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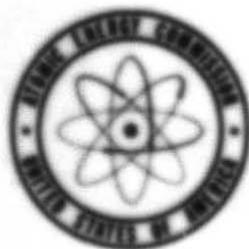
CHEMISTRY

UNITED STATES ATOMIC ENERGY COMMISSION

**PROCESSING OF URANIUM - MAGNESIUM
FLUORIDE SLAG— TECHNICAL INFORMATION
MEETING, DECEMBER 6, 1956**

**December 1956
[TISE Issuance Date]**

**Feed Materials Division
Oak Ridge Operations Office
Oak Ridge, Tennessee**



Technical Information Service Extension, Oak Ridge, Tenn.

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PHYSICAL PROPERTIES OF MAGNESIUM FLUORIDE SLAG

by

D. S. Arnold

National Lead Company of Ohio
Cincinnati, Ohio

Physical properties of magnesium fluoride slag have been compiled. X-ray diffraction and microscopic examinations indicating the nature of the uranium dispersion in the slag have been studied and are reported. These examinations demonstrate that the uranium occurs in the slag as highly dispersed very fine globules of either uranium metal or uranium oxide.

INTRODUCTION

Magnesium fluoride slag is generated as a byproduct in the production of uranium metal¹ in the reduction of uranium tetrafluoride with magnesium as indicated in the equation:



This is a thermite type reaction and therefore product collection depends upon separation by gravity flow of the uranium and the magnesium fluoride while in the molten state immediately following the reduction reaction. The bulk of the uranium flows, by virtue of its higher density, to the bottom of the reduction chamber leaving the magnesium fluoride slag at the top. Incomplete separation of the molten uranium from the slag results in freezing of free uranium metal droplets

in the slag as the charge cools. Side reactions of the uranium and magnesium with oxygen of the entrapped air result in the formation of uranium oxides and magnesium oxide which also collect in the magnesium fluoride slag. For practical purposes, however, the quantity of magnesium oxide formed is considered insignificant. A small amount of unreacted magnesium metal is also trapped in the slag as fine droplets or particles.

These conditions lead to the generation of a reduction slag containing from one to five percent uranium, which is substantially higher than that of many of the natural ore deposits. As a background for uranium recovery process considerations, this paper presents the results of physical studies of magnesium fluoride slag in the form of X-ray diffraction and microscopic examination, sieve analyses and as literature data on physical properties of the slag constituents.

Because of turbulence and viscosity factors during the metal-slag separation and rapid freezing, the slag as discharged from the reduction furnace vessel is necessarily very heterogeneous. The presence of the various metal and metal oxide inclusions results in a range of colors in various portions of the slag from each reduction charge. However, these lose their identity as the slag is crushed and ground during processing.

X-RAY DIFFRACTION STUDIES

The various constituents of the slag have been identified by X-ray diffraction studies⁷ and are listed in Table I. The samples tested were hand picked from the slag from a uranium reduction charge as it was discharged from the reduction chamber and for convenience the samples are identified by color. It is noted that uranium and magnesium metal was identified in the form of metal spheres while the uranium oxides occurred as powder and as slag discoloration.

TABLE I
DESCRIPTION OF VARIOUS SAMPLES OF SLAG AND RELATIVE INTENSITY
OF THE DIFFRACTION PATTERNS FOR THE PHASES PRESENT⁷

Sample No.	Color	Massive Appearance	Relative Intensity of Diffraction Pattern				
			Mg ⁰	UO ₂	U ₂ O ₅	U	Mg
1	Brown	Metal spheres	--	--	--	S	--
2	White	Metal spheres	--	--	--	--	VS
3	Brown	Solid	M-F	VS	--	--	--
4	Gray-Black	Solid	VS	M	--	F	--
5	Dark Gray	Solid	VS	--	--	--	--
6	Medium Gray	Solid Chert-like	VS	--	--	--	--
7	Light Gray	Solid	VS	--	--	--	--
8	White	Solid	S	--	--	--	--
9	Dark Gray	Powder	S	--	--	--	--
10	Black	Powder	S	--	M-F	--	--
11	Gray	Solid	M-F	--	--	--	--

VS - Very Strong

S - Strong

M - Moderate

F - Faint

VF - Very Faint

MICROSCOPIC EXAMINATION

Microscopic examination of various samples of hand picked slag is required for quantitative measurement and identification of the individual particles as dispersed in the slag. The results of microscopic examination of a number of samples of slag by R. A. Matuszeski and R. Richman of our Metallurgy Department are demonstrated in the photomicrographs of Figures 1 - 6:

- (1) Figure 1 is a sample of light gray slag of relatively uniform color with a few small metallic inclusions visible to the naked eye. The average size of the metallic inclusions in this sample was less than 0.009 mm.

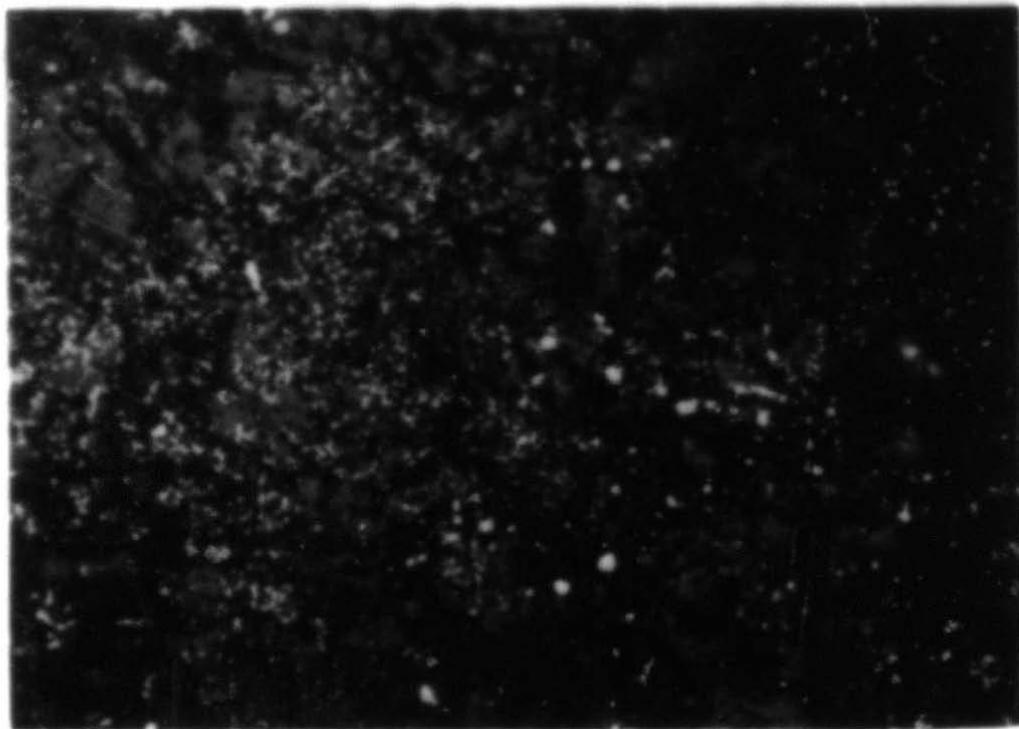


FIGURE 1 Light Gray Slag (Bright Field). White Areas are Included Metallics in Slag Matrix. Average Size Less Than 0.009 mm. (100X)

- (2) The slag represented in Figure 2 had a marble-like appearance of black, white and gray areas. A few of the small metallic inclusions (ranging from less than 0.009 to greater than 0.033 mm) were visible to the eye in this sample.

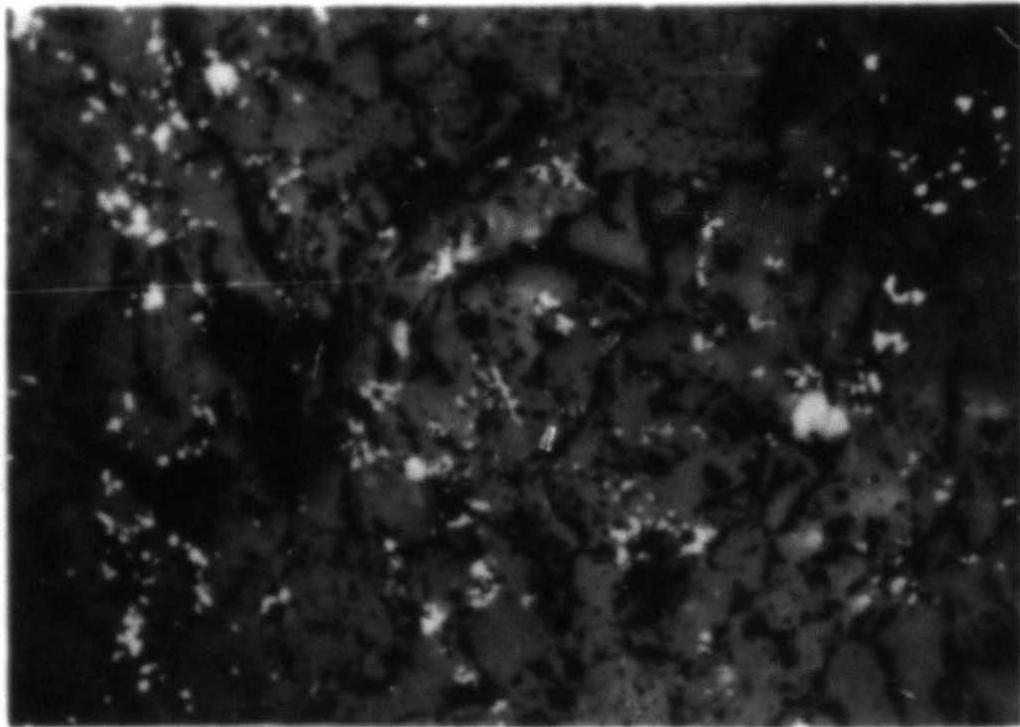


FIGURE 2 Black - Gray - White Slag (Bright Field). White Areas are included Metallics of Size Ranging from Less Than 0.009 mm. to Greater Than 0.033 mm. (100X)

- (3) A second marble-like sample but in general much darker than that of Figure 2 is shown in Figure 3 under bright field illumination and in Figure 4 in polarized light. The polarized light, it may be noted, provides an insight into the "sub-surface" nature of the inclusions, while the bright field shows only the surface exposure of the inclusions. The elongations and interconnections of the various small inclusions, as revealed in Figure 4, are of particular interest.

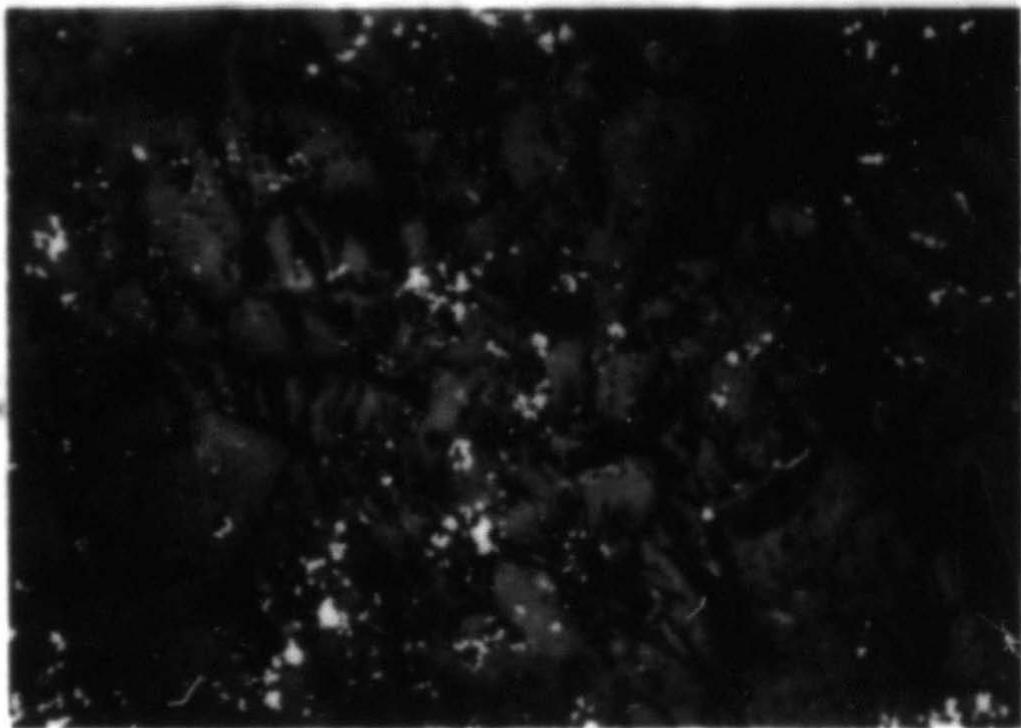


FIGURE 3 Black - Light Gray Slag (Bright Field). White Areas are Included Metallics of Size Less Than 0.009 mm. to Greater Than 0.033 mm. (100X)

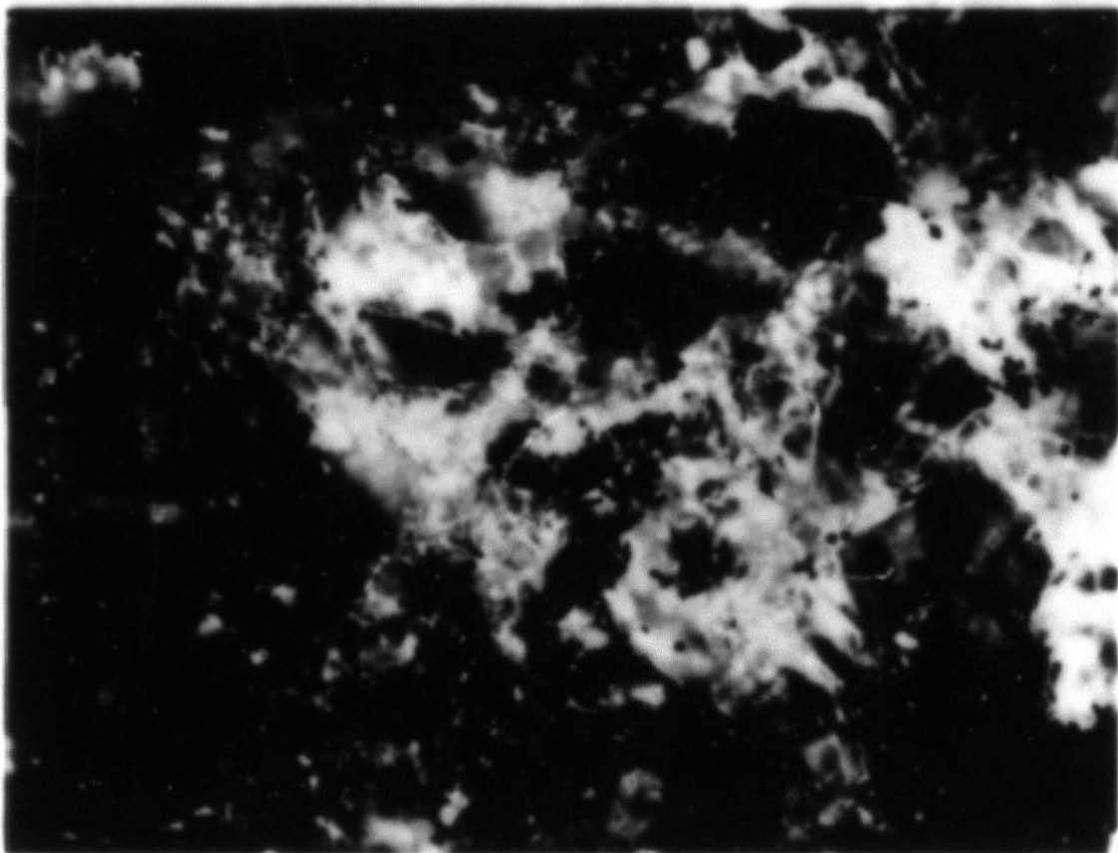


FIGURE 4 Black-Light Gray Slag (Polarized Light). Same Sample as Figure 3. (100X)

- (4) Figures 5 and 6 are photomicrographs of samples of all-white slag which had no metallic or dark particles visible to the naked eye. Of all the various slag fragments, these would be expected from visual inspection to have the lowest metal content. Chemical analyses of samples of this white slag gave 0.58 percent and 0.48 percent total uranium and 0.07 percent free magnesium metal.
- (5) Matuszeski found by microscopic studies of the fines, that even in the - 325 mesh screen fraction the metal occurs as inclusions in the slag. The metallics of this sample were found to be of size ranging from less than 0.009 μm to somewhat greater than 0.049 μm .

