ENGINEERING RESEARCH INSTITUTE
THE UNIVERSITY OF MICHIGAN
ANN ARBOR

THE ACID DISSOLUTION OF SOME

URANIUM ORE CONCENTRATES

Final Report on

Supporting Experimental Work

for the

Dow Nuclear Materials Plant Studies

H. A. Ohlgren
Lee Chajson
K. S. Sanvordenker

Project 2552

Dow Chemical Company

October 5, 1956

TABLE OF CONTENTS

LIST OF TABLES

1.0 INTRODUCTION

The staff of the Engineering Research Institute of the University of Michigan recently performed certain evaluations for the Dow Chemical Company on the processing of domestic uranium ore concentrates. In support of this work, preliminary laboratory studies on the nitric acid dissolution of ore concentrates were carried out.

The results of the early experimental work were submitted to the Dow Chemical Company in rough draft form as Memo #1 and Memo #2. These memoranda are included in the Appendix to this report for convenient reference. It will be recalled that the first memorandum (dated August 9, 1956) presented mainly qualitative information on the behavior of various uranium ore concentrates when contacted with nitric acid solutions. The second memorandum (dated September 4, 1956) reported some quantitative data on acid consumption and on uranium material balances.

This report, in conjunction with Memos #1 and #2 in the Appendix, is intended to bring up to date all of the laboratory work on the dissolution of uranium ore concentrates, including the analytical methods developed specifically for these studies.

2.0 ACID USED FOR DISSOLUTION

The cp nitric acid stock solution used in preparing the acid feeds for all of the experimental work was analyzed and found to be 15.9N in concentration. It should be noted that all the results reported in Memos #1 and #2 were based on an assumed concentration of 16.0N and, therefore, a slight correction is necessary.

3.0 DISSOLUTION RATES

3.1 Batch Dissolution

It was reported in Memo #2 that the uranium ore concentrates can be dissolved with nitric acid solutions of various strengths, and that the rate of dissolution was a function of the concentration of nitric acid solution.

With boiling 4M nitric acid, the dissolution is complete within 2 minutes whereas with 2M nitric acid, the dissolution takes about 20 minutes. Two representative runs supporting this conclusion are presented in Tables I and II, shown on the following page.

3.2 Continuous Dissolution

In view of the many advantages to be gained in developing a completely continuous system, a continuous glass dissolver was designed and tested in the laboratory. This vessel consisted of a 1" I.D. glass tube, 12" long, with a steam jacket 6" long at the bottom, fitted with connections for acid inlet and outlet. A reflux condenser was attached at the top to condense and return acid vapors.

The ore was fed at the top semicontinuously and the acid feed adjusted to a residence time of about 2 minutes. The steam jacket maintained the solution temperature at about 180°F.

For countercurrent dissolution, the ore was fed from the top through the reflux condenser and the acid solution from the bottom. The product was removed by the side connection, above the steam jacket.

In the con-current dissolution runs the ore was fed at the top as before, but the acid inlet was at the top instead of the bottom, while the product was removed at the bottom connection through a jack-leg. This type of operation appears better since it gives enough contact time and avoids the short circuiting of the ore into the outgoing product stream.

The only problem encountered in these systems was the wetting of the ores. The Anaconda acid and carbonate ores have bulk densities lower than that of water and the lumps of ore float on the surface for a few moments before wetting and sinking. These engineering problems can be satisfactorily resolved by suitable design of dissolution equipment.

TABLE I

DISSOLUTION OF 100 g. DURANGO ORE

IN 3.98M HNO$_3$

Sample No.	Contact Time (mins)	Specific Gravity (25℃)	Uranium (g/l)	Free Acid M	Acid Consumption (g/g of U)
S$_{21}$	2	1.300	143	1.92	.896
S$_{22}$	5	1.295	138	1.90	.95
S$_{23}$	10	1.297	139	1.92	.935

TABLE II

DISSOLUTION OF 100 g. DURANGO ORE

IN 1.99M HNO$_3$

Sample No.	Contact Time (mins)	Specific Gravity (25℃)	Uranium (g/l)	Free Acid M	Acid Consumption (g/g of U)
S$_{25}$	2	1.112	33	1.43	1.07
S$_{26}$	5	1.194	105	.26	1.04
S$_{27}$	10	1.234	136	*	.92
S$_{28}$	20	1.242	145	*	.86

*Acid deficient solutions. Material balance showed that essentially all the uranium is dissolved at the end of 20 minutes.

The samples taken during the continuous dissolution runs have been submitted to the Dow Chemical Company's analytical laboratories in Midland. A quantitative evaluation of the continuous dissolving runs must await the analytical results for these samples.

