaCl₂, and NH₄Cl
- (2) Solubilization of the uranium by an aqueous cure with H₂SO₄, followed by leaching with HCl-acidified acetone
- (3) Partial substitution of H₂SO₄ for HCl in the acid cure, to the extent of the CaCO₃ present.

Hydrochloric Acid by Metathesis. Formation of HCl, in situ, by the reaction of H₂SO₄ and a chloride theoretically offers some economies. The lowest priced chloride is NaCl, probably available at Salt Lake City for about \$0.01/lb. If complete metathesis were possible, according to the following reaction:

then 1.34 lbs. H₂SO₄ and 1.60 lbs. NaCl would be required to produce 1 lb. HCl, with a reagent cost of about \$0.031/lb. HCl. However, the possibility of forming difficultly soluble sulfates and thus tying up uranium at the temperatures and concentrations required to drive this reaction to completion appears quite likely. More probably, the stoichiometry involved would approach that for the formation of the acid sulfate:

in which event the reagent cost of the HCl would be approximately \$0.06/lb. of HCl, or nearly that of purchased HCl.

Early tests, in which one mole of H_2SO_4 was used per two moles of NaCl , showed only about 15 to 25 per cent extraction of uranium. This was confirmed quite recently on a sample of normal carnotite (A-51). When the molar ratio of H_2SO_4 to NaCl was 1:2, uranium extraction was 26 per cent. If conversion to HCl had been complete, HCl input would have been about 105 lbs./ton, more than adequate for 96 to 97 per cent extraction from this ore. When H_2SO_4 was added in 50 per cent excess, uranium extraction increased to 76 per cent. However, reagent cost under these conditions would be \$1.21/lb. uranium versus \$1.37/lb. uranium for the much more effective 105 lbs./ton of HCl . Furthermore, with $\text{H}_2\text{SO}_4 + \text{NaCl}$ there was no agglomeration, and settling rates were poor. It appears that the formation of HCl by reacting H_2SO_4 with NaCl is not applicable to the proposed process.

Some ammonium chloride would be available from the process, either as a dilute solution, if the primary precipitate were repulped in water, or as a condensable vapor, if the precipitate were calcined. Despite probable poor economics of recovery of ammonium chloride, a few exploratory tests were conducted with $\text{H}_2\text{SO}_4 + \text{NH}_4\text{Cl}$ to determine the levels of uranium extraction attainable. With normal carnotite (A-51) and an acid input equivalent to 105 lbs., expressed as 100 per cent HCl , uranium extraction was 64 per cent. Increasing H_2SO_4 input to 50 per cent excess above stoichiometric increased the uranium extraction very slightly, to 67 per cent. As was the case with NaCl , there was no agglomeration and settling was poor.

The most promising metathesis involving H_2SO_4 was that with CaCl_2 . However, unless CaCl_2 was added in quantities above stoichiometric for the H_2SO_4 , settling was poor. The addition of excess CaCl_2 also improved uranium extraction by 3 or 4 percentage points. Illustrative are the 87 and 90 per cent extractions obtained on normal carnotite ore (A-50) with an equivalent HCl input of 105 lbs./ton when stoichiometric and 25 per cent excess CaCl_2 was added. Unfortunately, the delivered price of CaCl_2 at Salt Lake City is estimated to be nearly \$0.03/lb. (100 per cent basis) and the cost of the H_2SO_4 and CaCl_2 required would be nearly the same as that for 105 lbs. HCl /ton, in spite of the lower extraction.

The economics of producing HCl by metathesis appears to be dubious. Coupled with the generally lowered uranium extractions, the possibilities of such a procedure seem to be distinctly unpromising.

HCl-Solvent Leach. Another approach aimed at minimizing HCl usage involved initial solubilization of the uranium by an aqueous H_2SO_4 cure, followed by leaching with HCl -acidified acetone. The first test of this method (on a very amenable normal carnotite ore, A-50) was quite encouraging, with a 90 to 92 per cent extraction and apparently minimum HCl consumption. However, later tests on a somewhat less amenable carnotite ore

SECRET

26

(A-51) gave only about 70 per cent extraction. This method appeared to have only very limited application and was not studied further.

Partial Substitution by Sulfuric Acid. The third approach, that of partial substitution of H_2SO_4 for HCl in the acid cure, appeared to be the most effective and practical means of reducing HCl demands, and was extensively investigated. As mentioned earlier, reaction of only about 0.4 to 0.6 per cent $CaCO_3$ with HCl is necessary to provide sufficient $CaCl_2$ for satisfactory settling. The balance of the $CaCO_3$ present may be reacted with H_2SO_4 , thus substantially reducing the quantity of HCl required, particularly for the higher lime ores. The resultant $CaSO_4$ (and $MgSO_4$) is essentially insoluble in acetone; its metathesis in a subsequent cure with HCl would not be expected to be rapid or complete. Subjecting an ore to a preliminary H_2SO_4 cure should, therefore, tie up most of the $CaCO_3$ in a form which is relatively inert with respect to the subsequent steps in the process.

Addition of sulfuric acid much in excess of equivalency with the lime is inadvisable, for two reasons. First, as was indicated by tests with sulfates in synthetic mixtures, as well as by experimental results on ores, the presence of excess sulfate may result in reduced uranium extraction. Second, if all of the lime is tied up as $CaSO_4$, no $CaCl_2$ is present to provide the desired settling characteristics in the acetone-leaching step.

Extraction of Uranium From High-Lime Ores. Lukachukai ore (A-30), the highest lime ore then available (13.2 per cent $CaCO_3$), was used for the preliminary tests of H_2SO_4 + HCl curing. Earlier work had shown that the HCl requirements for this ore were about 245 lbs./ton, for 99 per cent uranium extraction. Uranium extraction was still 99 per cent with 50 per cent substitution by H_2SO_4 , as indicated by Table 4. Settling rates were excellent. With 75 per cent substitution, uranium extraction was 98 per cent; settling rates were fair. Fortuitously, this latter ratio represented about 96 per cent equivalency with the $CaCO_3$, probably near the upper limit for satisfactory results. With 90 per cent of the acid requirements (114 per cent equivalency) uranium extraction was down only slightly, to 96.5 per cent, but settling rates were relatively poor.

Most of the leaching tests on Lukachukai ore were performed with anhydrous methyl ethyl ketone (MEK), then under investigation as an alternative solvent. This is not believed to have influenced the results, based on other experimental data.

SECRET

SECRET

27

The relative acid costs for treating a high-lime ore like Lukachukai with varying degrees of substitution of sulfuric acid are of interest. These estimates (Table 5), based on the results given in Table 4 and assuming a Salt Lake City location (the only location for which delivered prices of HCl are available) indicate that substitution of sulfuric to the extent of 96 per cent equivalency with the CaCO_3 can reduce acid costs for this ore from \$1.83 to \$0.87 per pound of uranium extracted.

Another ore with high lime content is A-71 (Steen ore, 12.5 per cent CaCO_3). Uranium extractions of 90 to 92 per cent were obtained on Steen ore (after roasting at 450°C . to destroy organic matter) with H_2SO_4 substituted to 95 per cent equivalency with the CaCO_3 (Table 4). Somewhat lower total acid requirements than those shown appear possible for Steen ore, perhaps along with a reduction in curing time.