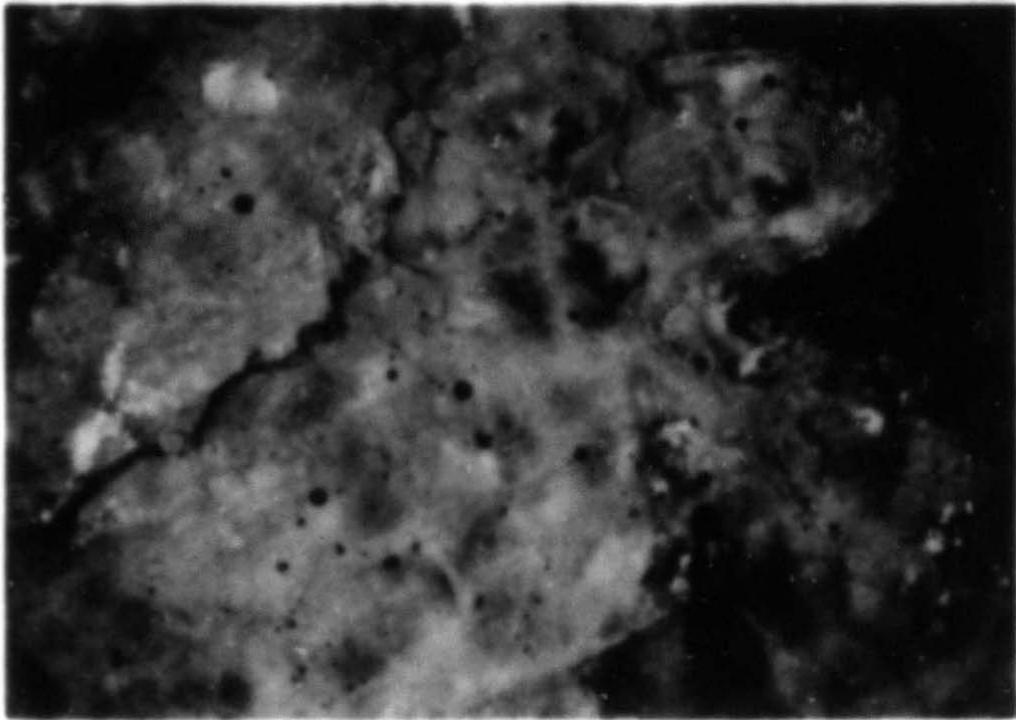


FIGURE 5 Porous Black - Gray - White Slag (Polarized Light). Both Light and Black Particles are Metallics of Size Less Than 0.009 mm. to Greater Than 0.020 mm. (100X)

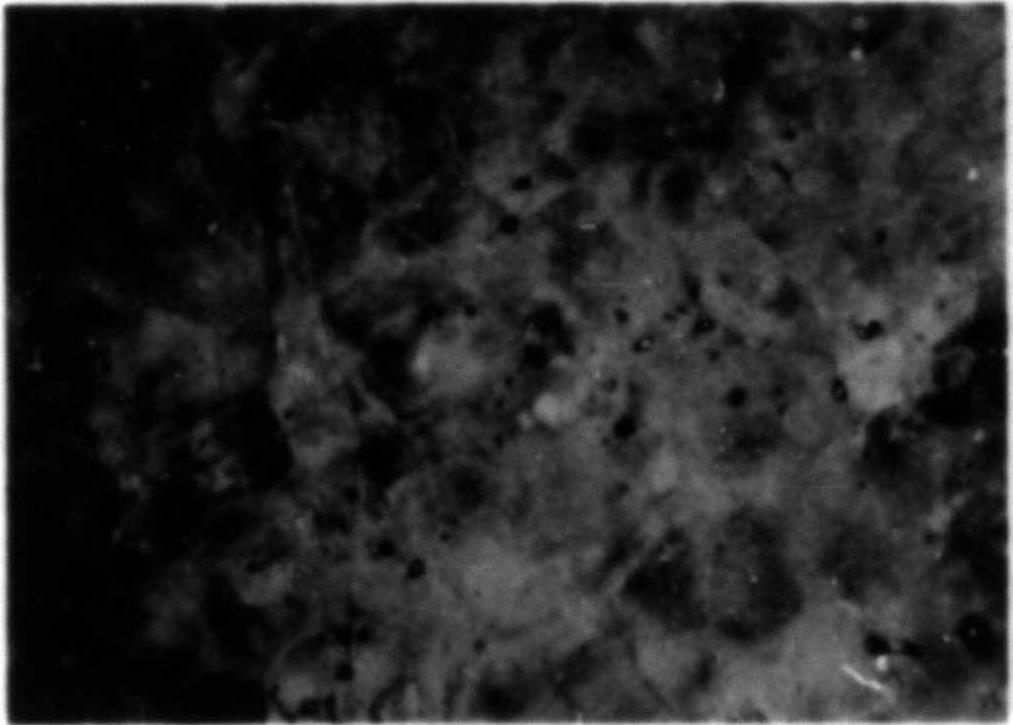


FIGURE 6 White Slag (Polarized Light). Light and Dark Particles are Metallics of Size Less Than 0.009 mm. to Greater Than 0.049 mm. (100X)

From these microscopic studies, it is seen that the uranium metal and oxides are dispersed in the slag as very fine particles.

SCREEN ANALYSIS

Further evidence of the high dispersion of uranium metal and oxides in the slag is found in the analyses of various screen fractions of laboratory crushed and ground slag as shown in Table II. The essentially uniform analyses of the various screen fractions is consistent with the conclusion of the high dispersion of finely divided uranium derived from microscopic studies.

TABLE II
CHEMICAL ANALYSIS OF VARIOUS SCREEN
FRACTIONS OF MAGNESIUM FLUORIDE SLAG

Sample No.	Screen Size	Total U (%)	Free U (%)	Free Mg (%)
1	+35m	2.7	2.5	0.3
	-35 + 200	2.3	1.1	0.1
	-200 + 270	2.1	1.9	0.1
	-270	2.4	1.7	0.1
2	+35m	3.7	-	-
	-35 + 48	1.8	0.5	0.3
	-48 + 65	1.3	0.7	0.2
	-65 + 100	2.1	1.5	0.1
	-100 + 200	1.3	0.7	0.2
	-200 + 325	1.4	-	-
	-325	2.0	-	-
3	-14 + 20	1.6	0.44	0.7
	-20 + 40	1.4	0.37	0.5
	-40 + 60	1.1	0.26	0.4
	-60 + 80	1.6	0.22	0.25
	-80 + 100	1.3	0.20	0.25
	-100 + 140	1.2	0.20	0.3
	-140 + 200	1.1	0.17	0.3
	-200 + 325	1.7	0.13	0.25
-325	2.0	0.09	0.3	

Typical particle size analysis and bulk density figures for the ground magnesium fluoride slag are listed in Table III. It is to be recognized that actual values may deviate from these with changes in crushing and grinding techniques.

TABLE III

**SIEVE ANALYSIS AND BULK DENSITY OF CRUSHED
AND GROUND MAGNESIUM FLUORIDE SLAG**

Screen Size	Sample No. 4	Sample No. 5
+20m	0%	0%
-20 + 100m	33%	50%
-100 + 200m	52%	48%
-200 + 325m	11%	2%
-325m	4%	0%
Apparent Density		
Bulk Density, g/cc	1.4	1.5
Tap Density, g/cc	2.1	2.2

PHYSICAL PROPERTIES

Physical properties of the individual constituents of the slag as identified above have been compiled from the literature^{2,3,4,5,6}. Uranium oxides have been nominally listed as UO_2 and U_3O_8 however it is probable that the uranium oxides in the slag exist as heterogeneous mixtures of these and intermediate oxides. Densities are given as ranges to reflect the effect of this variation and the effect of manner of preparation of the oxide.

TABLE IV

**PHYSICAL PROPERTIES OF CONSTITUENTS
OF MAGNESIUM FLUORIDE SLAG^{2,3,4,5,6}**

	MgF_2	Mg	U	UO_2	U_3O_8
Density, g/cc	2.97	1.74	18.9	8-11	7-8.4
Melting Point, °C	1265	651	1133	2100-2600	dec
Boiling Point, °C	2260	1110	3500	---	---
Hardness	5-6*	2.5*	70-100**	3.5*	3.5*
Crystal Structure	tetragonal, prism (sellaite)	hexagonal	Orthorhombic α Cubic γ	Cubic	Orthorhombic

* Scratch hardness, Mohs

** Rockwell hardness

CONCLUSION

In conclusion, a physical study of magnesium fluoride slag has shown it to be a relatively simple dispersion of very small uranium and magnesium metal particles and uranium oxides in the magnesium fluoride (sellaite) matrix. Physical properties of these slag constituents have been tabulated from the literature.

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CARBONATE LEACH RECOVERY PROCESS

by

R. G. Werkema

Mallinckrodt Chemical Works
Uranium Division
St. Louis, Missouri

This paper describes a process for recovering uranium from a magnesium fluoride slag by means of carbonate leaching. A detailed analysis is given of the operating variables in this process as determined in pilot plant operation. Included is an estimate of the operating cost and plant cost for processing 4000 tons of slag per year, based on this pilot plant data.

A magnesium fluoride slag is produced as a by-product from the manufacture of uranium metal. This slag contains small amounts of metallic uranium, metallic magnesium, and magnesium oxide. The uranium content of this slag is high enough to make its recovery economically feasible. The high fluoride content of this slag, together with the presence of a significant portion of the uranium as inclusions in magnesium fluoride crystals, have eliminated the possibility of using the slag directly as a refinery feed or of obtaining quantitative uranium metal recovery by a physical separation process; therefore, development work on this problem was directed at a recovery process which would achieve the following goals while operating at minimum cost: (1) reduction of the uranium content of this slag to less than 0.05 percent on a dry basis, and (2) production of a uranium product acceptable as a refinery feed having a fluoride content of about one part per one thousand parts uranium.

Uranium recovery can be accomplished chemically either by an acid digestion process or by a carbonate leach treatment. Both of these processes are based on solubilizing the uranium in order to separate it from the slag. The carbonate leach process was selected for investigation because it appears to offer the following advantages over acid leaching: (1) fluoride corrosion problems in the recovery and

subsequent refining operations should be less since magnesium fluoride is much less soluble in carbonate solutions than in acid solutions; (2) less filtration capacity should be required since filtration rates of carbonate slurries are usually considerably higher than those of acid slurries; and (3) drumming, storage, and handling of the final residue should be less expensive and more convenient than similar operations with an acid residue. The carbonate process selected involves the following basic steps: (1) grinding of the slag to expose uranium included in slag crystals; (2) air roasting of the slag to oxidize the uranium to U_3O_8 ; (3) leaching of the slag with a carbonate-bicarbonate solution containing an oxidant to convert the U_3O_8 to the soluble uranyl tricarbonate complex; (4) further grinding of the slag in part of the leaching circuit to complete the quantitative exposure of uranium to the leach solution; (5) washing of the leached slag cake to remove residual soluble uranium; and (6) caustic precipitation of the uranium from slag-free leach liquor to prepare a uranium bearing cake suitable as a refinery feed material. A flow sheet based on these principles is presented in Figure 1.

The first part of the process described by this flow sheet consists of a grinding and screening operation, which has two purposes: (1) to expose most of the uranium included in magnesium fluoride particles so that the subsequent roasting step will be effective; (2) to remove large metal particles of uranium and magnesium which are not readily disintegrated into a leachable form by grinding. After these steps, the slag is roasted in a continuous, indirect heated rotary kiln under an air atmosphere. The hot slag from the kiln is cooled before introduction into the wet grinding circuit.

The balance of the operation is wet processing involving the conversion of the uranium oxide to a soluble form and its precipitation from the leach solution. The leaching operation is carried out in two counter-current steps with further grinding of the slag being accomplished in part of the first leach step by a closed circuit ball mill and hydroclassifier system. Some of the product filtrate from the first cycle is combined with second cycle leach filtrate and reused in the first cycle, primarily as a diluent for the ball mill product to make the hydroclassifier operate properly.

The balance of the product filtrate from the first cycle is bled off to the precipitation step. Following a polishing filtration, the product liquor is treated with caustic to precipitate a di-uranate cake in a batch operation. The slurry from this step is filtered, and the cake, after a water wash, is an acceptable refinery feed material.

The pilot plant equipment used for the preliminary grinding and roasting steps in proving out this flow sheet consisted of an 18 by 30 inch Denver ball mill, a 20 by 36 inch 2-screen Gumpsifter, and an American Gas Furnace Company Model 20A rotary gas furnace modified for low temperature operation. The wet grinding and classification portion

of the leach step was carried out in a 16-inch by 32-inch Denver ball and a 36-inch diameter Denver hydroclassifier. Leached slag filtration and washing experiments were conducted on a 3-foot diameter by 1-foot wide Oliver rotary drum precoat filter. The pilot plant had sufficient tankage to permit semi-continuous operation at a slag feed rate of about 300 lbs./hr. to duplicate this flow sheet through the first stage leaching operation.

The majority of the equipment used in the pilot plant was mild steel. There was no evidence of any corrosion that could be attributed to the leach liquor.

Preliminary Grinding and Roasting

One of the primary objectives of the development work on this process was the determination of the preliminary grinding and roasting conditions necessary for optimum uranium recovery. Figure 2 shows the effect of roasting temperature on the leachability of the fluoride slag. Slags used for this experiment were roasted for three hours in a muffle furnace. The leach conditions used on this roasted material fall within the optimum leach range determined by laboratory work. Roasting at lower temperatures evidently did not completely oxidize the uranium metal particles, whereas roasting in the higher temperature range resulted in the formation of magnesium uranates, which were insoluble or only slightly soluble in the leaching media. Some work was done to determine the effect of the length of roasting time on uranium extraction. This work indicated that roasting for periods longer than three hours at the optimum roasting temperature of 900° F. resulted in the production of high uranium content residues.

In order to eliminate the effect of possible variations in the operations of the leach-grind pilot plant in determining the effect of preliminary grinding on slag leachability, a set of standard beaker leach procedures was set up for application to the roasted slag feeds prior to their introduction to the wet grind and leach system. One procedure consisted of subjecting the minus 325 mesh portion of the roasted slag feed to a 1-hour leach treatment. The ratio of the uranium assay of the slag feed to the residual insoluble uranium content of the slag from this 1-hour leach has been defined as the "roasting index". This index is partially a measure of the rate at which uranium can be leached and partly a measure of accessibility of the uranium in the slag.

The second standard leach procedure consisted of a vigorous 5-hour leach treatment of the unscreened roasted slag feed. Under the conditions employed, practically all of the uranium to which the leach solution had access should be leached. Thus, the ratio of the uranium content of the residue from this leach to the uranium assay of the slag feed is a measure of the relative inaccessibility of the uranium in the slag. For this reason, this ratio has been termed the "inaccessi-

bility 'factor'."

Figure 3 shows the correlation of roasting index with the fineness of preliminary grind. This graph shows an increase in roasting index as the fineness of grind of the roasted slag feed is increased.

Figure 4 shows a second correlation obtained from the use of the standard leaches. This figure shows the effect of fineness of preliminary grind of the roasted slag feed on the amount of uranium remaining in the roasted slag feed after a 5-hour standard leach. The trend is toward a decrease in inaccessibility with increased fineness of grind.

The combined effect of preliminary grinding and roasting and the leach-grind system in solubilizing uranium is represented by the insoluble uranium content of the cake from the first stage leach cycle. The solubilization reaction is still not complete since the average residence time for slag in the first stage leach system is about one hour. Since the roasting index is a measure of both accessibility and leach rate, a comparison of the roasting index with the fraction of original uranium not solubilized in the first stage serves to indicate the relative effectiveness of the first stage. This comparison is presented graphically in Figure 5.

Results obtained from both the leach-grind pilot plant and from laboratory work indicated that rapid leaching was achieved only when (1) the pH of the leach solution was less than 9.5; (2) the potassium permanganate concentration was greater than 2 g/l; and (3) the CO₂ concentration of the leach solution was more than 40 g/l. The data in this figure have been segregated to differentiate between those runs in which the leach liquor in the first stage was kept within these specifications and those runs in which it was not. Failure to keep the leach solution composition within the above limits resulted in poor first stage leaching. The data in this figure have also been segregated to show those runs in which the hydroclassifier overflow contained less than 99 percent minus 325 mesh solids.

Second Stage Leaching

The second stage leach step should reduce the insoluble uranium content of the slag below the value obtained in the first stage. The potential leach efficiency obtainable in the second leach stage is probably limited by the inability of the leach solution to make contact with a small amount of uranium trapped within the slag crystals. The inaccessibility of the uranium in the first leached cake residue was determined by a standard 5-hour beaker leach of that material. Figure 6 compares the inaccessible uranium, which is defined as the ratio of insoluble uranium content after the 5-hour leach to the original uranium content of the roasted slag, to the inaccessibility factor of the roasted slag feed. This graph shows that the wet grinding step

reduced the inaccessibility of the uranium by 60 to 70 percent.

The effects of second stage leach procedures less vigorous than the 5-hour beaker leach used to determine uranium inaccessibility have been evaluated by comparing the amount of uranium solubilized in acting on the first stage cake with that solubilized by the 5-hour leach on the first stage cake. Table I summarizes the average results of the three different second stage leach procedures.

Table I
Effect of Various Second Stage Leach Procedures

<u>Second Stage Leach</u>	<u>Fraction of Insoluble Accessible Uranium from First Stage Cake Solubilized, %</u>
None	0
1 hour Beaker leach at 160°F	53
3 hour Tank leach at 160°F	68
3 hour Beaker leach at 200°F	87
5 hour Beaker leach ^a at 200°F	100

^a Chosen as the basis for determining accessibility.