4.0 SOLIDS IN PRODUCT

The dissolver product formed on contacting the uranium-bearing concentrates with nitric acid contains an insoluble residue amounting to about 0.68% by weight of the ore. Spectroscopic analysis shows that the residue consists mainly of silica, with more than trace amounts of Al, Fe, Mg, Ti and Va, and with trace amounts of Cu and Ag. Quantitative data on this residue are presented in Table III below.

TABLE III

RESIDUE IN DISSOLVER PRODUCT SOLUTIONS

Loss in weight after ignition at 870°F	18%
Silica (SiO_2) in ignited residue	76%
Silica on basis of "as received" residue	62%
Uranium content of ignited residue	0.1%

5.0 STABILITY OF THE DISSOLVER SOLUTIONS

It was reported in Memo #2 that, on standing, the uranium solutions precipitate a white gelatinous material, resembling silica gel, amounting to about 2% of the ore. Analytical data on this precipitate are presented in Table IV below.

TABLE IV

SOLIDS FORMED IN DISSOLVER SOLUTIONS ON STANDING

Loss in weight on ignition	15%
Silica (SiO_2) in ignited residue	79%
Silica on basis of "as received" residue (dried at 110°C)	82%

The residue remaining after removal of silica could not be readily analyzed for uranium content due to its insolubility in nitric acid.

6.0 ACID CONSUMPTION

The batch dissolution data indicate that the nitric acid consumption is approximately 1g/g U. On the basis of the total ore fed, the nitric acid consumption is about 65g/100g ore. The acid consumption may be reduced by using low acid concentrations but at the cost of increased time of dissolution.

7.0 ANALYTICAL TECHNIQUES

Methods of analysis for uranium content, the free acid content, etc., of the dissolver product solutions, as well as the techniques for analysis of solid residues are presented below. Some of these have been developed at the University of Michigan laboratories, whereas others have been adapted from methods in the literature.

7.1 Analysis of Dissolver Product Solutions

7.1.1 Density

Density was determined by direct weighing using 2-ml. specific gravity bottles calibrated with distilled gas-free water. The results are reported for a temperature of 25°C. compared to water at 25°C. To obtain the "true" density, i.e., the density at 25°C. compared to water at 4°C. (density of water at 4°C = 1.000), the figures given should be multiplied by 0.99707.

Where the original sample was cloudy, it was centrifuged and the clear supernatant solution was used in the density determination. The contents of the specific gravity bottle were then quantitatively transferred to a volumetric flask and diluted to volume. Aliquots of the latter solution were usually used for the sodium hydroxide titrations and the uranium determinations.

7.1.2 Free Acid Determination

This determination when carried out in the presence of hydro-lyzable or precipitable metal ions is a tricky one and often is based upon a purely empirical procedure. A large number of such procedures have been proposed; these are usually based on the addition of a complex-forming anion whose purpose is to keep the metal ions from reacting with the hydroxide ions; none of these methods is generally applicable. Usually, each laboratory develops a particular procedure with which it attempts to live. Two procedures have been used. One is based on the procedure used at Fernald, and involves the addition of oxalate and titration to an arbitrary pH of 6.05.

The second procedure is one developed by the University of
Michigan. Based on a study made at Oak Ridge a number of
years ago on the hydrolytic behavior of uranium, it was
calculated that it might be possible to get a direct "free
acid" figure on the present solutions. The experimental
potentiometric titration curves showed for the diluted dis-
solution sample solutions (a) an initial pH of about 1.5,
(b) a gradual step with the inflection point of the rise at
about pH 3, and (c) a rising curve with a kink at about
pH 5 and a steep rise from pH 6 to 8; the kink at pH 5 was
also observed in the Oak Ridge work. The volume of NaOH
solution needed to reach pH 3 was originally used to calculate
the "free acid" molarity given in the reported data; the volume
of base needed to go from pH 3 to pH 8 was used to calculate
"equivalents of hydrolyzable metal" per liter of sample
solution.

A brief series of experiments was run to evaluate the two
procedures. A nitric acid solution (0.500$\underline{M}$ based on
titration with standard sodium hydroxide solution using methyl
red as indicator) was, after suitable dilution, titrated by
both procedures. The 80 $\pm$ 1 mg. of uranyl nitrate hexahydrate
(38 mg. U) was added to similar amounts of acid and the
titrations were repeated. The results are given in Table V below.