One of the 5-ton lots of ore received was from Stockpile 6, which is apparently a collection of miscellaneous high-lime ores. The sample studied in the laboratory (A-90) contained 14.1 per cent CaCO_3 . This ore cannot be handled with HCl alone, due to the excessive amounts of CaCl_2 produced. Uranium extractions ranged from 91 to 93 per cent when H_2SO_4 input was varied from 80 to 105 per cent equivalency with the CaCO_3 (Table 4).

Comparison aqueous leaches with H_2SO_4 and Na_2CO_3 gave slightly lower extractions. A 1-hour room-temperature leach at 25 per cent pulp density in dilute sulfuric acid (575 lbs./ton) extracted only 88 per cent of the uranium. Terminal pH was 0.73, and filtration was quite slow, probably because of the large amounts of CaSO_4 fines. A 1-hour leach at 90°C . in 10 per cent Na_2CO_3 (25 per cent pulp density) extracted 89 per cent of the uranium. These results suggested that the lower extractions from this ore by the HCl process arose from the nature of the ore rather than from defects of the process.

The possibility that liberation of the uranium was incomplete at the as-received minus 12-mesh grind was checked by tests at a minus 50-mesh and a minus 100-mesh grind (Table 4). Uranium extraction was still 91 per cent, although the finer particle size nearly doubled the HCl requirements. Essentially complete uranium extraction (98 per cent) was not achieved until an HCl cure at elevated temperature was employed. Concurrently, HCl requirements were more than tripled. Uranium extractions above the readily attainable 90 to 92 per cent appear to be uneconomic for this ore.

Comparison aqueous leaches were also made on the minus 50-mesh ore used for the above tests. With dilute sulfuric acid (575 lbs./ton) uranium extraction was also high, 96 per cent. However, extraction by a hot Na_2CO_3 leach was only 88 per cent, no better than the earlier test on minus 12-mesh ore. The indications are that, although this is a high-lime ore, the uranium

SECRET

SECRET

28

TABLE 4. EXTRACTION OF URANIUM FROM

Procedure: 25 g. or 50 g. of ore was mixed with
added the other acid and the ore cured
of acetone, filtered, and the

Ore		HCl Added, lbs./ton ^(a)			H ₂ SO ₄ Added		
Weight, g.	Mesh Size	Added as HCl	HCl Equiv. of Added H ₂ SO ₄	Total Equiv. HCl	Lbs./Ton	Conc., per cent	Equiv. to CaCO ₃ ^(b) , per cent
<u>A-30 Ore</u>							
25	-16	122	123	245	165	48	64
25	-16	61	184	245	247	48	96
25	-16	37	221	258	296	48	114
25	-50	122	123	245	165	48	64
25	-50	183	123	306	165	48	64
25	-50	61	184	245	247	48	96
25	-50	122	184	306	247	48	96
<u>A-71 Ore</u>							
25	-50	109	171	280	230	48	95
25	-50	144	171	315	230	48	95
25	-50	136	144	280	194	48	80
25	-50	171	144	315	194	48	80
25	-50	154	126	280	170	48	70
25	-50	189	126	315	170	48	70
<u>A-90 Ore</u>							
50	-12	101	214	315	288	96	105
50	-12	120	195	315	263	96	95
50	-12	129	186	315	250	96	90
50	-12	150	165	315	222	96	80
50	-12	150	165	315	222	96	80
50	-50	228	195	420	263	96	95
50	-100	228	195	420	263	96	95
25	-50	455	195	650	263	96	95

(a) 100 per cent HCl basis.

(b) Based on stoichiometric requirements for CaSO₄ of 19.6 lbs. H₂SO₄/ton for each per cent CaCO₃ content.

(c) Based on residue and head assays.

(d) Head assays of ores were:

	U, %	V, %	CaCO ₃ , %
A-30	0.46	1.16	13.2
A-71 (Roasted)	0.33	0.49	12.7
A-90	0.22	0.93	14.1

SECRET

SECRET

29

HIGH-LIME ORES AFTER AN $H_2SO_4 + HCl$ CURE

the designated acid and cured as shown; to this was again; this was then leached in 50 ml. acetone-washed residue assayed.

Curing Conditions					Leach-Liquor Acidity, N	Uranium, per cent	
First Cure	H ₂ SO ₄ Cure		HCl Cure			Residue Assay	Extraction(c)
	Time, min.	Temp., °C.	Time, min.	Temp., °C.			
(Lukachukai) ^(d)							
H ₂ SO ₄	15	R. T.	120	R. T.	0	0.006	99
H ₂ SO ₄	15	R. T.	120	R. T.	0	0.008	98
H ₂ SO ₄	15	R. T.	120	R. T.	0	0.016	97
H ₂ SO ₄	15	R. T.	60	R. T.	0	0.011	98
H ₂ SO ₄	15	R. T.	60	R. T.	0.02	0.008	98
H ₂ SO ₄	15	R. T.	60	R. T.	0	0.027	94
H ₂ SO ₄	15	R. T.	60	R. T.	0.09	0.018	96
(Steen) ^(d)							
H ₂ SO ₄	15	R. T.	60	R. T.	0.15	0.027	92
H ₂ SO ₄	15	R. T.	60	R. T.	0.34	0.031	90
H ₂ SO ₄	15	R. T.	60	R. T.	--	0.029	91
H ₂ SO ₄	15	R. T.	60	R. T.	0.27	0.041	87
H ₂ SO ₄	15	R. T.	60	R. T.	0.02	0.028	91
H ₂ SO ₄	15	R. T.	60	R. T.	0.11	0.035	89
(Stockpile 6) ^(d)							
H ₂ SO ₄	30	R. T.	30	R. T.	0.24	0.018	91
H ₂ SO ₄	30	R. T.	30	R. T.	0.20	0.017	92
H ₂ SO ₄	30	R. T.	30	R. T.	0.07	0.020	91
H ₂ SO ₄	30	R. T.	30	R. T.	0.03	0.015	93
HCl	15	R. T.	15	R. T.	0	0.020	91
HCl	20	R. T.	20	R. T.	0.02	0.023	91
H ₂ SO ₄	20	R. T.	20	R. T.	0.06	0.020	91
H ₂ SO ₄	30	R. T.	30	100	0.22	0.004	98

SECRET

TABLE 5. ESTIMATED ACID COSTS FOR TREATMENT OF LUKACHUKAI ORE

Analysis of Ore: 0.46 per cent uranium, 1.16 per cent vanadium,
13.2 per cent CaCO_3 , base requirement of acid
was 245 lbs. HCl /ton.