Wet Grinding Circuit Operation

The closed circuit grinding operation was investigated in order to determine equipment capacities and satisfactory operating ranges for slurry solids concentration in the various streams. The pilot plant hydroclassifier was originally intended to provide about the same particle size "cut" as a 325-mesh screen. From settling tests carried out on several samples of hydroclassifier overflow and underflow material, it was concluded that the actual cut in the pilot plant hydroclassifier took place at a particle diameter of about 30 microns, rather than 325 mesh or $\frac{1}{4}$ microns. Consequently, a sizable portion of the minus 325 mesh material was recycled to the ball mill. The average distribution of minus 325 mesh material in the hydroclassifier was 64 percent to the ball mill recycle stream, and 36 percent to the overflow.

In most runs trace amounts of plus 325 mesh material were found in the hydroclassifier overflow streams, amounting to less than one percent of the overflow solids. In the runs where more than one percent of the overflow solids were plus 325 mesh, one or more of the following conditions were responsible for the excessive oversize entrainment: (1) the concentration of solids in the overflow was 1.8 pounds per gallon or greater; (2) the underflow solids concentration was greater than 4.0 pounds per gallon; or (3) the ratio of underflow volume to cone wash volume was 1.1 or less. Overflow liquor rates up to 300 gallons per hour were successfully processed when the preceding conditions were not observed.

In order to describe the wet ball mill operation, a grinding efficiency was defined as the fraction of the plus 325 mesh material entering the ball mill ground to minus 325 mesh per pass. Figure 7 shows a plot of grinding efficiency versus the rate of slag flow through the ball mill for those runs in which hydroclassifier operation was satisfactory. This figure shows that increasing the solids flow rate through the ball mill decreases the grinding efficiency. Therefore, more solids must be recycled for additional grinding before they will pass the classification step. If the solids rate gets high enough, presumably a point will be reached at which the ball mill will be unable to keep up with the slag feed rate, and the system will choke up with unground solids. The upper limit for permissible slag rates may be calculated if the straight line relation in Figure 7 is assumed to apply and if the minus 325 mesh distribution in the hydroclassifier is assumed to remain at underflow to overflow ratio of 6:1 to 36. Figure 8 shows the results of this calculation for a 73 percent minus 325 mesh feed. The estimated maximum allowable slag rate for this system is about 310 pounds per hour.

The following criteria for satisfactory operation of the wet grinding and classification step are recommended: (1) Sizing of the ball mill to correspond to a slag feed rate of 155 pounds per hour on the 16-inch by 32-inch pilot plant mill at the rated plant capacity; (2) use of enough underflow recycle to give a solids concentration of about three pounds per gallon in the classifier underflow; (3) use of cone wash at 40 percent of the underflow rate; (4) use of enough dilution liquor to give a classifier overflow solids content of 1.5 pounds per gallon; and (5) use of a classifier having an area corresponding to an overflow of 16 gallons per hour per square foot. These recommendations provide a reasonable margin of safety from the limits of successful operation determined in the pilot plant. Table II lists the actual flows and compositions of the various streams, corresponding to operation at rated plant capacity according to these recommendations,

Table II

Wet Grinding and Classification System Standard Flows

Basis: 1 lb of 73% minus 325 mesh roasted slag feed

<u>Stream</u>	<u>Flow</u>	<u>Solids Content, lb/gal</u>	<u>Fraction of Solids minus 325 mesh, %</u>
Slag Feed	1 lb	-	73.0
Ball Mill Feed	0.78 gal	4.1	77.8
Ball Mill Discharge	0.78 gal	4.1	86.2
H. C. Overflow	0.66 gal	1.5	>99.0
H. C. Underflow	0.74 gal	3.0	80.3
Dilution Liquor	0.37 gal	-	-
Cone Wash	0.30 gal	-	-

Slag Filtration and Washing

A series of runs was made to determine filtration rate data required to size the precoat filters for this plant. Figure 9 shows the effect of slurry solids content and drum rotational speed on slag filtration rates. The filtration rates obtained are based on submerged filter area, and vary from 79 gallons per hour per square foot at 1.5 pounds dry solids per gallon and one rpm to 252 gallons per hour per square foot at 4.0 pounds per gallon and four rpm. Filtrations were carried out under 15 inches mercury vacuum and with a precoat cut of from one to two thousandths of an inch per revolution. The recommended amount of rotary filter area to handle a 1.5 pound per gallon slurry at 2 rpm is 6.2 square feet per ton of slag feed per day, allowing four hours downtime per cycle and a 50 percent safety factor over the size based on experimental rate data.

One of the primary functions of each filtration step is to permit washing out the soluble uranium from the slag cake. In order to determine the necessary wash rates for use in the plant, washing data were collected during the filtration runs. It was found that (1) washing efficiency appeared to improve with increased ratio of wash water to slag; (2) the efficiency increased when the liquor filtration rate increased; and (3) the efficiency decreased with increasing cake thickness. These effects were taken into account by computing a wash parameter "B," where B is defined as being (1) proportional to the ratio of wash water to slag and (2) proportional to the square root of the ratio of wash water filtration rate to cake thickness. The relationship between the fraction of soluble uranium not washed out and the washing parameter "B" is shown in Figure 10. The effect of slurry solids content and drum speed in the ratio of the washing parameter to the gallons of wash water per pound of wet slag cake is shown in Figure 11. This plot may be used to estimate the value of B, and, therefore, the washing efficiency for various ratios of wash water to slag at different filtration conditions. "Flooding" conditions limit the maximum effective washing to a value of B of about 0.3.

During these studies, the average water content of filter cakes was found to be 35 percent.

Diuranate Precipitation

The optimum conditions for diuranate precipitation from the bleed off liquors were found to be (1) a digestion temperature of 200°F; (2) a desired final caustic concentration of from 0.07 to 0.1 pounds per gallon excess; and (3) a digestion time of about 15 minutes after the final caustic concentration has been obtained. All bleed off liquors were polished prior to diuranate precipitation. The average fluoride content of the unwashed diuranate cake averaged 0.3 percent on a uranium basis, and a uranium precipitation efficiency of 99.8 percent was achieved.

Diuranate Precipitate Filtration

Based on previous experience with sodium diuranate cakes, pressure leaf filters are recommended for use in the plant diuranate filtration. Since this type of filter was not available to the pilot plant, filtration rate data were determined on a precoated plate and frame filter press for sizing of the plant filters as the best approximation possible at the time. Equation 1 shows the relationship between filtration volume and time for diuranate filtration at a pressure of about 30 psi.

$$t = 1.9V + (4.38/2)V^2 \quad (1)$$

where: t = filtration time, min.
 V = volume of filtrate collected
per unit filter area, gal/ft²
 S = slurry solids content, lbs/gal

Data covering the last 25 percent of volume filtered have been omitted in preparing this correlation, since the press was probably partially packed with cake during that portion of the runs, and the results are less reliable for extrapolation to pressure leaf filtration. The maximum overall diuranate filtration rate was about 2.4 pounds of wet cake per hour per square foot. This corresponds to a filtration batch of about 16 gallons per square foot if a 20 gU/l bleed off is employed and should give a cake thickness of about 1 1/4 inches. For a 4.6 percent uranium assay feed, the filter should be sized to give 16 square foot area per ton of slag feed per day, allowing a safety factor of about 2.

Reagent Consumption

An analysis of the reagent consumption encountered in the pilot plant work is given in Table III. This analysis was prepared by noting the amounts of bicarbonate, CO₂, permanganate, uranium, and water bled off from each run. It was assumed that the ratio of sodium to potassium in the bleed off liquors was the same as the actual reagent feed ratio.

Chemical Cost Estimation

Cost estimates have been prepared in order to determine the most economical method of operating to obtain the washing necessary to produce residues containing not more than 0.002 percent soluble uranium. These estimates were prepared according to the basis shown in Table IV. The following conclusions were drawn as a result of these estimates: (1) The slurry concentration in the second cycle should be 1.5 pounds per gallon since at higher solids content it becomes necessary to increase filter drum speeds to obtain adequate washing, and the increased cost of precoat offsets the reductions in leach tank capital investment; (2) normally both filters should be operated at 2 rpm.

Table III

Reagent Consumption Analysis

<u>NaHCO₃ Consumption</u>	<u>lb/lb U Leached</u>
Theoretical ^a required to dissolve U ₃ O ₈	1.49
Decomposed ^b to Na ₂ CO ₃ + CO ₂	1.34
Consumed by other reactions	<u>0.12</u>
	2.95
Wled off with product	<u>3.18</u>
	6.13
<u>K₂CrO₄ Consumption</u>	<u>lb/lb U Leached</u>
Theoretical ^a required to dissolve U ₃ O ₈	0.15
Consumed by other reactions	<u>0.21</u>
	0.36
Wled off with product	<u>0.21</u>
	0.57
<u>NaOH Consumption</u>	<u>lb/lb U precipitated</u>
Theoretical ^c required for neutralization and precipitation	1.4
Excess	<u>0.9</u>
	2.3
Ratio of product liquor volume to input water volume	0.86 gal/gal

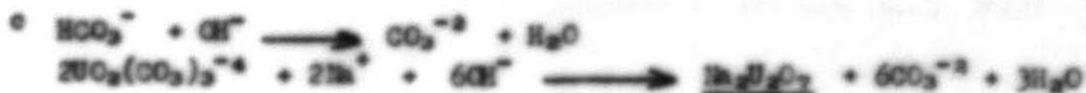
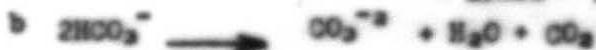
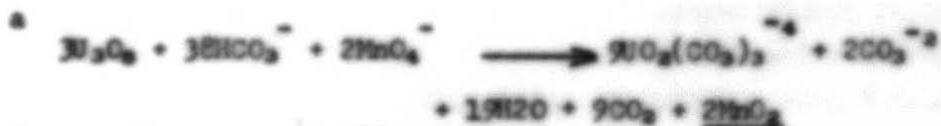


Table IV

Cost Estimate Basis

NaHCO₃

Fresh Liquor Concentration	1.0 M
Decomposed during Leach ^a	30% of Feed
Reacted ^b with U ₃ O ₈	1.49 lb/lb U
Converted to Carbonate by other Reactions ^c	0.12 lb/lb U
Cost	2.27 cents/lb

K₂CO₃

Decomposed during Leach	0.40 lb/lb U
Bleed off Concentration ^d	4.0 g/l
Cost	22.0 cents/lb

NaOH

Excess Required	0.1 lb/gal
Cost	3.4 cents/lb

Volume Loss during Leach^f 20%

Precoat (Hyflo)

Filter Cut	0.001 in/rev
Density of Precoat	20 lb Dry Hyflo/ft ³
Cost	2.5 cents/lb

Buildup Steam

Cost	50 cents/1000 lb water Evaporated
------	--------------------------------------

- ^a 22% decomposition occurred in the one stage pilot plant leach.
- ^b Theoretical requirements.
- ^c Experimental value, Table IV.
- ^d 0.36 lb/lb U were consumed in pilot plant.
- ^e This is twice the minimum specification of 2 g/l.
- ^f Pilot plant loss was 14 percent.

This speed is sufficient to give adequate filtration rates without excessive precoat cost; (3) If the feed assay is too low, the water fed to the system will be inadequate to sustain the desired wash rates. In order to reduce wash water requirements, the No. 2 filter should be speeded up to 4 rpm. If this proves inadequate, the No. 1 filter should also be speeded up. The increased precoat cost associated with the increased rotation speed is much less than the cost of boiling down water in achieving equal washing by that method. (4) If the feed assay proves too low for this scheme, the wash liquor rate on the first filter should be reduced further and the wash water rate on the second filter increased. The excess second filter wash should be boiled down.

The total cost of NaHCO_3 , $\text{K}_2\text{H}_2\text{O}_4$, NaOH , steam, and precoat for the above procedures have been calculated as a function of uranium level in the bleed off stream and uranium assay of the feed. Figure 12 shows the results of this calculation. For the 20 gU/l bleed off, normal operation will be adequate for feeds assaying 2.8 percent U or higher. By speeding up both filters and boiling down excess wash water, feeds assaying down to 1.2 percent U may be handled. Lower uranium assay feeds will require reduction of the bleed off level. Operation at 30 gU/l bleed-off should be more economical than at 20 gU/l unless the feed assay drops below 1.5 percent. At the 30 gU/l bleed off, it will be necessary to start the filter speed up and/or wash boil-down procedure at feed assays below 1.5 percent.

Plant Cost Estimate and Labor Requirements

A Cost estimate for a 4000-ton per year plant operating 300 days per year is presented in Table V. The size of this plant was arbitrarily chosen in order to present some idea of the cost of a carbonate leach recovery plant. The cost estimate given in this table is based on the cost of the process equipment, not installed. All other components of the physical plant cost were then estimated individually as equivalent to percentages of the equipment cost. These percentages were obtained from "Chemical Engineering Cost Estimation" by Aris and Newton.

It is estimated that seven operators/shift in addition to a foreman, a clerk, and a production engineer will be required to operate a plant of this capacity.

Table V

Carbonate Leach Recovery Process

Physical Plant Cost Estimate

Basis: 4000 tons/yr. capacity

Purchased Equipment	\$292,000
Equipment Installation	125,500
Piping	105,000
Instrumentation	43,800
Insulation	23,400
Electrical	43,800
Building	180,000
Land and Yard Improvements	5,000
Utilities	219,000
Physical Plant Cost	\$993,700
Engineering and Construction	29,800
Direct Plant Cost	\$1,023,500
Contractor's Fee Plant Cost	61,500
Contingency 15%	<u>153,500</u>
Total Plant Cost	\$1,238,500