TABLE V

COMPARISON OF ANALYTICAL PROCEDURES

Sample	"Free Acid" (U-M) $\underline{M}$	"Hydrolyzable Metals" (U-M) equivalents	"Free Acid" (Ox) $\underline{M}$
HNO_3	0.473 (pH 3)		0.444
	0.504 (max)		
HNO_3+U	0.481 (pH 3)	0.40	0.474
	0.510 (max)	0.34	
Calcu-lated	0.500	0.32	0.500
		(U = 2 OH)	

These experiments indicated that (a) the oxalate procedure gives low results, (b) the U-M procedure, when using pH 3 as an arbitrary equivalence point in the titration, gives low results for "free acid" but these are still better than those obtained by the oxalate method, (c) the U-M procedure for "free acid" gives good results if the maximum change in slope of the titration curve is used as the equivalent point, and (d) the "equivalents of hydrolyzable metal" are a very rough measure of the uranium content (and, obviously, of other precipitable metals present). The data given for the "free acid" in the Solution Samples by the U-M method are based on calculation from the maximum slope of the titration curve.

7.1.3 Uranium Determination

Most of the uranium determinations were done by an adaptation of the Brookhaven National Laboratories modification of the dibenzoylmethane spectrophotometric method. A few results were obtained by a titrimetric procedure (Jones reductor, aeration, addition of excess $Fe(III)$ and potentiometric titration with standard dichromate). At the present time the data are insufficient to express an opinion as to whether the photometric or titrimetric method is the more accurate; both methods have a precision of 1 or 2 relative per cent.

The uranium normality figure was taken as twice the uranium molarity so as to compare the data to the NaOH titration data.

7.2 Analysis of Solid Residues

7.2.1 Residue from Dissolution Experiments

This residue is ignited at 800°C to remove the volatile constituents. It is then fused with sodium carbonate, cooled, and dissolved in nitric acid. The insoluble residue (oxides of silicon, tin, etc.) is filtered and the solution analyzed colorimetrically for uranium content. The insoluble nitric acid residue is treated with hydrochloric acid and the extract subjected to emission spectroscopy to determine the constituents. The insolubles are probably all silica and will be investigated further.

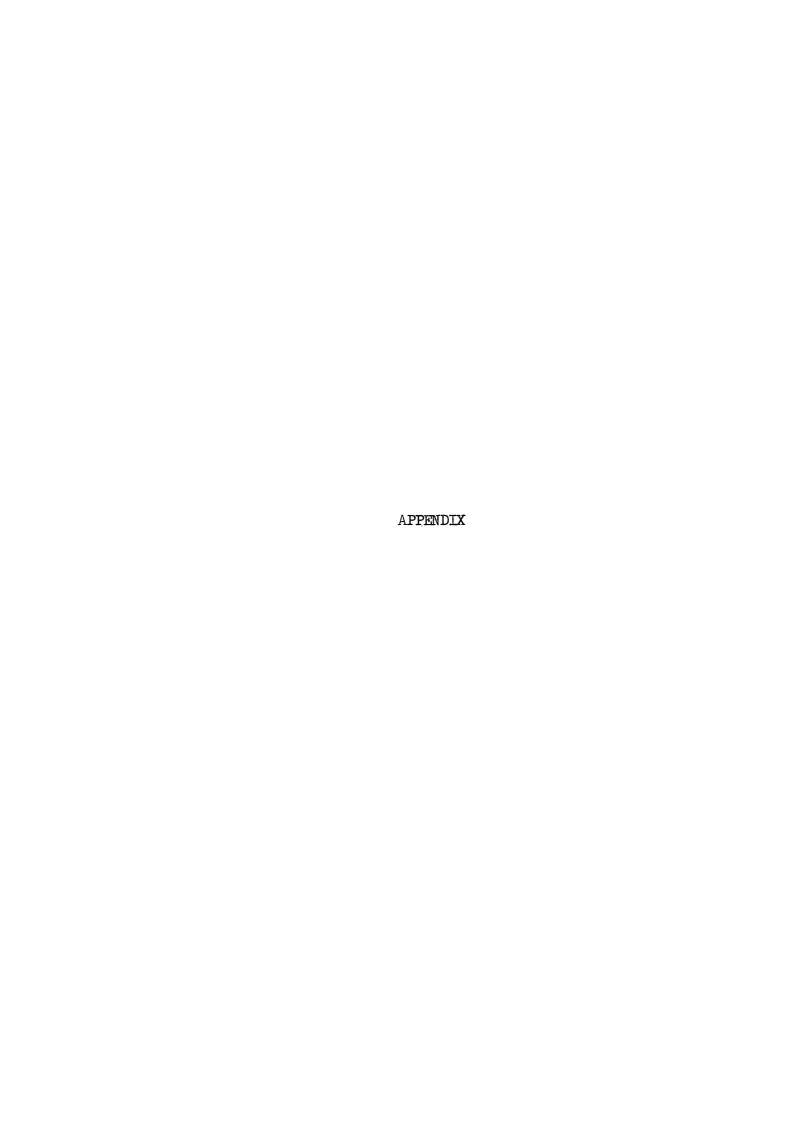### 7.2.2 Solid Precipitated from U Solutions on Storage