	Equivalence of H_2SO_4 to CaCO_3 , per cent		
	0	64	96
H_2SO_4 , lbs./ton of ore	--	165	247
HCl , lbs./ton of ore	245	122	61
Total Equivalent HCl , lbs./ton of ore	245	245	245
H_2SO_4 , dollars per ton of ore ^(a)	--	2.48	3.70
HCl , dollars per ton of ore ^(b)	<u>16.65</u>	<u>8.30</u>	<u>4.15</u>
Total Acid Cost, dollars per ton of ore	16.65	10.78	7.85
Uranium Extraction, per cent	99	99	98
Uranium Extraction, lbs./ton of ore	9.1	9.1	9.0
Acid Cost, dollars per lb. of uranium extracted	1.83	1.18	0.87

(a) Price of H_2SO_4 at Salt Lake City estimated to be about \$0.015/lb. (100 per cent basis).

(b) Price of HCl at Salt Lake City is \$0.068/lb. (100 per cent basis) based on quotation of \$29.00/ton for 20° Be . acid
f.o.b. Henderson, Nevada.

SECRET

30

SECRET

is tightly held, and an acid process may be necessary for maximum uranium extractions.

Substitution of H_2SO_4 to 95 per cent equivalency with the three ores shown in Table 4 left from 0.63 to 0.70 per cent $CaCO_3$ for formation of $CaCl_2$. Settling rates at this level appeared to be adequate for satisfactory operation.

Extraction of Uranium From Low-Lime Ores. While the greatest potential saving by substituting H_2SO_4 for HCl lies with the high-lime ores, it can also be used profitably with low-lime ores. The normal carnotites (A-50 and A-51), containing from 2.75 to 3.0 per cent $CaCO_3$, are examples of this, as shown by the results summarized in Table 6. Uranium extractions of from 94 to 96 per cent were obtained with A-50 after room-temperature cures with H_2SO_4 substitution up to 90 per cent equivalency with the $CaCO_3$. Settling rates at 90 per cent equivalency were only fair; at lower substitutions they were good. Much the same results were obtained with the more recent sample of normal carnotite ore (A-51). Up to 97 per cent uranium extraction was obtained after room-temperature cures with H_2SO_4 and HCl . Excellent uranium extraction was obtained even when H_2SO_4 was added in excess of equivalence with the $CaCO_3$, although settling rates were then unsatisfactory. The viscosity of concentrated H_2SO_4 and the generally small quantity involved make its addition to dry ore difficult, so that it is desirably added to already wetted ore. In a number of the above tests the ore was cured first with HCl , followed by a cure with concentrated H_2SO_4 . Equally effective uranium extraction was obtained, and tying up the lime as $CaSO_4$ first, before addition of the HCl , appears to be unnecessary.

If it is approximated that a uranium extraction of 95 per cent can be obtained with A-50 ore, using 90 lbs./ton equivalent HCl , and H_2SO_4 at 80 per cent of equivalency with the $CaCO_3$, the acid cost would be (using the same prices as before) \$4.57/ton or \$1.10/lb. of uranium extracted. With HCl alone, the corresponding acid costs would be \$6.10/ton or \$1.45/lb. uranium. For A-51 ore, again assuming 95 per cent extraction, 105 lbs./ton equivalent HCl , and H_2SO_4 at 80 per cent equivalency, the acid cost would be \$5.57/ton or \$1.09/lb. of uranium.

Miscellaneous Amenability Tests. Just before the laboratory investigation was concluded, three additional ore samples were received for amenability tests. These were Happy Jack copper-uranium shale from Stockpile 31 (A-80), Happy Jack copper-uranium sandstone from Stockpile 35 (A-81), and Utex ore from Stockpile 33 (A-90). Time permitted only one series of tests, and optimum conditions for maximum extractions were not

TABLE 6. EXTRACTION OF URANIUM FROM LOW-LIME ORES AFTER AN H₂SO₄ PLUS HCl CURE

Procedure: 25 g. or 50 g. of ore was mixed with one acid and cured for 5 to 15 minutes at room temperature; to this was added the other acid and the ore was cured again for 5 to 60 minutes at room temperature; this was then leached in 50 ml. of acetone, filtered, and the washed residue assayed.

HCl Added, lbs./ton ^(a)			H ₂ SO ₄ Added			Leach-Liquor Acidity, N	Uranium, per cent	
Added as HCl	HCl Equiv. of Added H ₂ SO ₄	Total Equiv. HCl	Lbs./Ton	Concentration, per cent	Equiv. to CaCO ₃ per cent ^(b)		Residue Assay	Extraction ^(c)
<u>A-50 Ore (Normal Carnotite)^(d)</u>								
49	21	70	29	48	50	0	0.013	94
84	21	105	29	48	50	0.02	0.010	96
39	31	70	42	48	75	0	0.012	95
74	31	105	42	48	75	0	0.009	96
69	36	105	49	48	90	0.09	0.011	95
<u>A-51 Ore (Normal Carnotite)^(d)</u>								
79.2	34.8	114	46.8	48	80	0.30	0.009	97
75	39	114	52.5	48	90	0.35	0.012	95
70.5	43.5	114	58.5	48	100	0.33	0.007	97
66	48	114	64.5	48	110	--	0.010	96
60	54	114	73	48	125	0.29	0.009	97
74	40	114	54	48	92.5	0.10	0.007	97
74	40	114	54	96	92.5	0.07	0.011	96
70.2	34.8	105	46.8	96	80	0	0.017	94
61.5	43.5	105	58.5	96	100	0.08	0.008	97
52.9	52.1	105	70	96	120	0.08	0.011	96

Footnotes appear on following page.

SECRET

SECRET

SECRET

33

Footnotes for Table 6.

- (a) 100 per cent HCl basis.
- (b) Based on stoichiometric requirements for formation of CaSO_4 .
- (c) Based on residue and head assays.
- (d) Head assays of ores were:

	<u>U, %</u>	<u>V, %</u>	<u>CaCO_3, %</u>
A-50	0.22	0.66	2.74
A-51	0.27	0.94	2.98

SECRET

28

SECRET

34

established. Further study would be required to determine the necessary treatments for the Happy Jack ores, as evidenced by the relatively low uranium extractions, summarized in the following tabulation:

<u>Ore</u>	Head Assay, per cent		HCl, lbs./ton ^(b)		Uranium, per cent	
	<u>U</u>	<u>CaCO₃^(a)</u>	<u>Added</u>	<u>Consumed</u>	<u>Residue Assay</u>	<u>Extraction</u>
A-80	0.20	1.4	105	70	0.089	56
A-80 Roasted ^(c)	0.20		105	65	0.051	75
A-81	0.26	1.8	105	70	0.084	68
A-90	0.11		280	230	0.019	83
A-90 Roasted ^(c)	0.11	7.1	245	210	0.012	89

(a) Spectrographic analysis.

(b) 100 per cent HCl basis.

(c) Roasted at 450°C.

Substitution of H₂SO₄ at 50 per cent equivalence with the CaCO₃ was also tested on Utex ore (A-90). Using 230 lbs. HCl/ton and 70 lbs. H₂SO₄/ton, uranium extractions were 82 per cent on raw Utex and 94 per cent on roasted Utex.