FIGURE 2

EFFECT ON GAS TEMPERATURE IN MUFFLE FURNACE DURING ROASTING ON SLAG LEACHABILITY

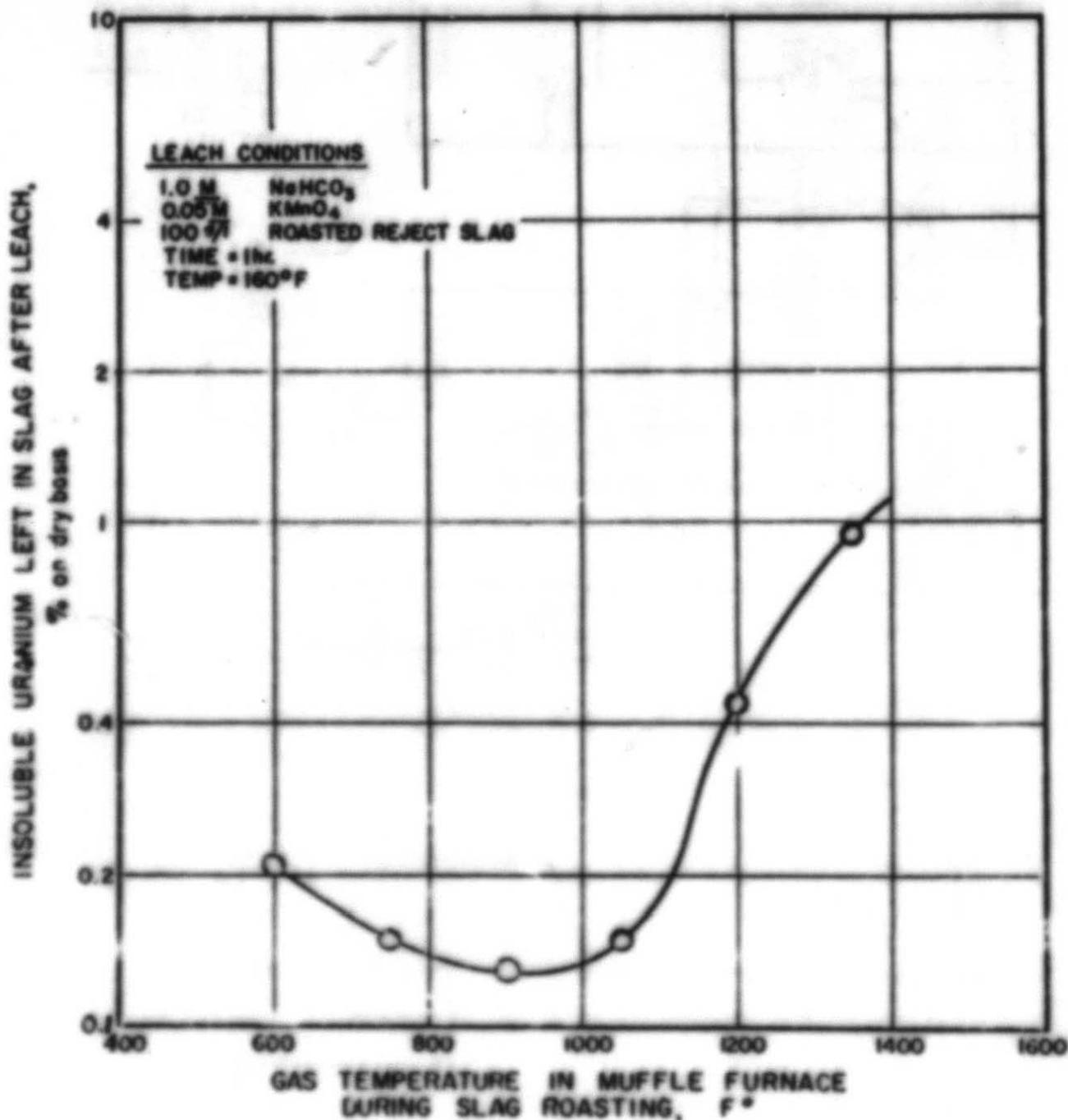


FIGURE 3

**EFFECT OF PRELIMINARY GRINDING
ON ROASTING INDEX OF
ROTARY FURNACE-ROASTED SLAG**

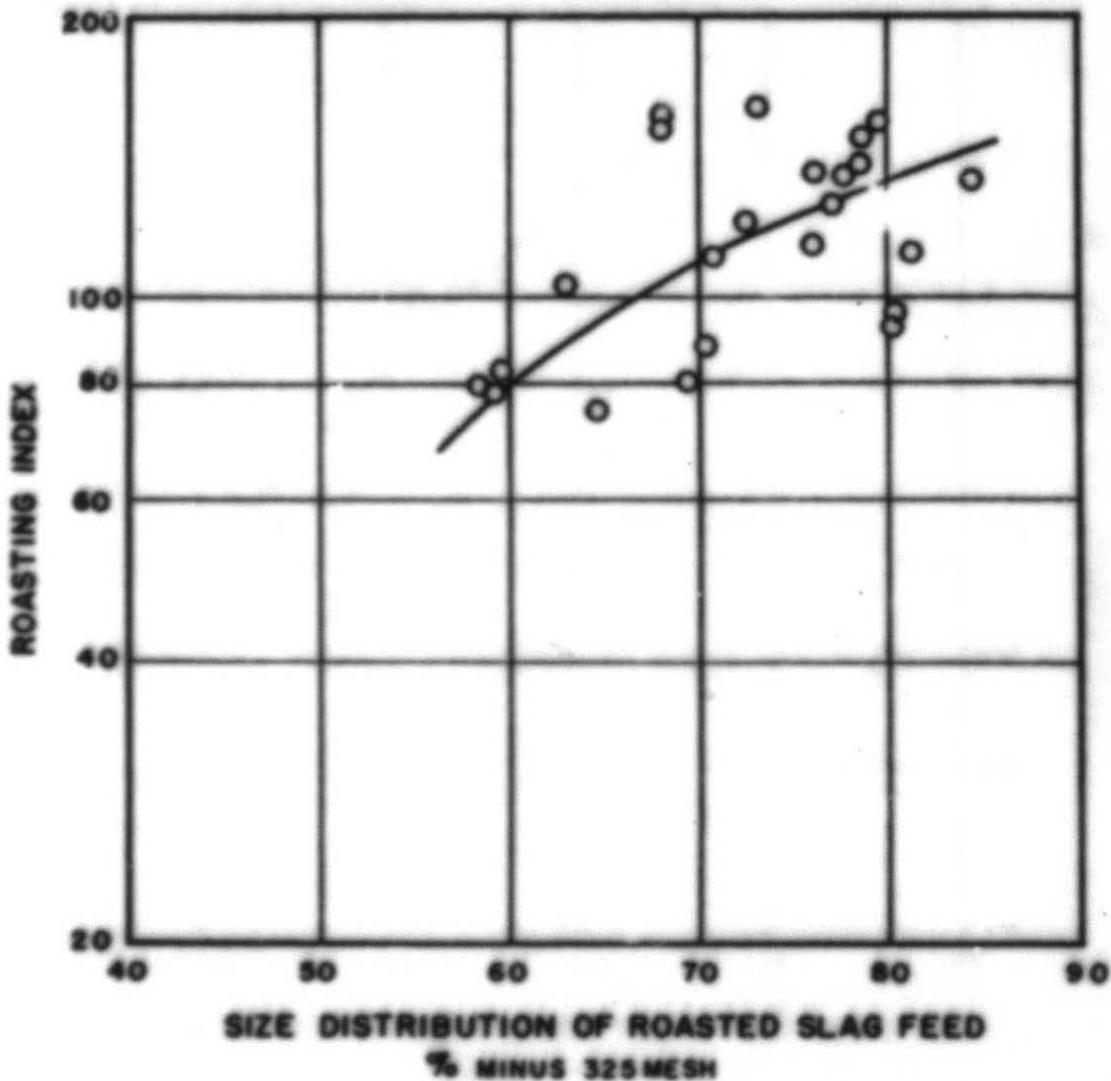


FIGURE 4

EFFECT OF PRELIMINARY GRINDING
ON SLAG LEACHIBILITY

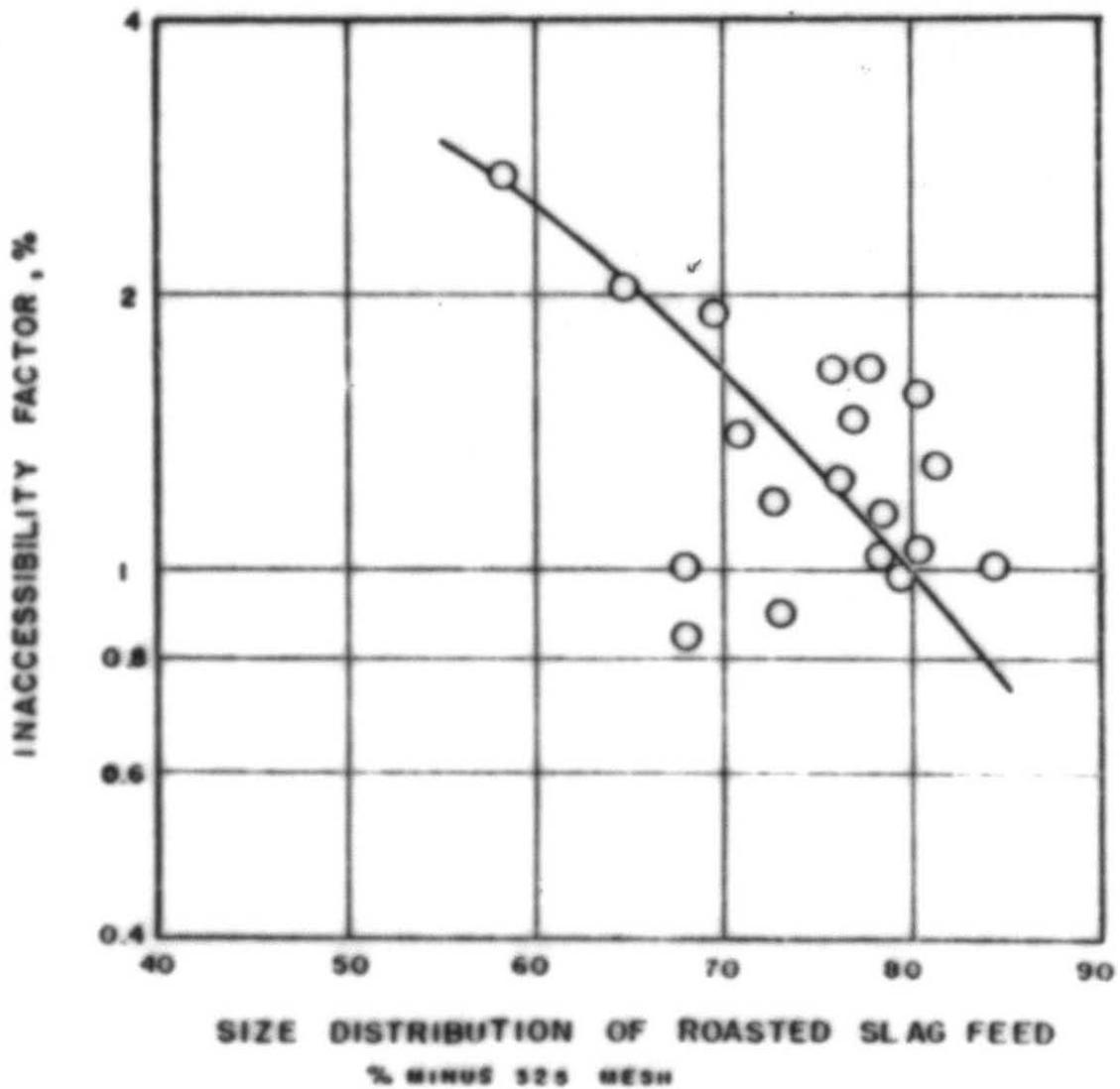


FIGURE 5

RELATION BETWEEN ROASTING INDEX
AND FIRST STAGE LEACHING

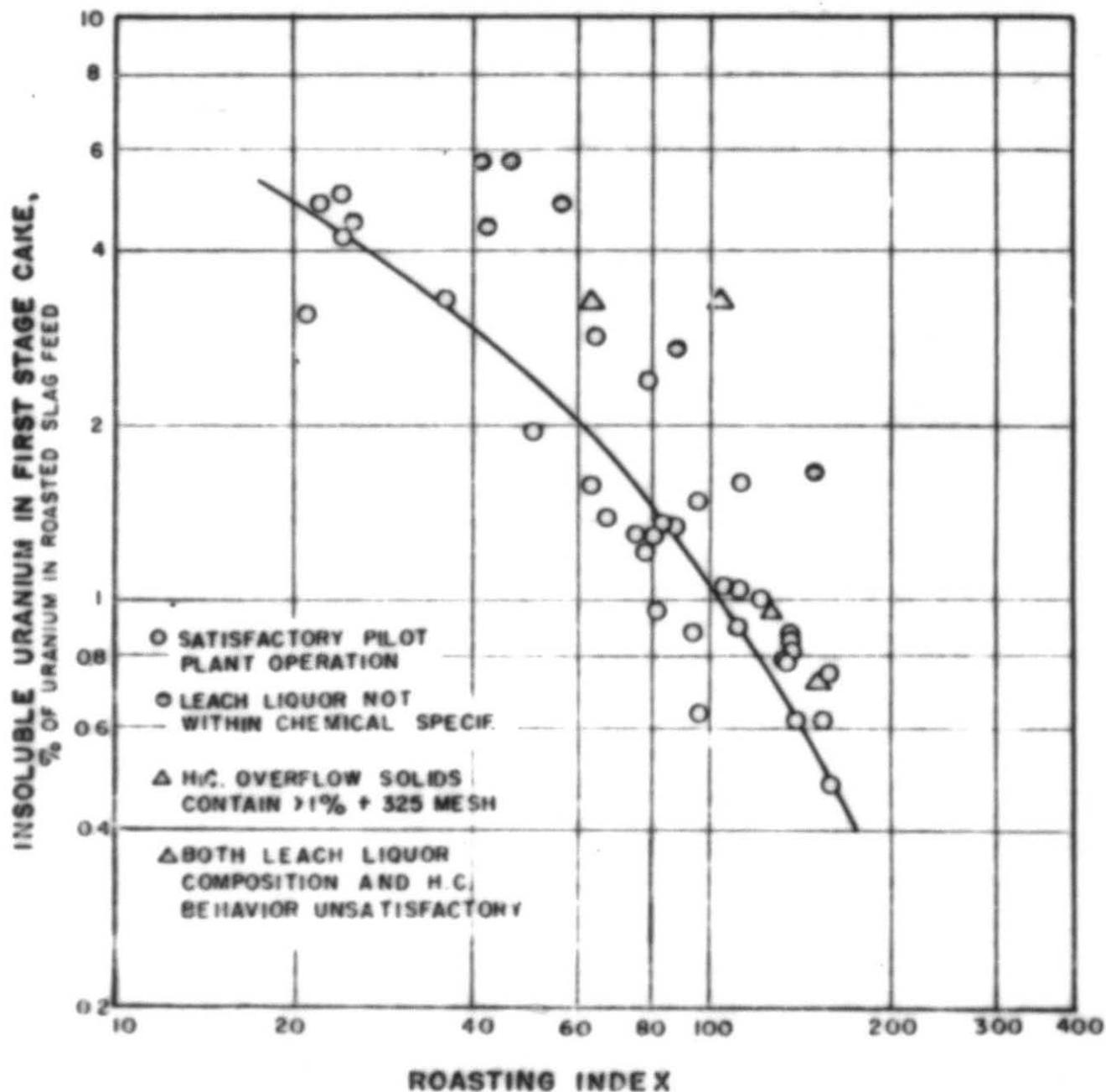


FIGURE 6

EFFECT OF WET GRINDING STEP
ON SLAG LEACHIBILITY