This gelatinous precipitate is first dried at 110°C and then evaporated with a mixture of hydrofluoric and sulfuric acids to volatalize silica. The remainder is not soluble in nitric acid, so that a method of U determination has not yet been developed.

A part of the precipitate is ignited at 870°C to determine the volatiles and the silica in the remainder determined by the above technique.

8.0 SUMMARY AND CONCLUSIONS

The laboratory work described in this report was of a "scouting" nature rather than a precise, systematic investigation of the variables involved. Consequently, the data must be considered preliminary and subject to confirmation and extension. Nevertheless, the results probably justify drawing the following conclusions:

a. There is no significant difference in the dissolution rates of the various domestic ore concentrates that were tested.

b. The fastest dissolution rates are obtained with a nitric acid concentration of four to five molar.

c. At this acid concentration all of the concentrates tested can be dissolved in less than five minutes, at boiling temperatures.

d. Approximately one gram of nitric acid is consumed for each gram of uranium dissolved.

e. The ore concentrates can be dissolved to acid-deficient conditions; hence, acid economy is possible if a proper flowsheet for the subsequent extraction steps can be developed.

f. The dissolution product contains a residue amounting to less than 1% of the ore, by weight. The residue is mainly silica and contains less than 0.1% uranium.

g. On standing, the dissolver product solutions precipitate a material, which is mainly silica, in amounts to about 2% of the ore concentrate, by weight.

h. Laboratory-scale continuous dissolution runs on uranium ore concentrates were successfully carried out. Since continuous dissolving offers many operational and economic advantages over the present batch techniques, further work on this concept is strongly recommended.

APPENDIX

1.0 INTRODUCTION

Three uranium concentrates, viz. (1) VCA Durango Lot A58, (2) Anaconda
Acid A 94 A, (3) Anaconda Carbonate A 97 C, were studied for their
dissolution kinetics in nitric acid solutions, on a laboratory scale
batch dissolution.

During the period in which the continuous countercurrent dissolution
apparatus is being fabricated, the experimental study was conducted
on a batch scale. The basic equipment consisted essentially of a
1000 ml flask equipped with a stirrer, a thermometer socket and a
reflux condenser. The conditions in the reactor were those of a
stirred pot reactor.

Suitable analytical techniques for the uranium concentration in
presence of the accompanying foreign matter are under a stage of develop-
ment. In absence of rigorous analytical data, quantitative results
cannot be presented; however, certain generalizations and the behavior of
the ores on acid treatment can be obtained from the experimental work
done so far. These results are of great use in the design of any pilot
plant dissolution equipment.

2.0 BEHAVIOR OF DURANGO ORE LOT A 58

The Durango ore is a fairly dense black powder with a bulk density of
about 2 g/cc and a packed density of about 3 g/cc. It readily dissolves
in concentrated nitric acid with voluminous NO_2 fumes accompanied by
heat evolution. A little white residue remains undissolved. The dis-
solution proceeds slower in diluted nitric acid solution up to $4.0M$ HNO_3,
the dissolution being complete in about 20 minutes time. The rate of
dissolution increases as the dissolution proceeds. This suggests that
the rates of dissolution increase at higher temperatures caused by the
heat evolution or, as some literature references indicate, the uranyl
nitrate formed in the initial stages acts as an accelerator of the
reaction.

At elevated temperatures, viz. boiling nitric acid solutions, the
dissolution rates are very fast, and the reaction proceeds to completion
within 5 minutes of start. The concentration of nitric acid or the
acidity does play an important part. Thus, with a nitric acid strength
of $2.4M$, the solution seems to hydrolyze forming a brown precipitate,
presumably of hydroxides of uranium. A nitric acid concentration of about
$4.0M$ seems to be the best compromise.

As the concentration of uranium in solution increases, so does the
viscosity and specific gravity of the solution. The viscosity is
important for subsequent handling of the solutions. The conflict of
interests lies in the desirability of a high uranium concentration in
the solution and a low enough viscosity for ease of handling the
solution. Visual judgment suggests that a concentration of about 120-150
g/U^{238} in solution is the optimum.