Vanadium Recovery. Vanadium recoveries are extremely variable with the HCl-acetone process. Vanadium chlorides appear to be quite soluble in acetone, and extraction of vanadium in this form by the acetone leach appears to be essentially complete. The available data indicate that the often low over-all recovery is due primarily to a failure to solubilize the vanadium in the initial acid cure. Vanadium present as carnotite and other amenable forms is evidently readily solubilized, but in many ores the vanadium is present in a refractory form, possibly as a vanadium mica, which is virtually untouched by normal treatment procedures. Some of the early test data indicated that vanadium solubilization could be materially improved by fairly drastic treatment, although at a rather high cost. Use of a fluoride, such as Na₂SiF₆, in the acid cure appeared to be effective. Salt-roasting was also effective, but at the expense of greatly diminished uranium extraction.

Since the Atomic Energy Commission regarded the recovery of vanadium as being of secondary importance to the main problem, this phase of the problem was not thoroughly investigated. Further work would undoubtedly disclose methods by which vanadium recoveries could be improved. However, as indicated by the experimental data available, high vanadium recovery may not be economically sound.

SECRET

SECRET

35

Corrosion Problems. Acidic chloride systems are severely corrosive and materials of construction would offer some problems in the proposed process, although these difficulties would be minimized by the compact nature and the few pieces of equipment requiring corrosion- and/or solvent-resistance. A rubber or refractory liner would probably be suitable for the acidulator, where an aqueous chloride system is encountered. No data were available on materials which would withstand both the solvent action of acetone and the corrosive action of HCl. Brief experimental testing of several rubbers by the Resin and Rubber Chemistry Division at Battelle indicated that neoprene had the lowest swelling (40 per cent) of any of the types tested, which was adjudged satisfactory for tank linings, etc., where high strength is not necessary. Its abrasion resistance is high, and it is readily bonded to metals. Neoprene was used for gasketing material in the pilot plant, where it appeared to perform satisfactorily, and it is believed that it would be suitable throughout the acetone circuit where acidity is also present. The fact that the extraction step is carried out in a substantially nonaqueous system should minimize the corrosion problem.

Recovery of Uranium From Leach Liquors

Of the several possible methods for recovering uranium from acetone leach solutions, precipitation with anhydrous NH_3 was regarded as the most practical and least costly, from the standpoint of both capital and operating costs. This method, therefore, received the most attention; other methods were studied only briefly.

Neutralization. Complete neutralization with NH_3 produces a precipitate of intermediate grade, from 3 to 7 per cent uranium. The precipitate is voluminous but settles rapidly and is easily filtered, presumably because of the low degree of hydration. Depending on the composition of the ore, the primary precipitate may also contain from 1 to 5 per cent vanadium, 10 to 20 per cent iron, 0.5 to 3 per cent calcium, and 60 per cent or more of ammonium chloride. Indicative are the analyses of primary precipitates from a number of ores, summarized below:

	Primary Precipitate, per cent ^(a)				
	U	V	Fe	Ca	Cl
Temple Mountain (A-11)	3.2	1.75	13.7	<0.5	40.9
Lukachukai (A-30)	3.3	1.5	12		43.9
Normal carnotite (A-51)	4.5	2.2	11.7	2.8	37.8
Normal carnotite (A-51)	4.5	2.1	18.6	1.5	38.8
Blend of miscellaneous ores	4.1	2.25	12		39.1

(a) Dried at 105°C.

SECRET

The ammonia demand is dependent primarily on the concentration of chlorides in the leach solution, and based on the few laboratory tests in which it was measured, will be of the order of 3.5 to 5 grams/gram of uranium. Precipitation of the uranium is complete at pH 7. Neutralization of leach solution was found to be straightforward, and offered no difficulties. Although the precipitate is only partially hydrated, some water is removed from the system by the precipitation, which will assist in maintaining the water balance of the acetone circuit in a large-scale operation. Acetone may comprise possibly 50 to 60 per cent of the wet precipitate; in practice, this would be volatilized and recovered for return to the leaching circuit.

To be a suitable refinery feed material, the uranium concentration should be 25 per cent U_3O_8 or more, the vanadium content less than 10 per cent of the uranium, and both ammonia and chloride concentrations should be at very low levels, probably <0.1 per cent.

Chloride Removal. The chloride content of the primary precipitate is high, principally because of the NH_4Cl brought down with the precipitate. It is hypothesized that only a gross separation of chlorides is necessary initially, and that if the bulk of the chloride is eliminated at an early step, the balance of it is satisfactorily eliminated in the subsequent processing steps. Washing tests have shown that the chloride content can be reduced effectively by repulping in water. Repulping at a 25 per cent pulp density removed about 75 to 80 per cent of the chloride per pass. Five such repulpings reduced chloride content from 39.4 to 0.08 per cent in one test, a removal of 99.9+ per cent. Elimination to this extent in the preliminary step is more than is necessary. More nearly typical, though still more than needed, was the reduction from 39.4 to 1.2 per cent (99 per cent removal) by two repulpings at 15 per cent pulp density. Calcium elimination was not as complete; approximately 85 per cent was removed in the above test. Evidently not all of the calcium is present as the soluble chloride and its complete elimination by washing may not be possible. The washed cake will contain, on a dry basis, from 10 to 15 per cent uranium, with the water-insoluble compounds proportionally increased.

Hydration of the primary precipitate upon repulping converts it to a somewhat slimy precipitate, less readily filtered than the original one. Hot digestion improves its filterability.

Calcination will remove chloride present as ammonium chloride, but not that present as calcium chloride. Ammonium chloride is readily volatilized and is effectively eliminated by calcination at $400^{\circ}C$. Since there is no reduction in calcium content, the grade of the calcined cake is slightly under that from repulping and washing. Calcination has the advantage that a dry shippable product, containing 10 per cent uranium or more, results directly.

SECRET

37

A calcined feed is quite amenable to a subsequent uranium-vanadium separation by a sawdust-soda ash fusion. However, insoluble residues are high when calcined cake is dissolved in acid for separation by fractional precipitation.

Upgrading by Stepwise Neutralization of Aqueous Solutions. One method of upgrading the uranium concentration is the stepwise neutralization of an aqueous H_2SO_4 solution of the primary precipitate, precipitating and filtering off iron vanadate previous to precipitation of the uranium. Elimination of vanadium is good by this procedure, which also reduces the iron content of the final product. The ferric vanadate precipitate has some tendency to redissolve, the tendency being accentuated by boiling or by prolonged standing. A short digestion, at a temperature below the boiling point, appears to improve both vanadium removal and the filterability of the precipitate.

In one series of tests, precipitation with NH_3 to a pH of 2.1 to 2.2 reduced vanadium from nearly 100 per cent, on a uranium basis, to 3 to 4 per cent. From 0.17 to 0.22 per cent of the uranium in solution was lost to the ferric vanadate precipitate. Increasing the pH to 2.5 reduced the vanadium to 1.8 per cent of the uranium, but the loss of uranium increased to 0.5 per cent.

Neutralization of the filtrate from the ferric vanadate precipitation to pH 7 with additional NH_3 precipitates the uranium. Most of the remaining chloride is eliminated in the precipitation and washing of the precipitate. The minor quantities remaining are removed by the calcination of the precipitate, so that the final product contains less than 0.1 per cent chloride.