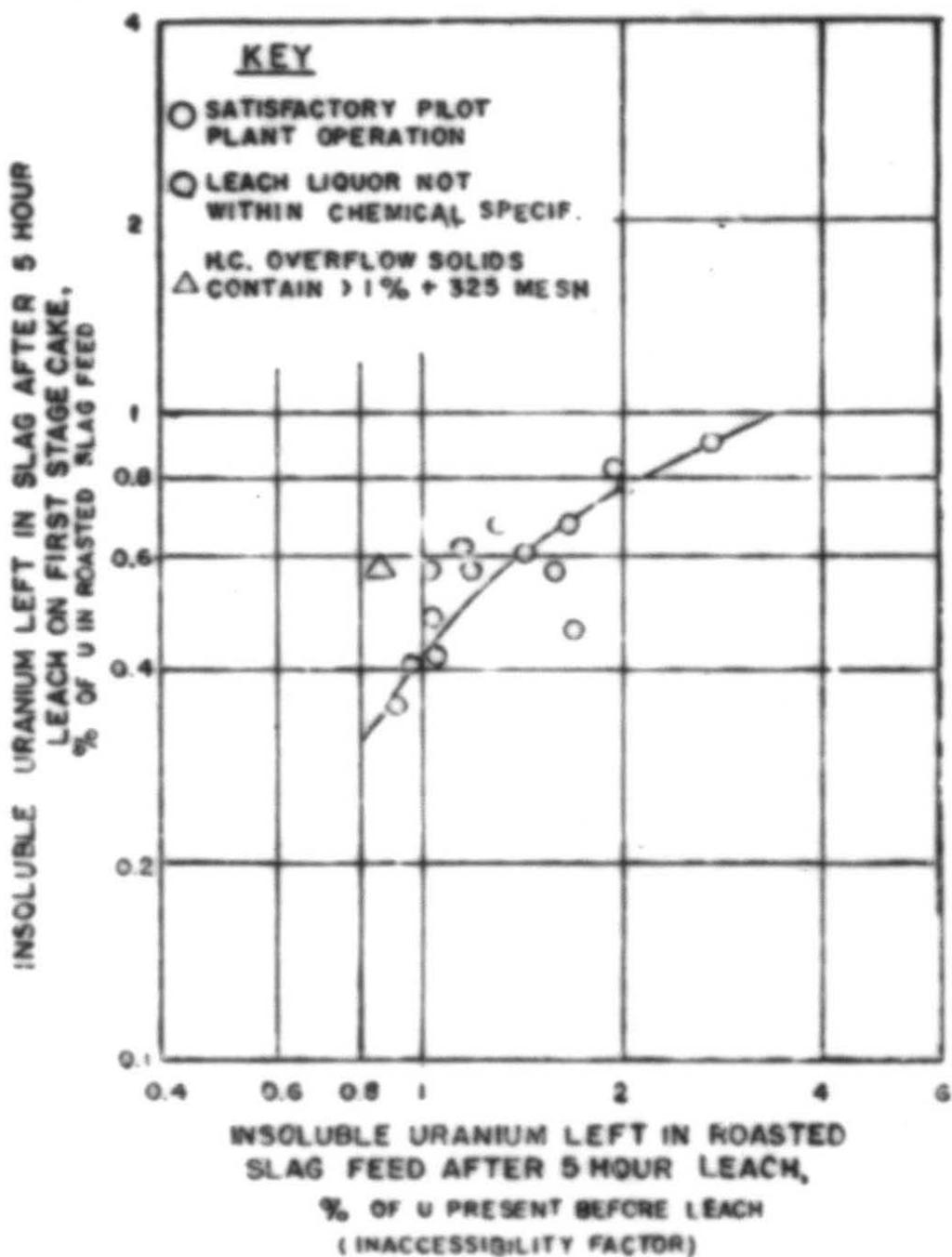


FIGURE 7

EFFECT OF SLAG FLOW
ON GRINDING EFFICIENCY

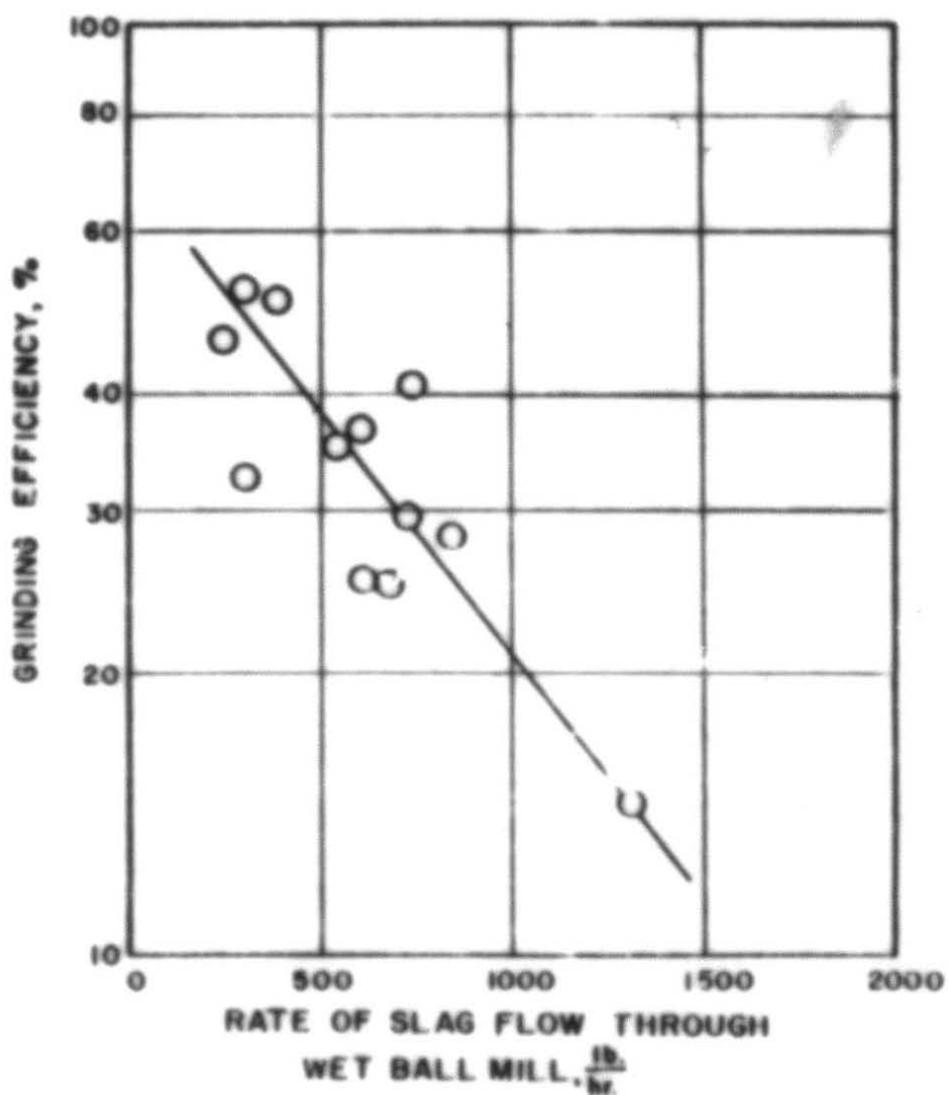


FIGURE 8

RELATION BETWEEN SLAG FEED RATE
AND BALL MILL LOAD

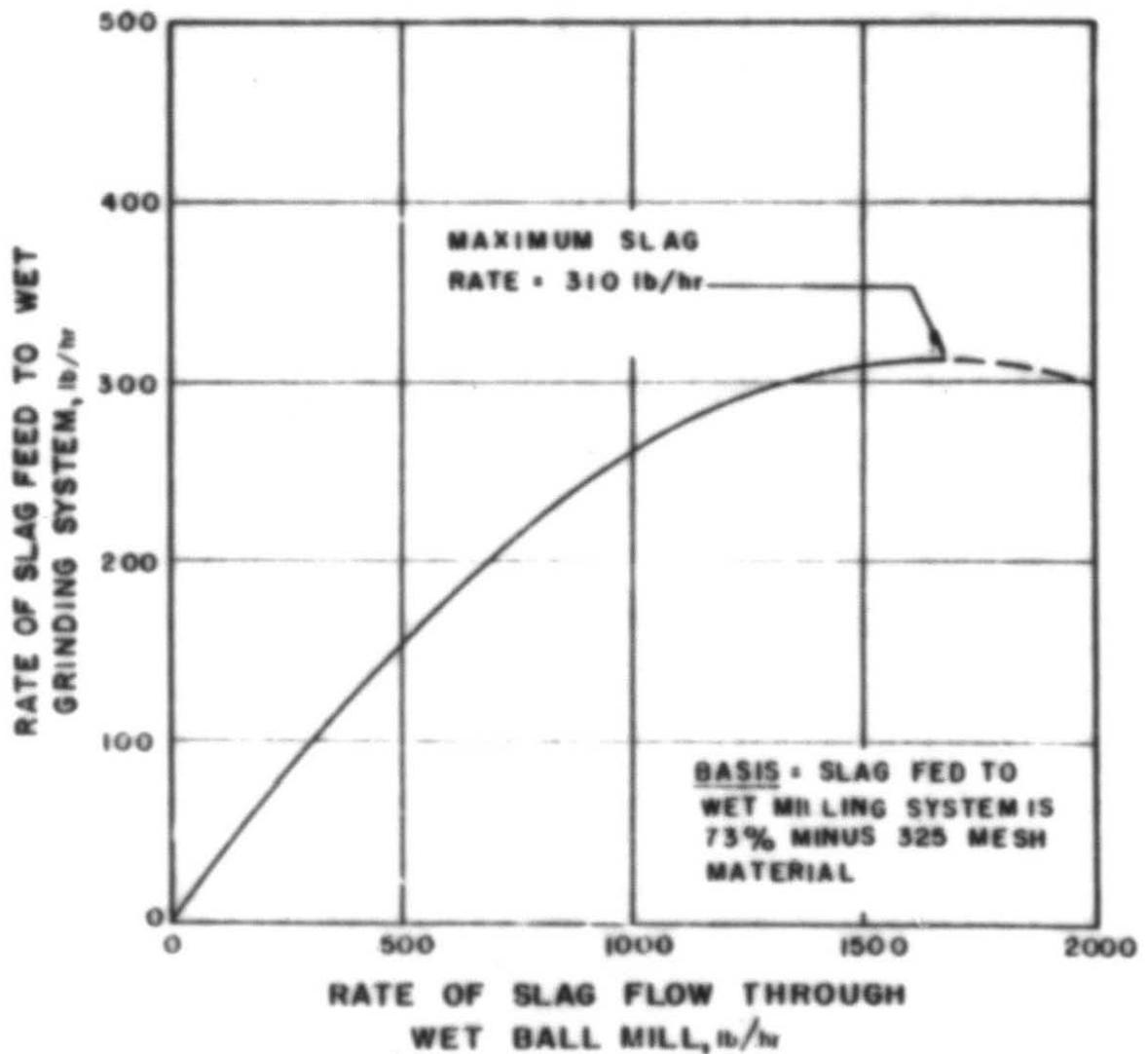


FIGURE 9

ESTIMATED EFFECT OF DRUM ROTATION SPEED ON SLAG FILTRATION RATES

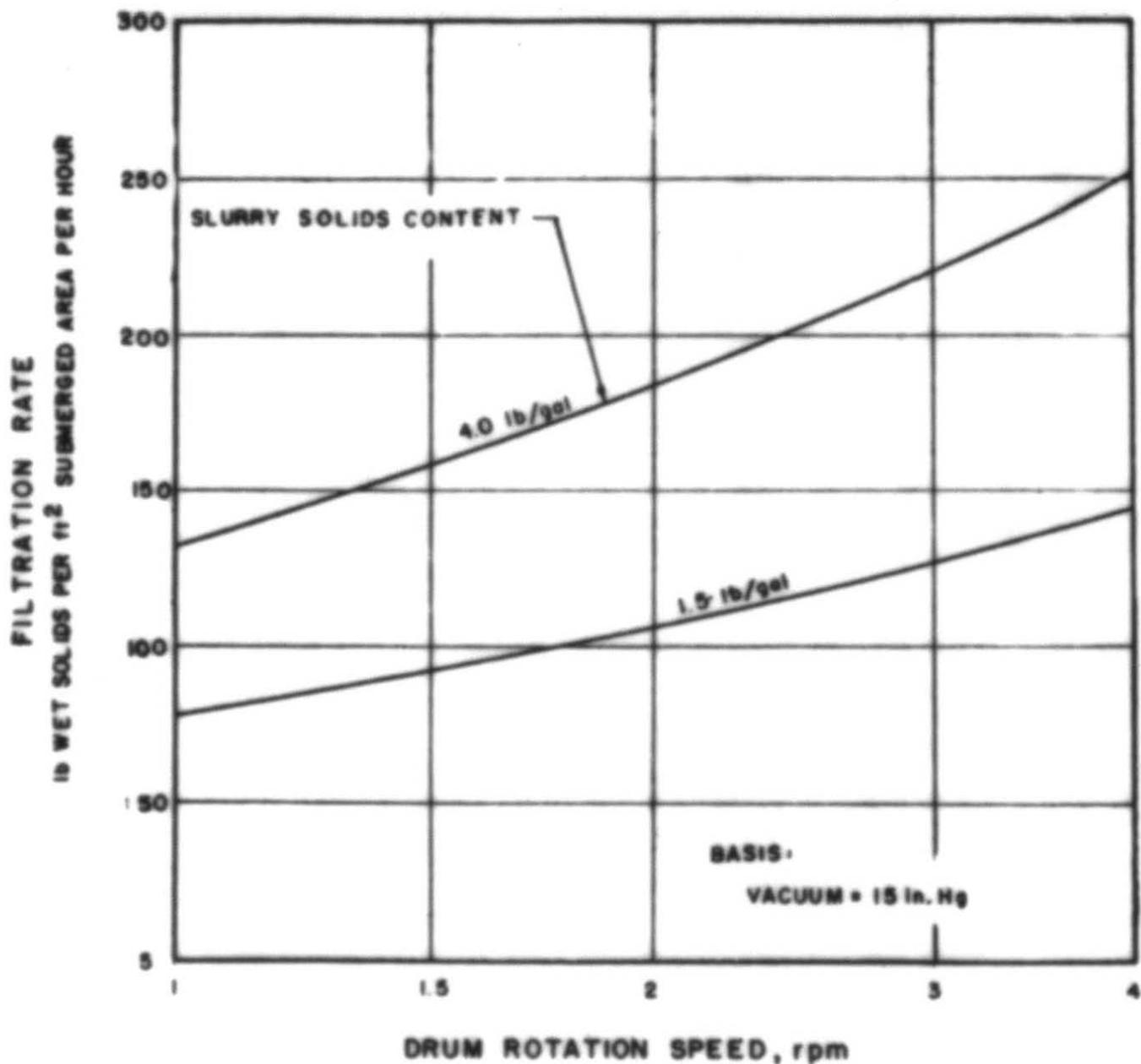


FIGURE 10

WASHING EFFICIENCY CORRELATION

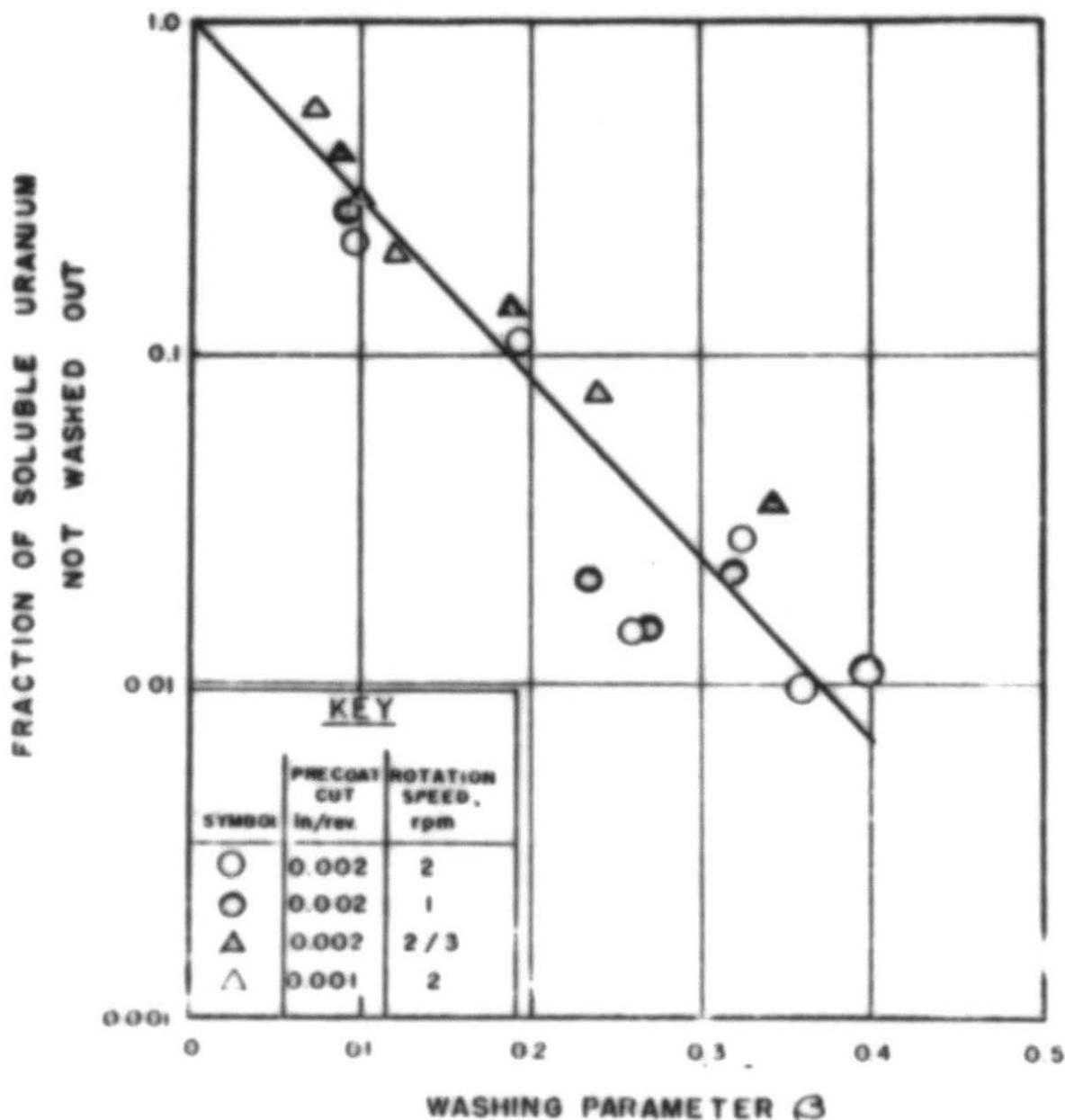
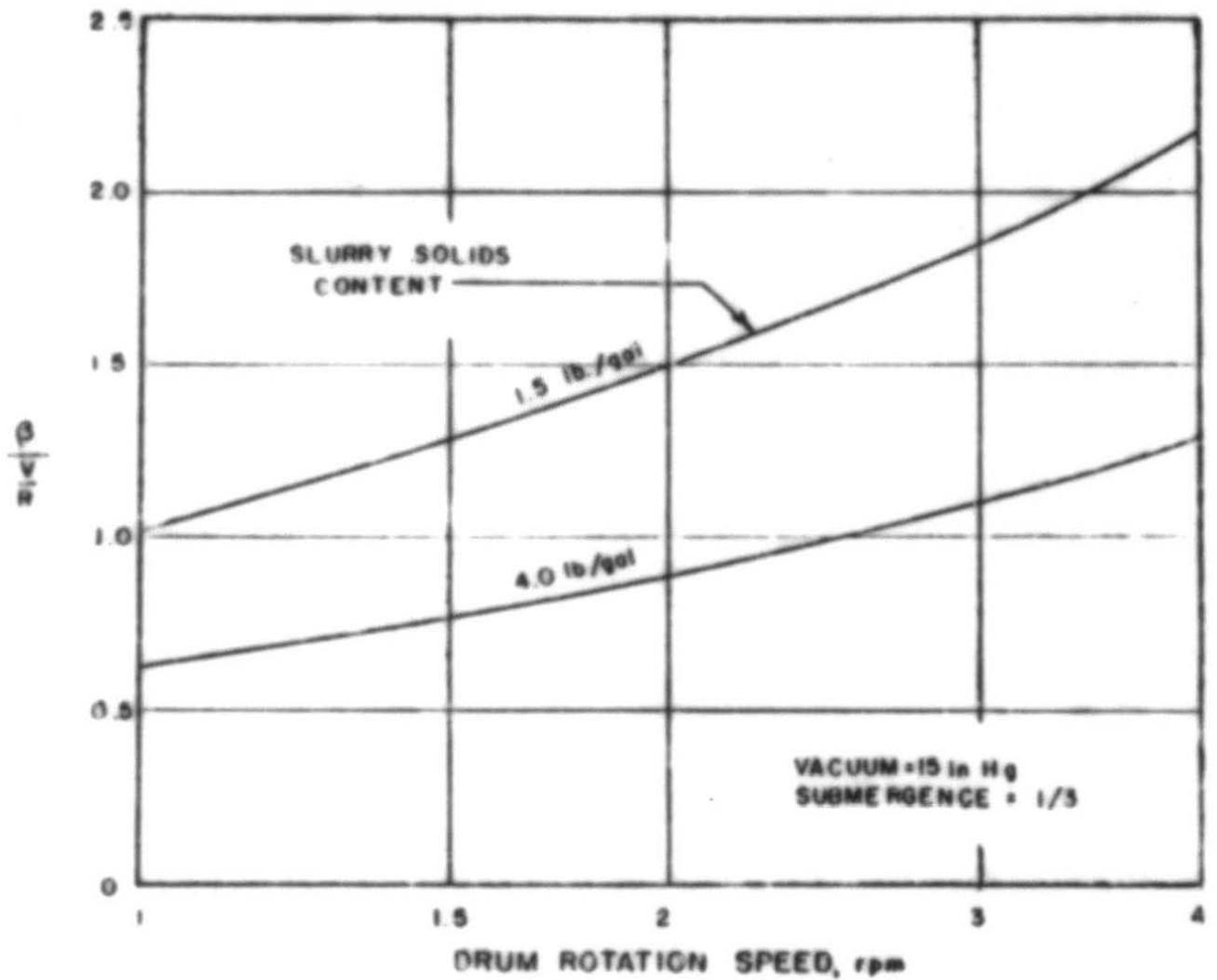
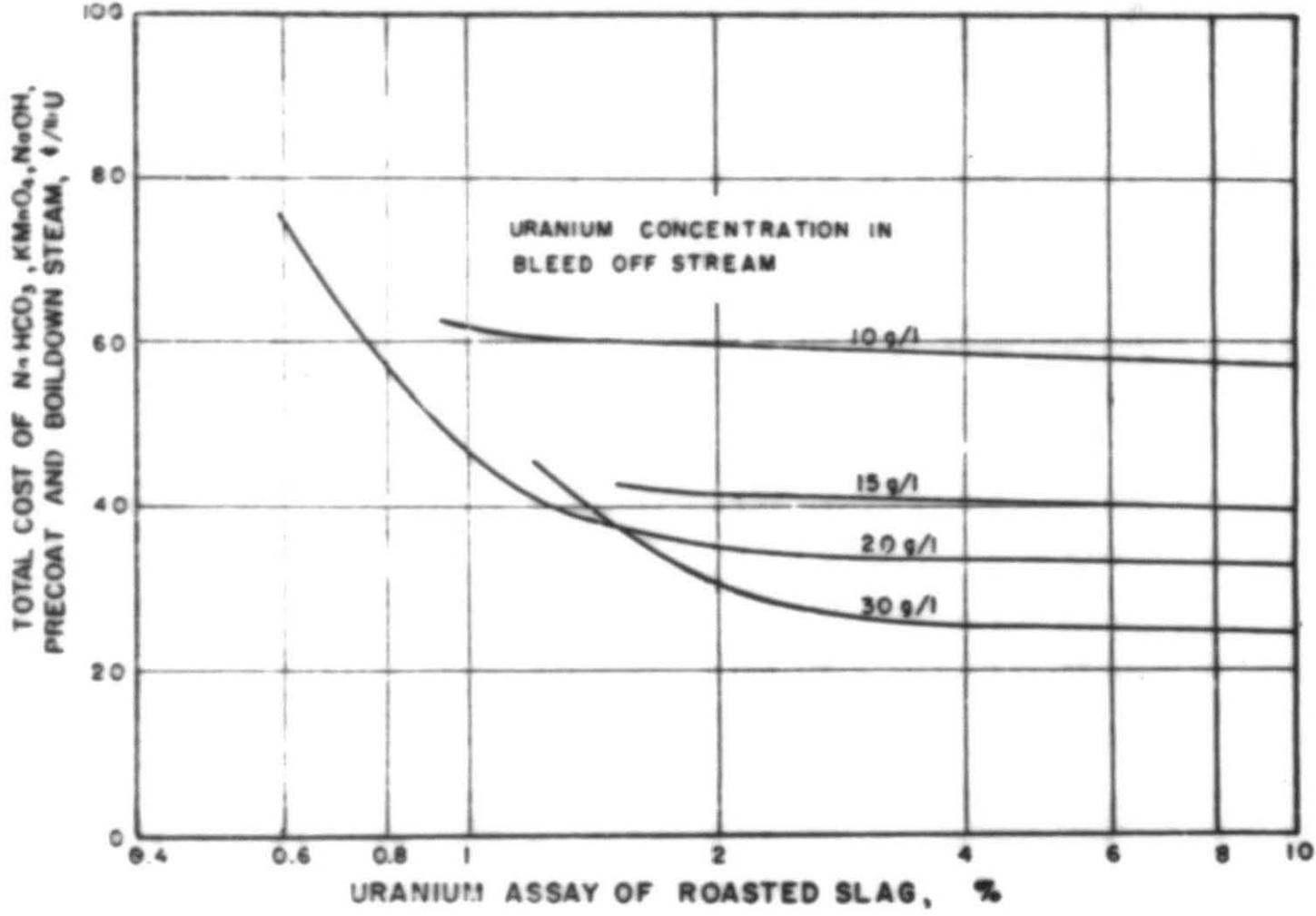