The solution is difficult to filter and the separation of the slime may be done by operations like centrifuging rather than by the conventional filter cloth. A little frothing is observed during dissolution.

3.0 BEHAVIOR OF ANACONDA ACID AND THE CARBONATE ORES

The acid ore is a yellow, light, fluffy powder. The bulk density is about .5 g/cc and the packed density about .7 g/cc. The powder lumps float in water and a wetting agent may have to be used in large scale operation.

The carbonate ore is also light yellow, having a bulk density of about .8 g/cc and a packed density of about 1.1 g/cc. The powder floats in water, although it poses a problem not as serious as the acid ore.

Both the ores dissolve easier in dilute nitric acid than in concentrated nitric acid; at room temperatures, the best concentration of nitric acid solution seems to be 3$\underline{M}$. The dissolution is accompanied by only a little NO_2 evolution and a little heat evolution. The dissolution is much faster than the Durango ore. The solutions present no problem of filtration and the separation of the slime should be fairly easy.

The acid ore forms a yellow solution whereas the carbonate ore forms a dark, brownish solution. The carbonate ore solution seems to be more viscous than the acid ore solution and tends to reprecipitate a slime on cooling. At elevated temperature, the dissolution is complete within 2-5 minutes.

4.0 SUMMARY

The dissolution of the ores proceeds without much difficulty in both cold as well as hot nitric acid. The optimum concentration of nitric acid seems to be about 4-5$\underline{M}$, and the dissolution rates are fastest at boiling temperatures. The optimum concentration of U^{238} in solution seems to be about 120-150 g/l. A little residue is left behind undissolved in all cases.

The Durango ore solution is difficult to filter. The Anaconda acid ore floats in water and may present a slight problem in continuous dissolution. A little frothing is observed in all cases, the maximum frothing occurring with the Durango ore.

1.0 INTRODUCTION

The previous report (dated August 9, 1956) dealt with the behavior of some Durango and Anaconda uranium-bearing ores when contacted with nitric acid solutions. The information reported was based largely on qualitative experiments conducted on a batch scale. The analytical techniques which were under development at that time are now completed, making it possible to present some quantitative results.

2.0 URANIUM MATERIAL BALANCE

It is encouraging to note that well over 99% of the uranium present in the ore can be dissolved by $4\underline{M}$ nitric acid within 2-3 minutes time, at boiling temperatures. The loss of uranium in the residue is about 0.005%.

An experiment with 110 g. of Durango ore dissolved in $4\underline{M}$ nitric acid gave the following results:

	Actual Weight (Grams)	Percent Basis
Uranium contained in 100 g. ore	67.4	100
Uranium in filtered solution	66.0	97.9
Uranium in filtration liquor (wash)	0.72	1.06
Uranium in solids	0.0034	0.005

3.0 DISSOLUTION RATES

An observation reported in the previous memorandum has been since confirmed: The dissolution of Durango ore in boiling $4\underline{M}$ nitric acid is essentially complete within 2 minutes. Samples withdrawn after 5 minutes and after 10 minutes showed no appreciable changes in concentration of uranium or in the free acid content when compared to the 2 minute sample.

The dissolution time is a function of the nitric acid concentration. An experiment conducted with a $2\underline{M}$ nitric acid solution showed a dissolution time of about 20 minutes, the dissolution being substantially complete at the end of that period.

4.0 ACID CONSUMPTION

Experiments conducted to determine the acid requirements show that approximately 75 g. HNO_3 are consumed per 100 g. of the ore. The dissolution of the uranium in the ore can be achieved to the full extent, even in an acid deficient solution. This was demonstrated by dissolving an ore sample in $2\underline{M}$ nitric acid. The final solution at the end of 20 minutes contained essentially all the uranium in the ore, although the solution reprecipitated a brown precipitate, which has not yet been identified.

The success in dissolving to an acid deficient solution is encouraging since it opens the possibility of achieving acid economy by developing an acid deficient flowsheet.

5.0 STABILITY OF DISSOLVER SOLUTIONS

On storage, some of the uranium solutions become viscous with the appearance of a thick gelatinous precipitate. On filtration and washing, it was observed that the precipitate resembled silica gel; this will be confirmed by analysis. It is possible that the silica in the ore is colloidal when in solution and passes through the filter paper. This may explain the difficulty observed in filtering the Durango ore. On cooling and standing for some time, the colloidal matter precipitates out, forming a gelatinous mass. The dry weight of the precipitate represents about 2% of the total Durango ore.

A more extensive program on stability tests is planned.