The stepwise neutralization procedure was carried completely through on a 1-liter batch of acetone leach solution having the following analysis:

Grams/Liter					
U	V	Fe	Ca	Al	Cl
1.38	0.78	3.6	1.67	0.30	14.2

This was precipitated with anhydrous NH_3 , filtered, and repulped with 250 ml. of water, digested hot for a few minutes, filtered, and given two 100-ml. washes. After repulping, the precipitate retained only 16 per cent of the initial chloride content; the two washes reduced this to 1.5 per cent. The washed precipitate was redissolved in H_2SO_4 , a small amount of oxidizing agent ($KClO_3$) added, diluted to 500 ml., and precipitated, in this instance, with concentrated NH_4OH . After digestion at the boiling point for 10 minutes, the ferric vanadate was filtered off. The pH of the filtrate (cooled to room temperature) was 2.0. The filtrate was further neutralized to pH 7.6 with

SECRET

32

SECRET

38

concentrated NH_4OH , the precipitate filtered and calcined. The calcined product had the following analysis:

<u>Constituent</u>	<u>Per Cent</u>
U_3O_8	64.9
V_2O_5	0.71
Fe_2O_3	28.6
SiO_2	2.1(a)
MnO_2	1.4(a)
CaO	0.4(a)
NH_4	<0.001
Cl	<0.1

(a) Spectrographic analysis.

Vanadium content of the final product was 0.72 per cent of the uranium, well under maximum specifications. Both ammonia and chloride contents were also satisfactory. Iron content is somewhat high, but in view of the low salting strengths of current refinery feeds, this may not be a disadvantage. The only significant loss of uranium was to the ferric vanadate precipitate, amounting to 2 per cent of the uranium. Based on other data, this would have been less than 0.5 per cent if anhydrous NH_3 and lower digestion temperatures had been used.

If the uranium-vanadium separation is to be made by stepwise neutralization of an acid solution of the primary precipitate, removal of chlorides by repulping is preferable to removal by calcination. Attempts to dissolve calcined (350 to 500°C.) primary precipitates resulted in high acid-insoluble residues, amounting to 30 to 40 per cent. These consisted principally of iron oxide, with appreciable quantities of vanadium, but also contained from 1 to 2 per cent uranium. These residues were quite refractory, and were essentially insoluble even in boiling concentrated nitric acid. The uranium loss to this insoluble residue was as high as 11 per cent, but was 5 per cent even at the lowest calcination temperature.

Selective Dissolution. Since V_2O_5 is not readily soluble in dilute nitric acid, selective dissolution of the uranium from a calcined primary precipitate was briefly investigated as one means of securing a vanadium separation.

SECRET

SECRET

39

It was found that an attack sufficiently drastic to dissolve the uranium also dissolves appreciable amounts of the vanadium, so that no effective separation is possible.

Selective dissolution by a carbonate leach was also examined, quite briefly, near the conclusion of the investigation. Leaching with hot Na_2CO_3 or $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ solutions extracted only about 93 per cent of the uranium from a washed primary precipitate. Part of this loss may have been due to entrapped mother liquor since the residue was extremely difficult to filter and wash. From 85 to 95 per cent of the vanadium remained in the residue, so that a satisfactory vanadium separation was achieved. Separation from iron is also obtained by a carbonate leach, and the uranium product would be expected to be of high grade. Whether uranium losses could be reduced to tolerable levels is a question unanswered by the preliminary tests. Leaching tests with $(\text{NH}_4)_2\text{CO}_3$ showed comparable uranium losses, and resulted in the same general conclusions.

Soda Ash-Sawdust Fusion. One of the currently used methods for obtaining a uranium-vanadium separation is the soda ash-sawdust fusion method. In this method, yellow cake (sodium uranyl vanadate), the primary product recovered from the leach solutions, is fused with soda ash, with reducing agents such as sawdust and fuel oil added. The fused melt is chilled, ground, and leached in hot water, which dissolves the sodium vanadate, the uranium remaining as black oxide (U_3O_8). A high-grade product results when yellow cake is the feed, since U_3O_8 is essentially the only compound present which is insoluble in the sodium carbonate leach solution.

Preparation of only the primary precipitate at the mill site, with the vanadium separation being accomplished by a soda ash-sawdust fusion at a central mill, was considered as one of the possibilities for the acetone leach process. The grade of the final product from this method does not approach that obtained from fractional precipitation, because of the large amounts of iron present and the fact that iron elimination is negligible. Vanadium removal is good, a typical value for vanadium in the final product being 3 to 4 per cent of the uranium.

Some of the more recent work, not described in the progress reports, indicated that the above vanadium values could be bettered. This work indicated also that better separations were obtained when the feed had been calcined, that calcium did not interfere at the levels encountered in calcined primary precipitates, and that the addition of oil as a reducing agent was very deleterious. Although the early fusions had used only sawdust, later information from the Plateau had stated that fuel oil was also added to the charge, and this modification was included in the procedure. When oil was added, vanadium separations were very poor. Apparently the oil graphitized within the mass, forming a nearly impervious coating over some of the

SECRET

particles, which either prevented formation of sodium vanadate or prevented its dissolution in the subsequent leach.

Based on laboratory fusion tests of calcined primary precipitates obtained from early pilot-plant runs on normal carnotite ore, the final water-leached product would have an analysis approximately as follows:

<u>U₃O₈</u>	<u>V₂O₅</u>	<u>Fe₂O₃</u>	<u>CaO</u>	<u>Cl</u>
14-18	0.2-0.6	70-75	6-7	<0.1

The negligible elimination of iron by this process is apparent. Although vanadium specifications could be met, attainment of minimum uranium concentrations may be somewhat difficult.

Distillation of the Acetone Solution. Distillation of the acetone, leaving an aqueous residue of metal chlorides, is one method of recovering uranium from acetone-leach liquors. A number of disadvantages of this method are apparent. The large quantities of acetone which must be distilled per pound of uranium recovered, the associated heavy cooling-water demands, the possibility of excessive acetone degradation, and the increased cost and complexity of plant, are some of the more important ones.

Distillation was therefore tested only briefly. In one test, acetone leach solution was distilled, both as is (0.01 N free acid) and after neutralization with NH₃ to pH 7-8. No significant differences in volumes of acetone recovered were observed; within the limits of experimental error, there appeared to be no serious deterioration of the acetone upon distillation of slightly acid leach liquor. The test method was not definitive, but it is believed that appreciable deterioration would have been indicated, if existent.

Stepwise Neutralization of Acetone Solution. Preparation of a high-grade product directly from the acetone would be advantageous, if feasible. In one approach to this, fractional precipitation with NH₃ of a sample of acetone leach liquor from the pilot plant was examined. The selectivity observed in fractional precipitation of aqueous sulfuric acid solutions was not found in the acetone solution. Based on the analyses of the fractions, a large part of the uranium apparently precipitated as a uranyl vanadate; about one-half of the uranium and most of the vanadium came down below a pH of 3. Precipitation of the uranium was complete at a pH of 6.5, at which point all other ions precipitated by NH₃ were also down.