FIGURE 11

ESTIMATED EFFECT OF DRUM ROTATION SPEED ON WASHING PARAMETER



ESTIMATED EFFECT OF ROASTED SLAG ASSAY AND URANIUM LEVEL IN BLEED-OFF STREAM ON SLAG PLANT OPERATING COSTS



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FIGURE 12

RECOVERY OF URANIUM FROM MAGNESIUM FLUORIDE SCRAP
BY FLUORIDE VOLATILITY

by

G. I. Cathers and D. E. Ferguson

Oak Ridge National Laboratory
Oak Ridge, Tennessee

The present method of recovering uranium from the magnesium fluoride scrap obtained in the production of uranium metal consists of obtaining a nitrate solution by dissolving or leaching, precipitation, and solvent extraction procedures. An alternate method that has been investigated for scrap processing is fluoride volatility. It was found that reaction of MgF_2 slag with elemental fluorine at $400^\circ C$ volatilized 99% of the contained uranium, provided that good gas-solid contact was obtained. Based on these laboratory results, a process which consists of grinding, screening, fluorinating with fluorine gas at $400^\circ C$ in an agitated reactor, and collecting the product UF_6 in a cold trap appears to be an attractive method for treating the MgF_2 scrap.

INTRODUCTION

Relatively large quantities of uranium-containing magnesium fluoride scrap are produced in the reduction of uranium to the metal. The present method of recovering uranium from this scrap consists of obtaining a nitrate solution by dissolution or leaching, precipitation, and solvent extraction. This wet chemistry method has the outstanding advantage that it can successfully handle the large variety of scrap that is produced. However, it has the disadvantage of requiring costly chemical conversions to return the salvaged uranium to the metal production line.

An alternate method that appears attractive for MgF_2 scrap recovery is fluoride volatility. Basically this method has the advantage that the product, UF_6 , may be returned directly to either the metal production line or to a diffusion plant. For the reduction

slag this method would represent a large improvement over the wet method.

The paper presents a general discussion of the applicability of fluoride volatility to the slag recovery problem and the results of laboratory studies on the fluorination of metal reduction slag.

FLUORINATION OF MgF_2 SLAG

Several investigators have studied the feasibility of recovering uranium from magnesium fluoride slag by a fluoride volatility process. Tests were made with ClF_3 , BrF_3 and F_2 as fluorination agents. The use of ClF_3 was studied at Mallinckrodt.¹ In one series of laboratory tests with slag that had been previously hydrofluorinated (Table I), about 94% of the uranium was recovered in 30 min at 350-420°C with a 50-100 fold excess of ClF_3 . However, this recovery is not high enough for slag containing more than 1% uranium, since an acceptable residual content is only 0.05%.

In a similar set of tests with slag that had not been hydrofluorinated and with the ClF_3 diluted with helium, increasing the fluorination temperature increased the uranium recovery up to 380°C; above this temperature no increase in uranium recovery was noted up to 620°C. No data were obtained on the consumption of ClF_3 in these experiments. In none of these tests was adequate uranium recovery obtained in 60 min with a 35-fold excess of ClF_3 . These scouting experiments with ClF_3 were discontinued before the suitability of the fluorinating agent was firmly established. It should be noted that beds of slag in excess of 1 in. thick were used in these experiments and good contact with the ClF_3 probably was not obtained.

The use of elemental fluorine for volatilizing UF_6 from MgF_2 slag has been studied on a laboratory scale at Oak Ridge National Laboratory² and Mallinckrodt.¹ In the tests conducted at ORNL, reaction of a thin layer of slag (0.05 in.) with fluorine gas volatilized 97% of the uranium in only 0.05 hr at 500°C (Table II). Increasing the reaction time to 3 hr reduced the residual uranium in slag of -100 mesh particle size to about 1% of the initial value of 1.5-2.0 wt %. In two other tests a reaction temperature of 370°C was equally effective. Uranium could not be adequately recovered with slag of particle size greater than 100 mesh. Also volatilization of uranium was not adequate when fluorine was passed over a static bed of ground slag with a bed depth of 0.5-1.5 in. This was attributed to the heavier UF_6 gas collecting in the lower part of the bed and preventing good contact with the fluorine.

These results indicate that it is possible to recover uranium from MgF_2 bomb-reduction slag by reacting with elemental fluorine at 370°C provided that the slag is ground to pass through a 100 mesh screen and provided that the slag is agitated to ensure good contact with the reacting gas.

Table I

Fluorination of MgF_2 Slag with ClF_3

Slag previously hydrofluorinated; screen analysis (wet): 3% of +200 mesh; 13% of -200 to +325 mesh; balance, -325 mesh

Reacted for 30 min with 50-100 fold excess ClF_3

Temperature (°C)	U in Slag (Wt %)	
	Before	After
350	1.80	0.098
420	0.84	0.048
350	0.90	0.061
350	1.70	0.19

Untreated slag; screen analysis (dry): 56% of +200 mesh; 15% of -200 to +325 mesh; balance, -325 mesh

Reacted for 60 min with a mixture of helium and ClF_3 ($He/ClF_3 = 2/1$), 35-fold excess ClF_3

Temperature (°C)	U in Slag (Wt %)	
	Before	After
100	1.8	0.92
190	1.8	0.42
310	1.8	0.24
380	1.8	0.17
500	1.8	0.19
620	1.8	0.17

Table II

Fluorination of MgF_2 Slag with F_2

Initial U concentration in slag, 1.5-2.0%

0.05-in.-thick bed of slag reacted with F_2

Time (hr)	Temperature (°C)	Particle Size (mesh)	Uranium in Residue (%)
0.05	500	-100	0.049 ^a
0.5	500	-100	0.048 ^b
1.0	500	-100	0.040
3.0	500	-100	0.020 ^a
3.0	370	-100	0.025 ^b
3.0	500	-35, +60	0.17
3.0	500	Unclassified	0.16
3.0	500	-60, +100	0.11

^aAverage of three runs.^bAverage of two runs.

The use of liquid BrF_3 as a fluorinating agent was tried in two experiments at Argonne National Laboratory³ by contacting slag with liquid BrF_3 at the relatively low temperature of 125°C for 6 hr. Uranium recovery was greater than 95%.

APPLICATION OF FLUORIDE VOLATILITY TO SCRAP PROCESSING

A schematic flowsheet for uranium recovery from MgF_2 slag by reacting with elemental fluorine is shown in Figure 1. Fluorine was selected in place of ClF_3 or BrF_3 because of the comparative ease of separating F_2 and UF_6 and recycling the F_2 . In the case of the interhalogen fluorinating agents, fractional distillation or an equally complicated step would be required to separate the fluorinating agent from the UF_6 . The process consists of grinding and screening the scrap to less than 100 mesh to ensure that intra-particle diffusion does not limit the uranium recovery, reacting with fluorine gas at 400°C to form volatile UF_6 in an agitated reactor to ensure good gas-solid contact, collecting the UF_6 in a cold trap, and recycling the excess F_2 to the fluorinator. While this process has been tested only in laboratory scouting experiments, it has been shown to be chemically feasible in the case of the MgF_2 slag and liner material. The fluoride-containing scrap from the UF_6 and metal reduction steps could also be processed along with the slag without extensive pretreatment.

More development work will be required to establish optimum operating conditions for the slag process and the pretreatment required to obtain maximum recovery with a minimum fluorine consumption. Hydrofluorination prior to fluorination may drastically reduce the consumption of expensive fluorine gas. No attention has been given to the recycle of unused fluorine. Undoubtedly, volatile impurities will build up in the recycled gas and will require a disposal system.

From the standpoint of equipment this process introduces no novel problems. Engineering development certainly would be required to establish the best design and operating procedure for the fluorinator, and it may be necessary to use a cyclone separator and filter to prevent entrained solids from being carried over with the product. Suitable materials of construction are available in the high-nickel-base alloys, such as Inconel or Monel. Operation of the process at essentially atmospheric pressure throughout would probably be most practical in order to avoid in-leakage of air into the system, and to minimize the out-leakage of fluorine and UF_6 .

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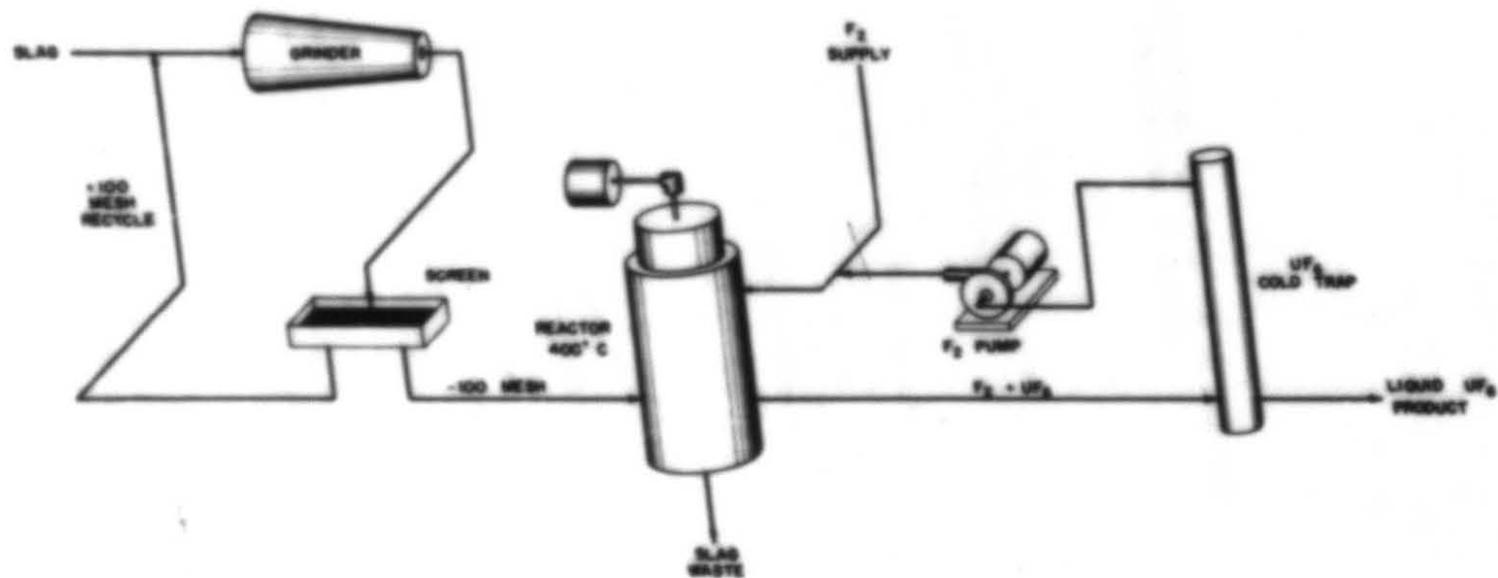


FIGURE 1
SCHEMATIC FLOWSHEET FOR URANIUM
RECOVERY FROM REDUCTION SLAG

RECOVERY OF URANIUM FROM MAGNESIUM FLUORIDE
WASTES BY ION EXCHANGE

by

I. R. Higgins
Chemical Technology Division
Oak Ridge National Laboratory

The most attractive ion exchange flowsheet for the recovery and partial purification of uranium is based on the sorption of uranyl ion as a chloride complex on anion resin and its elution with water. This step is attractive because of the low cost of elution and the preparation of uranium in a form relatively free from bulk ions. This product is suitable for either precipitation or electrolysis.

If it is desirable to recover both HF and uranium from MgF_2 scrap, the scrap is treated with H_2SO_4 , retorted to recover HF, and uranium recovered from the residue by ion exchange. Uranyl sulfate is extracted on anion resin from $MgSO_4$ solution. The sulfate on the resin is replaced by chloride using concentrated brine or $\sim 8\text{ M HCl}$ forming a uranyl chloride complex. The uranyl chloride complex is eluted with water as UO_2Cl_2 which can be precipitated as diuranate or reduced to UF_4 by the Excer process.