Sulfate Precipitation of Acetone Solution. One other method of recovering uranium directly from acetone leach solutions, which was briefly tested, involved its precipitation as a sulfate. In connection with the study of the use of sulfuric acid it had been noted that addition of K_2SO_4 or $(NH_4)_2SO_4$ to a uranyl sulfate solution in acetone produced insoluble crystalline precipitates, apparently double salts of uranium. Attempts to apply this mechanism as a means of recovering uranium from acetone leach solutions were only moderately successful. Although precipitation of fair amounts of uranium was very readily accomplished, quantitative precipitation was not obtained even with large excesses of reagent. Further, the selectivity was poor and substantial percentages of the vanadium were also precipitated. Ammonium, sodium, and potassium sulfates were tested (0.5 M concentration) as both neutral and 0.5 M H_2SO_4 solutions. One other serious objection to the method was the dilution of the acetone by the water accompanying the sulfate salt. No reaction occurred when the sulfates were added as anhydrous salts.

Ion Exchange. Adsorption by ion-exchange resins is one feasible method of recovering uranium directly from acetone leach solutions, with the further advantage that a very high-grade product results. In general, although distribution coefficients may be quite high, adsorption rates are slower than in aqueous media, a fact verified experimentally by earlier tests with a strong-base resin (IRA-400) in methanol leach solution. Later tests with acetone leach solution also confirmed the conclusion that only the strong-base resins had satisfactory distribution coefficients for uranium; coefficients were of the order of 300 to 500. Distribution coefficients for vanadium were negligible, and a sharp separation should be possible.

The low adsorption rates would necessitate low throughputs and the capital investment for an ion-exchange plant of sufficient capacity would undoubtedly be high. Ion-exchange adsorption also did not fit in with the goal of a plant of minimum complexity. Primarily for these reasons ion-exchange adsorption from acetone leach solutions was not studied further. However, it should no doubt be reconsidered if the process is carried further at some later date.

Nonaqueous Extraction With Other Solvents

Several alternative solvents, primarily alcohols and higher ketones, for acetone in the HCl-solvent leach process have been considered. The earliest work on the HCl process involved the use of methyl alcohol, which is as good a solvent as acetone for uranyl chloride, and apparently a better one for uranyl sulfate. Its solubility for uranyl sulfate is not quite high

SECRET

42

enough, however, to provide satisfactory uranium extraction from all-sulfate systems. Calcium chloride solution is miscible with the lower alcohols (methyl, ethyl, N-propyl, and isopropyl) and agglomeration and rapid settling were not observed. Satisfactory agglomeration was obtained with n-butyl and n-amyl alcohols, and presumably would be obtained also with still higher alcohols. Uranium extractions with anhydrous butyl and amyl alcohols were comparable to those with acetone and either could be used, although their relatively high viscosities hinder settling rates. The high boiling points (over 100°C.) would probably make recovery from the tailings more difficult.

The use of other ketones of higher flash point and lower volatility than acetone might be desirable in a plant. The most attractive of these, from a price standpoint, are methyl ethyl ketone (MEK) at about \$0.11/lb., and methyl isobutyl ketone (MIBK, or hexone) at about \$0.13 to \$0.16/lb., both moderately more expensive than acetone at about \$0.08/lb. MIBK systems had excellent settling characteristics, but, based on the results of the few tests of its use, uranium extractions were reduced. Uranium extractions and settling behavior with anhydrous MEK were comparable to acetone. However, unlike acetone, MEK forms an azeotrope with water, and a plant leaching circuit might eventually attain the equilibrium level of 10 to 11 per cent water. When water-saturated MEK was used for leaching tests, distribution of the metal chlorides to the solvent displaced some of the water, so that a discrete aqueous phase resulted. Since uranium and vanadium concentrations in this aqueous phase were high, losses of metal values to the tailings were serious. The feasibility of using MEK would hinge on the water balance of the leach circuit, and whether water concentrations could be kept below levels which result in the formation of an aqueous phase. If this were not possible, recovery of anhydrous MEK would be necessary, which would add substantially to the cost of using this solvent.

Acetone remains the most satisfactory solvent of those tested to date. Its most serious disadvantage is its low flash point; on the other hand, this same volatility aids in its recovery from the tailings. One advantage is that acetone does not form an azeotrope with water, and occasional solvent dehydration or purification could therefore readily be accomplished by distillation. A more extensive investigation of possible alternative solvents should be considered before any large-scale pilot-plant operations are initiated.

Some of the recent work at the Oak Ridge National Laboratory has indicated that a number of the long-chain amines are promising solvents for the extraction of uranium from sulfate solutions. One of these, tri-n-octylamine in a hydrocarbon solvent, was tested briefly, with unpromising results. Extraction of uranium from H₂SO₄-cured ore was low and the desired agglomeration and rapid settling were not obtained. Both uranium extraction and settling behavior were better with HCl-cured ore, but neither approached that attainable with acetone.

SECRET

SECRET

43

The original objective of the investigation was to discover a readily liquefiable gas or low-boiling liquid which could directly extract uranium from Western ores. The results of this work were negative and they are described but briefly in this report; details of the work may be found in the early quarterly progress reports.

Among the readily liquefiable gases tested were ammonia, nitrogen dioxide, sulfur dioxide and trioxide, and chlorine, at pressures up to 1000 psi. None was found to be an effective solvent for carnotite. Even in those cases where an apparent reaction occurred, the end product was insoluble in the liquid.

Ammonia and SO_2 were the most thoroughly investigated, both alone and with additives. A considerable number of potential complexing agents are soluble in liquid ammonia. A very few of these, chief of which was thioglycolic acid, solubilized carnotite when added first, the resultant product being soluble in liquid ammonia. No solubilization occurred when the additive was added last. Results with liquid SO_2 were negative with all additives tested.

Study of low-boiling liquids as solvents for synthetic carnotite revealed none which would dissolve carnotite directly. Several reacted with carnotite to form products soluble in water or certain organic solvents, including methyl and ethyl alcohols, and acetone. Among these were sulfur chloride (S_2Cl_2), thionyl chloride (SOCl_2), and thiophosphoryl chloride (PSCl_3). The evidence indicated that solubilization depended on the presence of HCl , formed as a result of hydrolysis of part of the chloride reagent. The presence of water was therefore necessary, although the normal water of hydration of carnotite appeared to be sufficient. No reaction occurred when the carnotite was anhydrous, and only incomplete reaction when the carnotite was partially dehydrated by drying at 105°C . U_3O_8 reacted only incompletely, under all conditions.

Conversion of carnotite to uranium and vanadium chlorides thus appeared to be a simple acid dissolution. HCl in any of the same solvents likewise dissolved carnotite. The use of HCl would be preferable from the standpoint of both cost and reactivity with the solvent.

The conclusion drawn from the initial work with readily liquefiable gases and low-boiling solvents was that the uranium is quite strongly bound and not subject to attack by complexing agents. Presumably this is also the case for the other complex minerals found in Western ores. The most promising means of solubilizing uranium appeared to be by attack with a mineral acid, which could be carried out in nonaqueous media, or with more refractory ores, probably preferably by an acid-cure preceding the non-aqueous leach. Exploration of this approach ultimately resulted in the development of the HCl -acetone process.

SECRET

53 18

High-Temperature Chlorination

Another nonaqueous extractive method involves volatilization of the desired metal values by a high-temperature vapor-phase chlorination, using either Cl_2 or CCl_4 . Although such an approach has been investigated for other uranium ores, in most cases the associated gangue materials were also reactive, and consumption of chlorinating agent by the gangue materials was excessive. Since about 80 per cent of a carnotite ore may be silica, which is not readily chlorinated, chlorination of carnotites appeared to offer more favorable conditions. Chlorination of carnotite had not apparently been investigated heretofore, and was examined in some detail.

Preliminary qualitative tests indicated that treatment of synthetic carnotite with an excess of Cl_2 at 600°C . for 1 hour volatilized the vanadium, but essentially none of the uranium. At 1000°C ., both uranium and vanadium were volatilized completely upon treatment with an excess of Cl_2 . The vanadium appeared as a reddish liquid, probably VCl_4 , and the uranium deposited as a yellow solid (presumably uranyl chloride, UO_2Cl_2) at the cold end of the tube. Chlorination at 1000°C . converted UO_2 , UO_3 , and U_3O_8 to black substances (crystalline in the case of the UO_2) with no observable volatilization.

UO_2 , UO_3 , and U_3O_8 were successfully volatilized at temperatures of 500 - 1000°C ., using variously CCl_4 , S_2Cl_2 , and Cl_2 plus carbon.

The effect of CCl_4 and S_2Cl_2 on synthetic carnotite at 600 - 800°C . was to volatilize the vanadium readily, leaving behind a greenish-black substance. This uranium-containing substance appeared to have a low vapor pressure; it was still relatively nonvolatile at 800°C . It is thought that it may have been a double salt of perhaps the composition $\text{KCl} \cdot \text{UCl}_4$. It was readily soluble in hot or cold water. Sodium diuranate formed a similar residue when chlorinated with CCl_4 at 600°C . Hydrogen chloride failed to volatilize uranium from synthetic carnotite at 1000°C . Likewise, a salt-carbon sintering at 1000°C . volatilized essentially no uranium, though perhaps 60 per cent of the vanadium.

Preliminary tests with 5-gram samples of Western ores in a horizontal-tube furnace indicated that nearly complete volatilization of both uranium and vanadium can be obtained by chlorination with Cl_2 at 1000°C . Removals of uranium and vanadium were from 93 to 98 per cent with Temple Mountain (A-10), Lukachukai (A-30), and normal carnotite (A-50) ores; somewhat lower values were obtained on some ores. Residue assays indicated that at 1000°C ., Cl_2 did not react with the Al_2O_3 in the matrix; the chief Cl_2 consumers were iron, calcium, other minor alkalis, uranium, and vanadium. Calculated "order of magnitude" values on this basis indicated that Cl_2 consumption might range from 100 to 400 lbs./ton of ore.

Reducing-chlorinating agents, such as CCl_4 , are often effective at lower temperatures than Cl_2 itself. Preliminary test work with roasted Temple Mountain ore (A-10) indicated that solubilization of the uranium of up to 90 per cent could be attained at temperatures as low as 300°C . Volatilization was negligible at this temperature; but was 84 per cent at 600°C . and 92 per cent at 700°C . These temperatures were substantially lower than the 900 - 1000°C . required with Cl_2 . The "reaction start" temperature for vanadium appeared to be between 400 and 500°C . At 500°C . vanadium removal was 94 per cent. CCl_4 would be expected to react with Al_2O_3 , where Cl_2 does not, thus increasing reagent requirements. Spectrographic assays of the above residues confirmed this, indicating a "reaction-start" temperature also of about 500°C . for the Al_2O_3 . At 500°C . and above the residues contained only 0.02-0.2 per cent Al_2O_3 . The water-leached residues also contained essentially no calcium or iron, indicating complete chlorination of these metals.

Most of the ore-chlorinating studies, after the initial boat tests, were conducted in a vertical Vycor reactor (1 by 22 inches) externally heated by a tube furnace. Degree of agitation of the bed varied from completely fluidized to quiescent. Since volumes of vapor required for the reaction were insufficient for fluidization, nitrogen was used to make up the difference after experimental data had shown that CCl_4 could safely be diluted with N_2 by as much as 95 per cent. Air could not be tolerated, because oxidation of the uranium chlorides resulted.

Effectiveness of utilization was low when a fluidized bed was used, and much of the chlorinating agent passed through the bed unreacted. Although longer retention times would exist in a commercial scale unit, it does not appear that complete utilization could be attained, and recycle of the chlorinating agent would constitute a major problem. With relatively deep beds, lower flow rates provided quiescent beds and long retention times of the chlorinating agent. These conditions were more favorable for the apparently rate-controlling diffusion of the chlorinating agent (and/or the volatile chlorides), and efficiency of utilization was much improved. In one such deep-bed test, chlorinated with CCl_4 at $\sim 600^\circ\text{C}$., analysis of the residue indicated 94 per cent volatilization from the bottom third of the bed, 76 per cent for the center third, and 61 per cent for the top third. These data indicate that it should be possible to design a continuous vertical reactor which could, operated countercurrently, produce satisfactory uranium volatilization at 600°C . with near-stoichiometric quantities of CCl_4 . This would eliminate the problem of recycling large excesses of chlorinating agent.

CCl_4 has the advantage over Cl_2 in that operating temperatures can be several hundred degrees lower, for a savings in heat costs. On the other

SECRET

46

hand, Cl_2 is a cheaper source of chlorine, and has the further advantage that less would be consumed, since it does not appreciably attack Al_2O_3 . Cl_2 plus carbon could also be used, in which case the temperature could be lowered, but at the expense of attacking the Al_2O_3 . Satisfactory materials of construction would be a major problem with either reagent.

Although precise measurements of chlorinating-agent consumption were not feasible in the small-scale laboratory tests, the indications were that they were at least as high as the calculated theoretical values. Even at this level, it was apparent that reagent costs would be substantially higher than for the HCl -solvent leach process then being developed. In addition, whereas the leaching process utilizes largely conventional equipment, the volatilization process would require a major design effort before suitable equipment could be built. When continued improvement of the HCl -solvent leach process increased the potential cost differential even more, further study of the volatilization of uranium was abandoned.

RECOMMENDATIONS FOR FUTURE WORK

Future work on nonaqueous extractive methods should undoubtedly center about the HCl -acetone process. Much more remains to be learned about continuous operation, preferably on a larger scale than the ton per day pilot plant operated for a short while at Battelle, and particularly with respect to material balances of the various streams, so that a better evaluation of the economics of the process can be made.

The prime objective of any future laboratory studies would be to devise methods of further reducing acid costs since this seems to constitute the largest single drawback of the proposed process. Methods of obtaining a higher grade concentrate at an earlier step in the process would also be desirable; in this connection further study of ion-exchange is needed. Due to the variations in amenability of the Western ores, additional study of optimum treatment procedures for the various types of ore would be needed in any extension of the program.