If HF recovery is not required, the MgF_2 scrap is leached with HCl and the uranyl chloride complex sorbed directly from the strong chloride solution ($\sim 8\text{ M}$ containing suspended MgF_2). Again the uranium is eluted with water as UO_2Cl_2 .

Uranium may also be recovered from a carbonate leach by ion exchange. The principal advantage of ion exchange over precipitation is the elimination of a clarification step because the eluted product is carbonate solution similar to the original leach. In addition, dilute leach solutions can be concentrated to 25 g U/l.

INTRODUCTION

Continuous ion exchange processes are being developed at ORNL for the recovery, concentration, and partial purification of crude uranium. The bulk of the studies have been concerned with ore leach pulps, but this paper will be confined to bomb liner scrap recovery studies.^{1,2,3,4} The ion exchange flowsheets have been designed to prepare feed for the Excer process.^{4,5,6} If electrolytic reduction by the Excer process is not desired, the partially purified ion exchange product may be precipitated as diuranate by standard methods.

ION EXCHANGE TREATMENT OF CHLORIDE LEACHED MgF_2 SCRAP

Scrap uranium is presently being recycled at FMPC by hydrochloric acid dissolution, filtration and precipitation. Using essentially the same dissolution procedure, ion exchange is proposed for elimination of the filtration step and for the preparation of a higher purity product. When MgF_2 scrap was dissolved in 8 M HCl, with $NaClO_3$ as an oxidant, magnesium was dissolved to 1.5 g/l and F to 0.8 g/l.³ Even in 8 M HCl fluoride has some affinity for the anion resin but is scrubbed out with fresh 8 M HCl, which is required anyway to displace contaminants in the void volume. The uranium is eluted with water. Product concentrations of UO_2Cl_2 of over 200 g U/l has been demonstrated in continuous operation in a Higgins contactor. If it is desired to precipitate at this point, alkali may be added. A NaU_2O_7 cake, prepared from UO_2Cl_2 and washed with water contained only 0.01 wt % chloride. If the Excer route is preferred, the UO_2Cl_2 is ready for electrolysis after adding HF.^{4,5,6}

The barren waste is used as a source of high chloride for feed makeup. Calcium oxide or $CaCl_2$ is added to prevent a buildup of SO_4 or F. A crude solid-liquid separation, with no washing, is sufficient to remove the CaF_2 or $CaSO_4$ since a bleed stream is necessary anyway (See Fig. 1).

ION EXCHANGE TREATMENT OF SULFATE LEACHED MgF_2 SCRAP

Magnesium fluoride scrap could be leached with sulfuric acid and only the uranium recovered, but if digested in HF distillation equipment, this valuable by-product would also be recovered. In either situation the uranium occurs in a $MgSO_4$ solution with varying amounts of MgF_2 as slurry depending on the completeness of the HF recovery. The anion exchange recovery of uranium is identical to that of sulfate ore leach, the uranium being sorbed as the sulfate complex. By displacing the sulfate with strong chloride, 5 M or greater, the uranium is eluted with water and treated as in the previous discussion. The sulfate leach system has the advantage of a less expensive acid. No recycle of leach liquor is required, as in the chloride system, because

uranyl sulfate is anionic in dilute solution. The sulfate system has the disadvantage of continually going through a sulfate-chloride exchange on the resin, which reduces the overall production rate below that which is possible with an all-chloride system (Fig. 2).

ION EXCHANGE TREATMENT OF CARBONATE LEACHED SCRAP

Mallinckrodt is presently using a Na_2CO_3 , NaHCO_3 , KMnO_4 leach of calcined MgF_2 bomb liner scrap. The final leach slurry is filtered and the uranium precipitated as diuranate. This carbonate leach material was tried on the 2-in.-dia. Higgins contactor. The KMnO_4 was reduced to MnO_2 with H_2O_2 to prevent sorption of permanganate ion on the anion exchange resin. The MnO_2 and MgF_2 slurries were treated on 20-40 mesh resin with no indications of plugging.¹ Eluting systems were not thoroughly investigated but 1 M NaHCO_3 was found to be effective.

This carbonate cycle fits anion exchange very well, but this system does not have any great advantage over precipitation. Purification is not needed because carbonate dissolution is a purification step in itself. Concentration is not required because the feed and product solution strengths are essentially the same. The diuranate precipitation step is not avoided by using ion exchange. If filtration of the MgF_2 slurry, separation of traces of MgF_2 from the uranium solution, or loss of uranium by adsorption on the MgF_2 particle are difficult problems, the resin-in-pulp treatment would be of value. If the carbonate leach were used on very dilute uranium sources, ion exchange would serve as a recovery-concentration step (Fig. 3).

PERFORMANCE OF A 2-INCH HIGGINS CONTACTOR USING A CONTAMINATED SULFATE LEACH AND THE STRONG CHLORIDE-WATER ELUTION SYSTEM

The high-chloride sorption and water elution system for treating uranium sources is presently being studied using a 2-in.-dia. Higgins contactor. Synthetic sulfate ore leach or scrap feeds were prepared, containing recycle sulfate-chloride ion exchange wastes and electrolytic cell supernate from a previous Excer run containing UO_2F_2 and HF. The recovery of uranium was >99.8% when using 4 ft of Permutit SK-20-40 mesh resin loaded to 44 g U/l (Fig. 4).

In the presence of a high concentration of chloride ion (>5 M), it is theoretically possible to displace sulfate equivalent with an equivalent amount of chloride. A 3 ft column section was used for this purpose and proved to be too short. Further work also remains to determine the level to which sulfate must be reduced to prevent uranium losses. Nevertheless, from the approximate one equivalent capacity of the resin, the sulfate in solution has been reduced in 3 ft to 0.006 M with a consumption of six equivalents of HCl (as 8 M), to 0.028 molar with 4 equivalents, and to 0.36 molar with three equivalents (5 M NaCl) (Fig. 5).

The water elution of uranium from resin loaded with uranyl chloride anion complex is very rapid and complete as compared to elution of a sulfate loaded resin with 1 M chloride. On dilution, the UO_2Cl_2 has essentially no affinity for the resin. The concentration of product that is withdrawn depends upon initial uranium concentration in the resin phase. The maximum product concentration that can be removed is the maximum loading capacity of the resin in the strong chloride solution multiplied by 2.5, the void volume factor. When using 8 M HCl for scrubbing sulfate, uranium product concentrations of over > 200 g U/l, as UO_2Cl_2 , have been achieved (Fig. 6).

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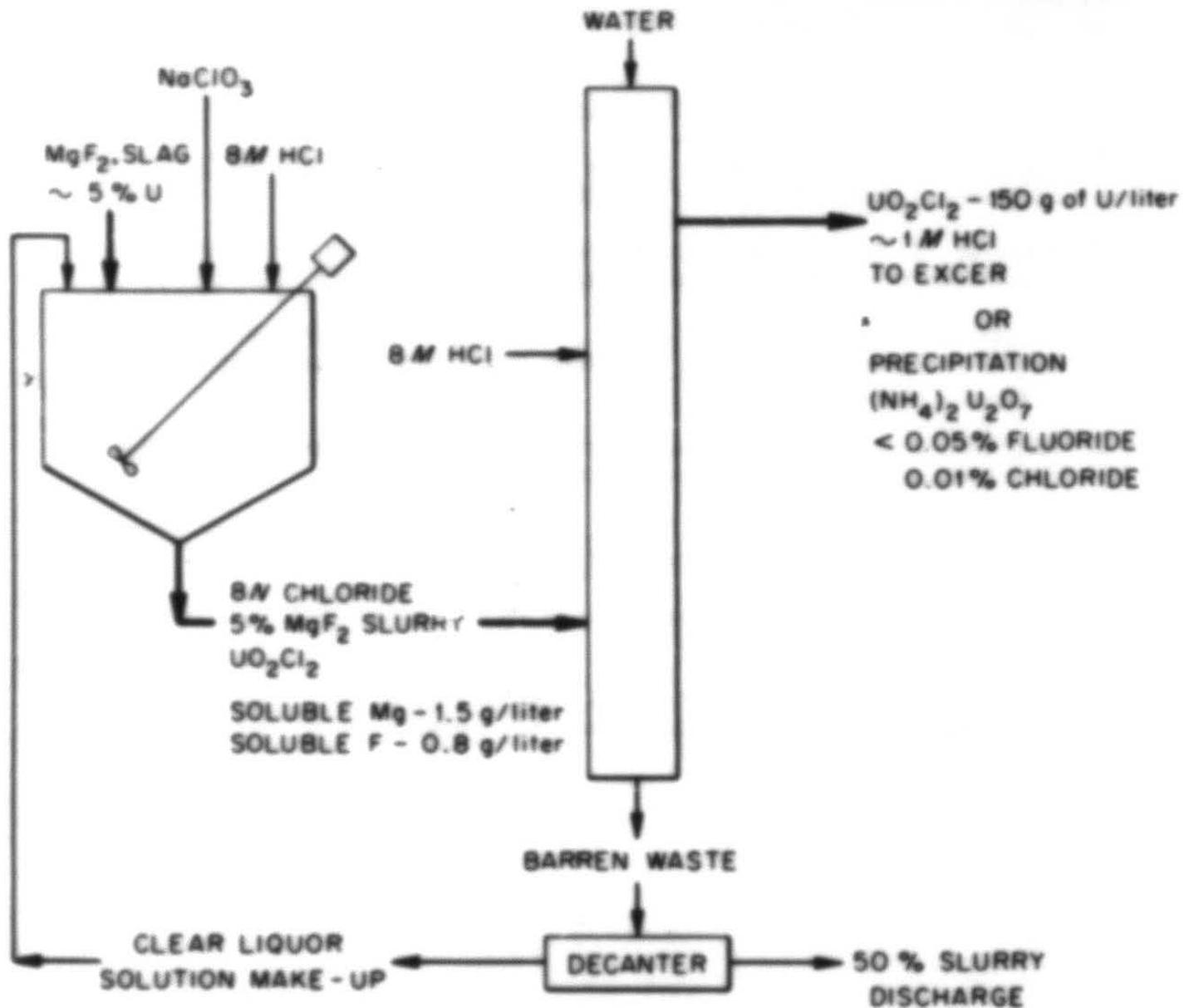
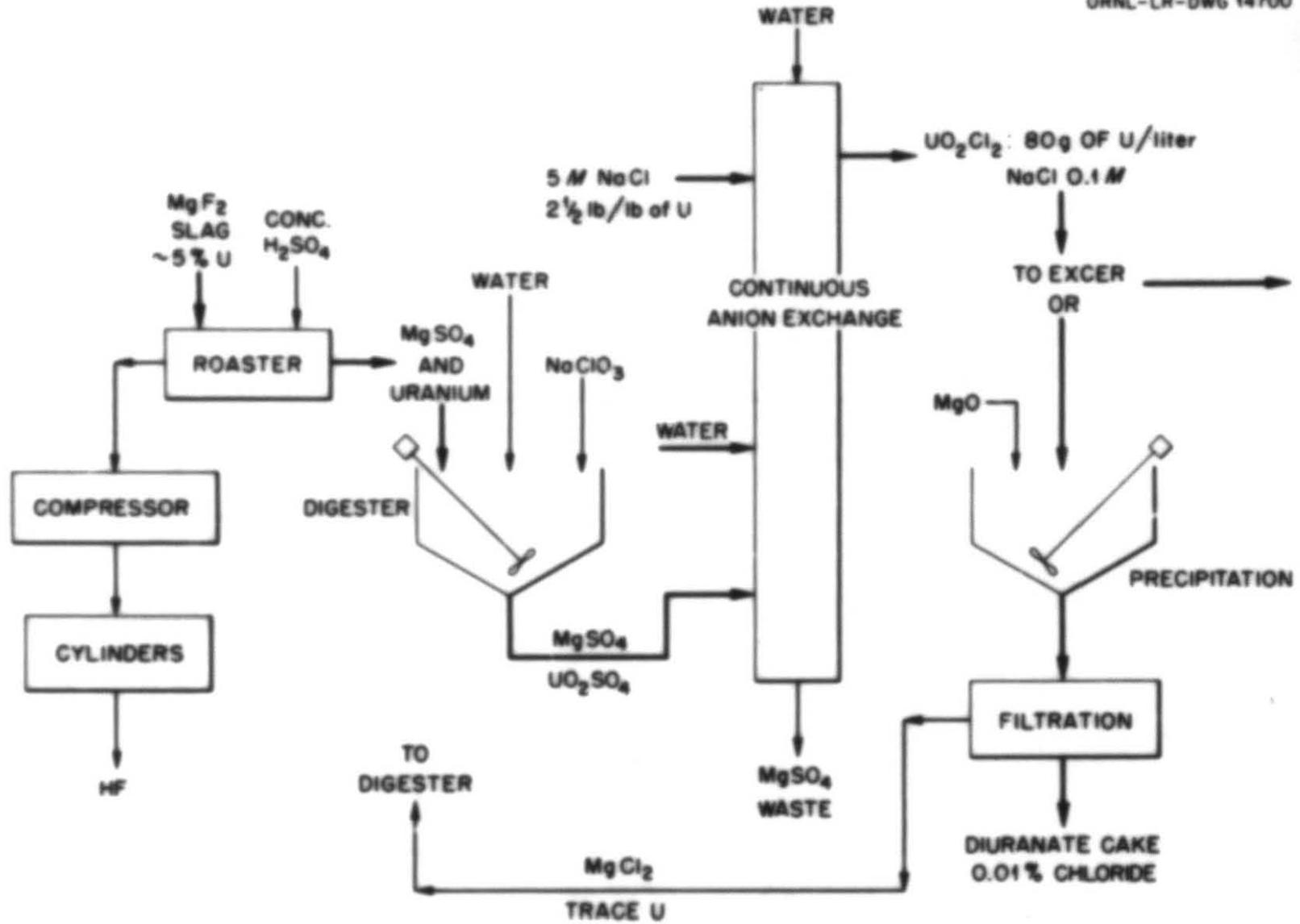


Fig. 1. Flowsheet for Recovery of Uranium from Bomb Liner Slag, Chloride Leach.

Fig. 7. Flowsheet for Recovery of Uranium and Anhydrous HF from Bomb Liner Slag.



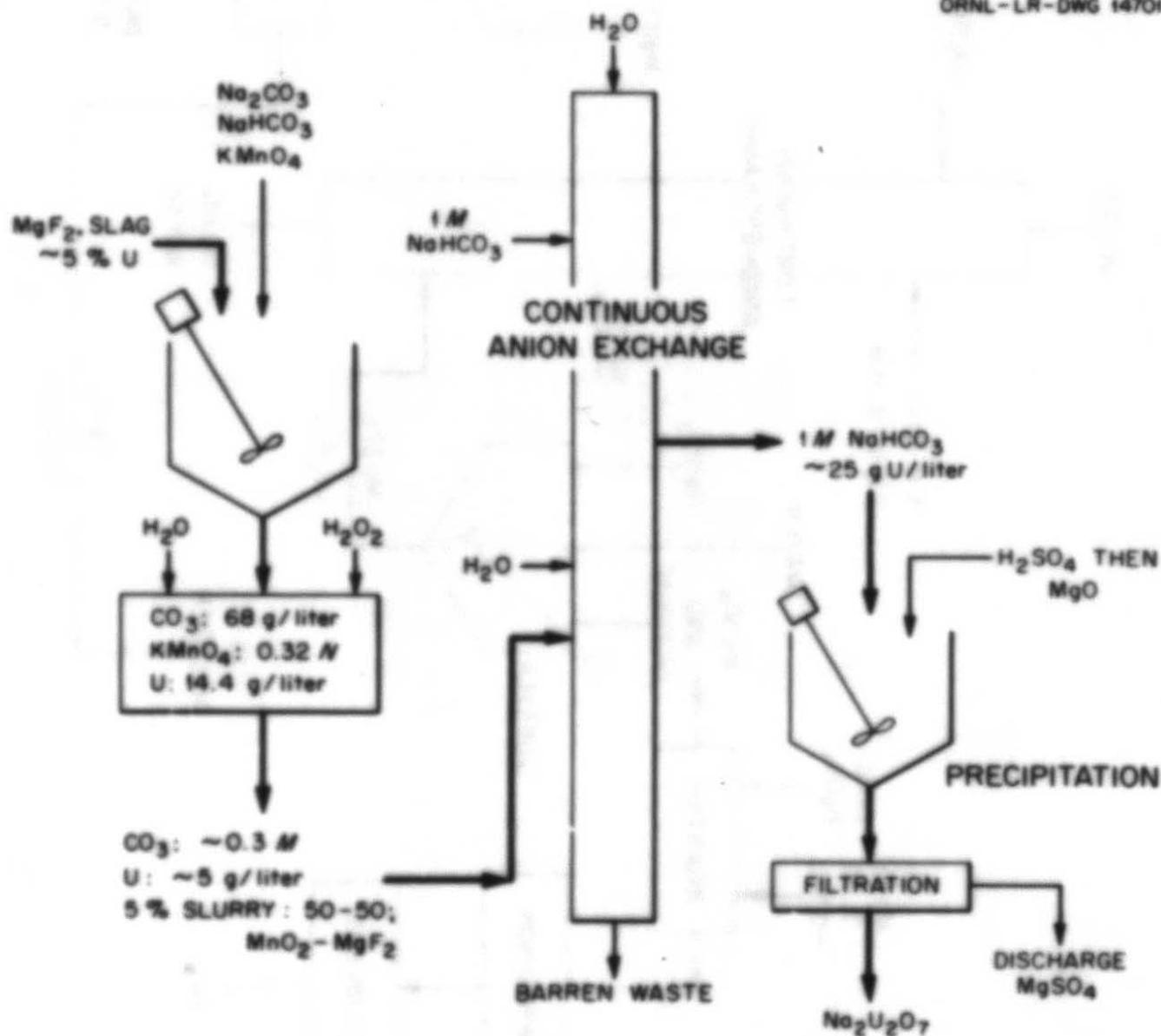


Fig. 3. Flowsheet for Recovery of Uranium from Bomb Liner Slag. Carbonate Leach.