Additional study of materials of construction, if only to confirm the suitability of already selected materials, would be advisable.

A general tidying-up of process details, not possible during the current investigation, would be another objective of future work. This would be particularly desirable if additional larger scale operations were contemplated, since many of the now unanswered questions could be answered more economically in the laboratory.

RAE:SJK:AEB/NLC/bt/jj

SECRET

SECRET

47

APPENDIX

Analyses of Ores

Most of the ore samples used for the test program originated from the operations at Monticello, Utah. Two samples of Temple Mountain ore were obtained from The Vitro Chemical Company at Salt Lake City, Utah. Several other ore samples from Grants, New Mexico, were analyzed but were given only limited study. The ores on which complete chemical analyses are available are shown in Table 7.

Except for the 5-ton lots of ore, the usual procedure was to grind the ores by passing them through a small jaw crusher and then through a McCool disk grinder, after which representative samples were split out for analysis. The Vitro samples were mill-feed samples, and were not further reduced. The 5-ton lots had likewise been ground before shipment and required no additional grinding. Screen analyses are also shown in Table 7.

Uranium distribution was determined for a number of the samples. The uranium in normal carnotite ores appeared to reside largely in the fines. For example, A-50 ore which had 12.3 per cent by weight of minus 325-mesh material, contained 45.2 per cent of the uranium in this fraction. In A-11 ore (Temple Mountain) both uranium and vanadium distributions followed the weight distribution fairly closely. Steen ore (A-71) also had a uranium distribution quite close to the weight distribution. This was not appreciably altered by grinding to minus 50 mesh. Somewhat finer grinding may be required to liberate the uranium from these latter ores than is needed for the normal carnotites.

List of Related Reports

The following progress reports entitled "Nonaqueous Extractive Methods for Western Uranium Ores" have been issued:

BMI-264, January 15, 1953, by R. A. Ewing, M. Pobereskin,
R. B. Kimball, and A. E. Bearse.

BMI-265, April 15, 1953, by R. A. Ewing, M. Pobereskin,
R. B. Kimball, and A. E. Bearse.

SECRET

~~SECRET~~

48

~~CONFIDENTIAL~~

TABLE 7. CHEMICAL AND SCREEN

BMI Number:	A-10	A-11	A-12	A-20	A-30	A-40
Stockpile:	--	Vitro	Vitro Calcines	--	--	--
Ore Type:	Temple Mountain	Temple Mountain	Temple Mountain	Sinbad-Muddy River	Lukachukai	7-Mile Canyon
<u>Chemical Analysis,</u>						
SiO ₂	80.4	79.8	87.0	74.1	75.1	55.5
CaCO ₃	1.34	1.6	2.1	6.1	13.2	23.6
Al ₂ O ₃	3.70	5.8	6.2	7.13	3.66	10.3
Fe ₂ O ₃	1.51	1.8	1.6	2.84	1.29	2.66
Total SO ₄	3.38	3.9	0.64	3.33	0.16	2.66
SO ₄ ⁼	--	0.9	0.4	--	--	--
PrO ₅	0.13	--	--	0.12	0.06	0.10
Total C	6.6	4.1	0.7	--	--	--
CO ₂	1.27	1.0	0.9	4.42	5.77	9.50
L.O.I.(c)	9.8	--	--	7.4	6.4	12.0
Cu	--	--	--	--	--	--
U	0.51	0.26	0.24	0.09	0.46	0.12
V	0.56	0.60	0.54	0.02	1.16	0.05
<u>Screen Analysis,</u>						
-8+16	2.2	3.5	4.2	4.5	0.2	1.4
-16+30	15.8	15.6	15.7	15.0	2.2	13.7
-30+50	29.2	30.2	28.3	26.1	13.6	21.6
-50+70	16.3	14.8	15.1	15.0	9.5	10.0
-70+100	14.2	15.8	17.5	12.4	25.8	11.7
-100+200	10.7	12.0	12.5	10.5	33.5	13.4
-200	11.6	8.1	6.7	16.5	15.2	28.2

(a) 5-ton lots.

(b) After drying at 105°C.

(c) Loss on ignition at 1000°C.

~~SECRET~~

~~SECRET~~~~UNCLASSIFIED~~

49

~~CONFIDENTIAL~~

ANALYSES OF WESTERN ORES

A-50	A-51	A-60	A-71	A-90	B-10	B-20	B-30
29	29	--	33	6	Bluewater 1	Bluewater 2	Bluewater 3
Normal Carnotite	Normal Carnotite ^(a)	Copper- Uranium	Steen (Utex)	Misc. High- Lime ^(a)	Limestone	Blue Peak	Silver Spur
<u>per cent^(b)</u>							
86.7	--	71.0	70.5	--	8.9	76.9	89.5
2.74	3.0	5.13	12.5	14.1	90.8	3.34	1.21
3.11	--	7.61	7.9	--	0.90	11.0	5.20
1.62	1.00	4.96	2.5	1.85	0.41	1.88	0.89
0.44	0.24	5.05	0.63	0.57	0.35	1.75	0.22
--	0.09	4.7	0.15	0.21	--	--	--
0.16	--	0.18	--	--	<0.05	<0.05	<0.05
--	--	0.50	1.7	2.37	--	--	--
3.52	1.4	0.81	3.1	6.8	37.5	0.76	0.63
2.5	--	7.3	--	--	38.2	4.1	1.4
--	--	1.12	--	--	--	--	--
0.22	0.27	0.22	0.32	0.22	0.18	0.10	0.16
0.66	0.94	0.02	0.48	0.93	0.06	0.05	0.14
<u>per cent</u>							
tr	9.2	0.2	--	9.5	0.2	0.1	0
0.7	10.8	4.6	15.2	12.1	3.8	2.4	0.1
18.4	13.4	24.3	19.1	17.8	16.7	14.8	7.9
12.3	13.0	12.6	11.0	14.0	8.6	12.5	10.9
24.4	23.8	14.6	14.5	16.4	11.2	27.3	33.4
25.0	{29.8}	17.3	19.6	{30.2}	16.9	26.4	40.9
19.2		26.4	20.6		42.6	16.5	6.8

~~CONFIDENTIAL~~~~SECRET~~~~UNCLASSIFIED~~

~~SECRET~~

50

BMI-271, July 15, 1953, by R. A. Ewing, M. Pobereskin,
R. B. Kimball, and A. E. Bearse.

BMI-273, October 20, 1953, by R. A. Ewing, M. Pobereskin,
R. B. Kimball, and A. E. Bearse.

BMI-276, January 20, 1954, by R. A. Ewing, R. B. Kimball,
S. J. Kiehl, Jr., and A. E. Bearse.

BMI-277, April 20, 1954, by R. A. Ewing, R. B. Kimball,
S. J. Kiehl, Jr., and A. E. Bearse.

BMI-278, October 20, 1954, by R. A. Ewing, D. D. Foley, A. E.
Bearse, and R. B. Filbert, Jr.

RAE:SJK:AEB/jj

UNCLASSIFIED

~~SECRET~~