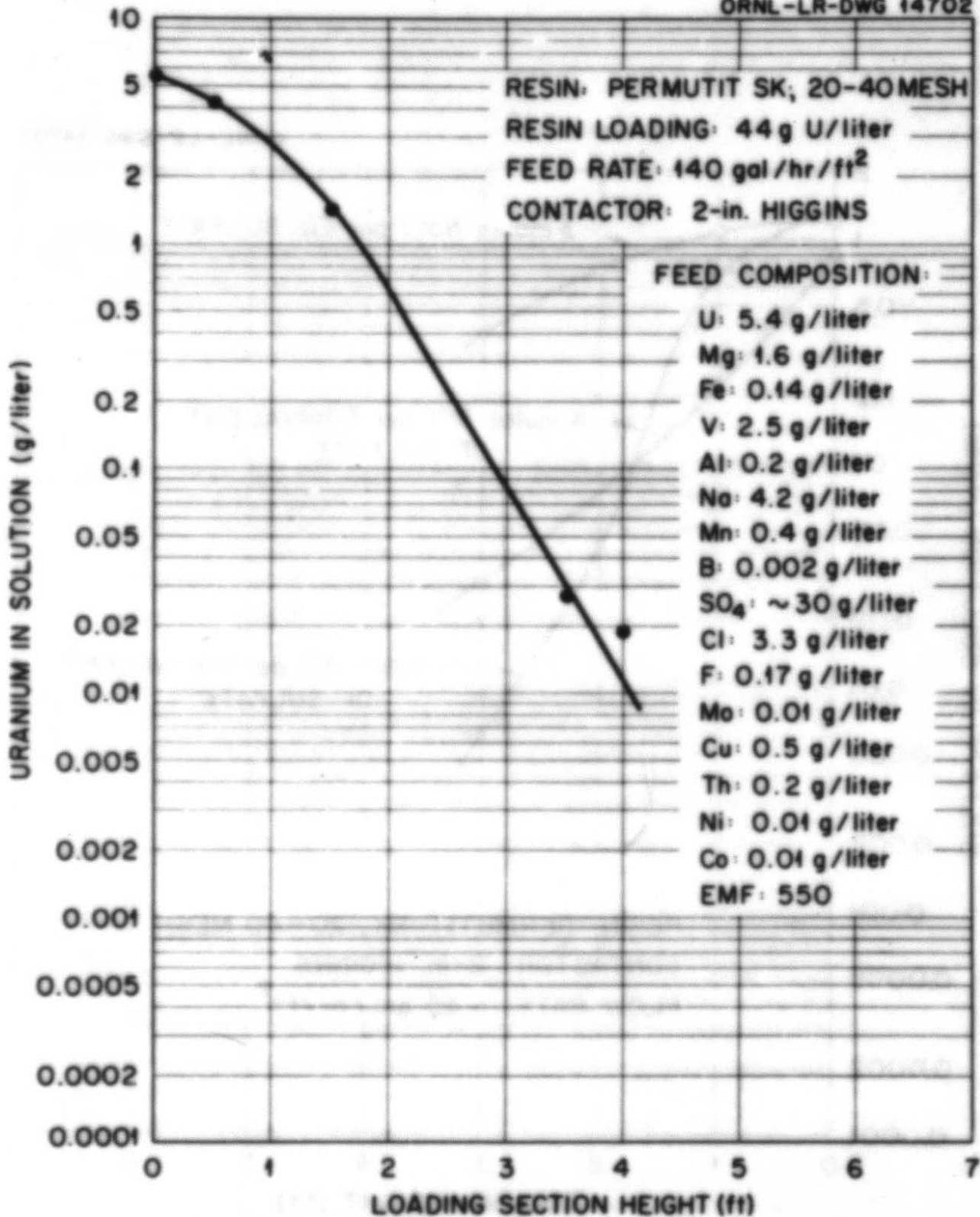


Fig. 4. Loading Column Height Required to Maintain Low Uranium Loss from Sulfate Leach.

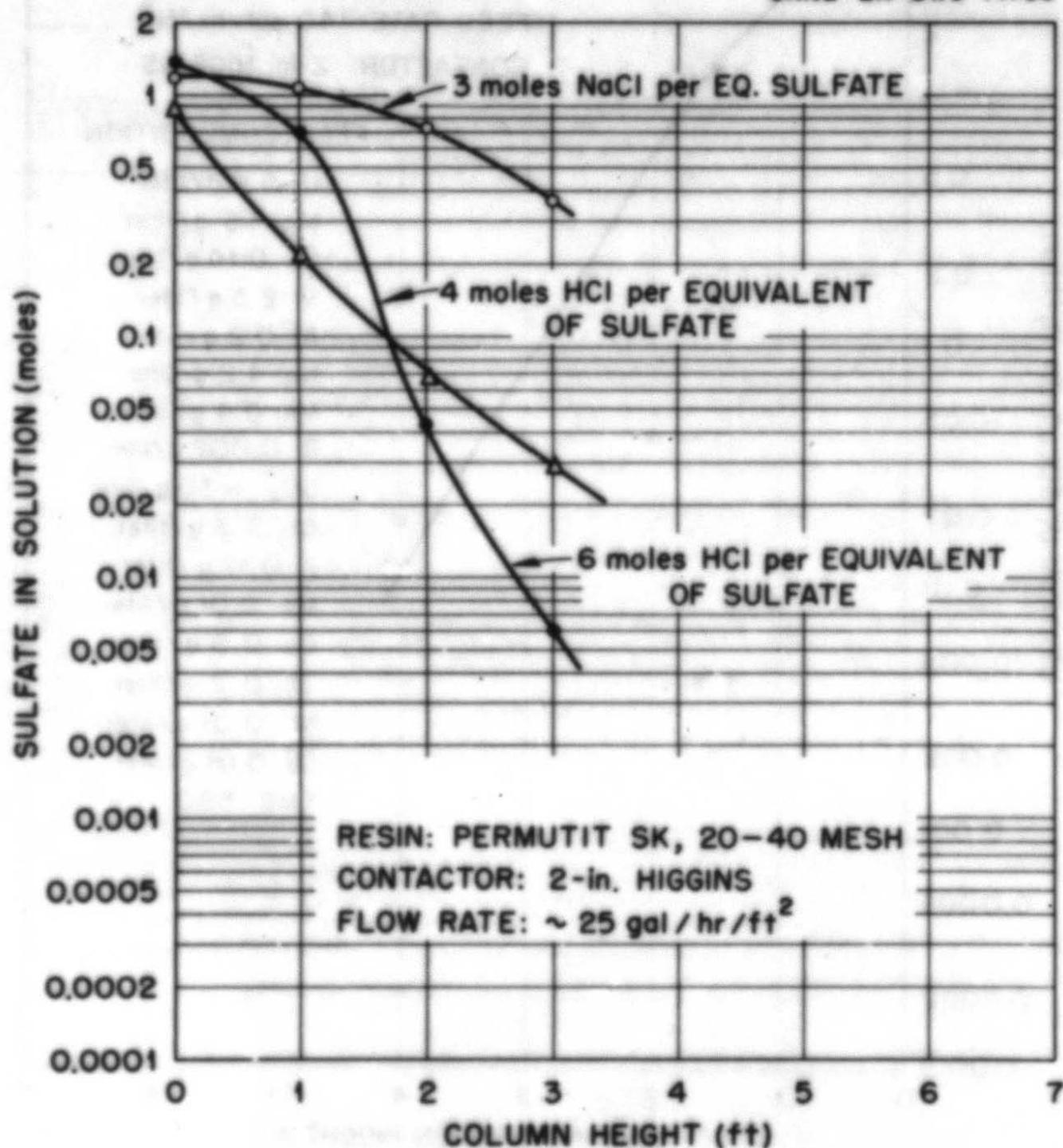


Fig. 5. Elution of Sulfate from Uranyl-Sulfate-Loaded Resin with 8 M HCl or 5 M NaCl.

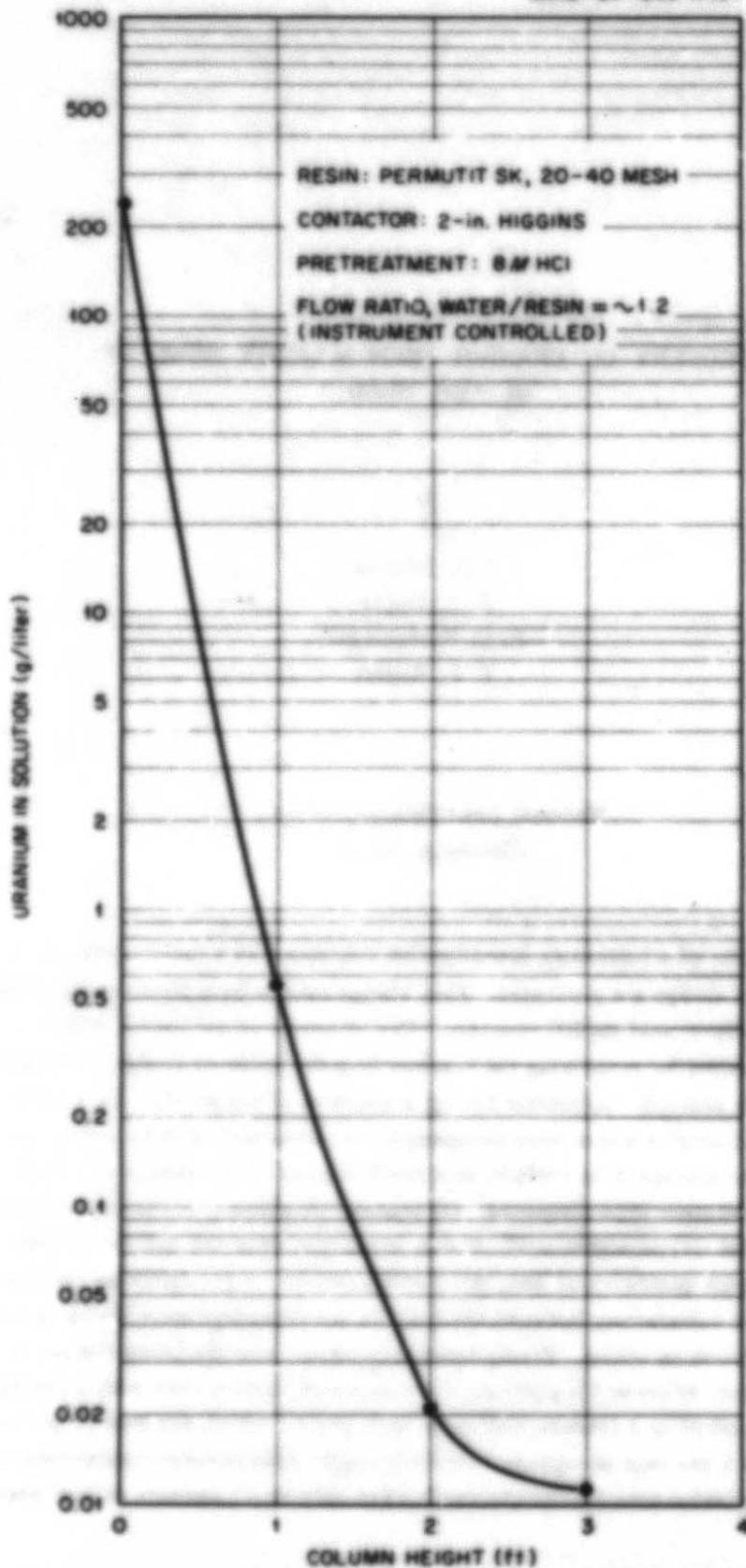


Fig. 6. Column Height Required to Elute Uranyl-Chloride-Loaded Resin with Water.

RECOVERY OF URANIUM FROM SULFATE RESIDUES OF MgF_2 SLAG

by

E. R. Johnson
R. L. Doyle
E. O. Rutenkroger
T. F. Rupert

National Lead Company of Ohio
Cincinnati, Ohio

The results of a laboratory investigation concerned with the recovery of uranium from sulfated sludge are presented. This sludge results from the roasting of MgF_2 slag with sulfuric acid for HF recovery. The objective of the investigation was to develop a method for recovering the uranium from the sulfated sludge in the form of a high-grade uranium concentrate having a minimum of impurities. This investigation included studies which were designed to determine the relative merits of precipitating the uranium from sulfuric acid leach liquors of the sludge as (1) an ammonium diuranate type compound, (2) uranous phosphate, (3) uranyl ammonium phosphate and (4) peruranic acid. It was found that when the sulfated sludge contained large quantities of iron, the uranous phosphate precipitation technique was the most satisfactory because the iron did not coprecipitate with the uranium from the reduced solutions. Precipitation of uranium from the leach liquors by this technique, followed by slurring the uranous phosphate cake with a caustic solution, resulted in a uranous hydroxide type product which assayed 67 per cent uranium and 4 per cent phosphate. Similarly, high grade uranium concentrates were produced by techniques (1) and (3) above when only small amounts of iron were present.

INTRODUCTION

During the production of uranium metal considerable quantities of MgF_2 slag are generated as a by-product of the UF_4 reduction operation. Slag suitable for reuse as a bomb liner material is prepared by subjecting the slag to a series of crushing and classification operations. The surplus liner material and the classification rejects are available for processing for the recovery of contained uranium values. This recovery can be effected satisfactorily by both the Mallinckrodt Chemical Works' carbonate leach technique¹ and by the National Lead Company of Ohio's hydrochloric acid leach-phosphate precipitation process.²

Since HF is commonly produced by the reaction between calcium fluoride and sulfuric acid, it appeared reasonable that magnesium fluoride (the major slag component) might be of similar commercial value. Since the Atomic Energy Commission is primarily interested in uranium recovery from the slag, the National Lead Company of Ohio was directed to conduct a series of exploratory studies, in the laboratory, to determine how the calcines (sulfated sludge) resulting from such an HF recovery treatment might best be processed for the recovery of contained uranium values.

This report describes the results of these exploratory investigations.

EXPERIMENTAL RESULTS AND DISCUSSION

A. Material Tested

Initially, a series of experiments was conducted in the laboratory in which synthetically prepared leach liquors were used. It was the purpose of these studies to examine the effects of the components of the sludge on the various uranium recovery techniques and to determine optimum conditions for uranium recovery. These leach liquors were generally prepared by dissolving $MgSO_4 \cdot 7H_2O$, UO_2SO_4 , and $Fe_2(SO_4)_3$ in very dilute sulfuric acid, the resultant acidity of the solution being approximately pH 1.0. The quantities of these components were varied during experimentation so that the effects of these variations on uranium recovery could be studied.

One group of investigators (A) submitted several samples of sulfated sludge (resulting from the treatment of MgF_2 slag with sulfuric acid for HF recovery) for use in uranium recovery studies. One of these samples was obtained from a pilot plant sulfation of a large sample of MgF_2 slag. It was estimated by these investigators that 65 per cent of the fluoride content of the slag was volatilized as HF during this run.

Prior to this pilot plant sulfation, the MgF_2 slag had been ground to the following particle size distribution:

Sieve No	Per Cent on Sieve	Cumulative Per Cent
+ 100	1.2	1.2
+ 200	18.0	19.2
+ 270	8.2	27.4
+ 325	39.3	66.7
- 325	33.3	100.0

The sludge resulting from this sulfation trial was reported to contain 32 per cent H_2SO_4 and 14.3 per cent insolubles. This sample of sulfated sludge was designated as A-1.

The other samples submitted by this group were obtained during their laboratory scale HF recovery studies. Several of these samples were composited to produce a mixture which contained 32.1 per cent H_2SO_4 and 11.3 per cent insolubles. This composite sample of sulfated sludge was designated as A-2.

Another group of investigators (B) submitted two 800-gram samples of sulfated sludge produced during their experimental work. One sample (designated B-1) was the product of a small vertical pot reactor, and the other (designated B-2) was the product of a small rotary kiln. In both cases, the MgF_2 slag had been ground to - 325 mesh prior to sulfation.

B. Leaching Tests

1. Water Leach

In most of the experimental uranium recovery work conducted, the leach liquors used were obtained by leaching the sulfated sludge samples with water at 90°C in the presence of an oxidant ($NaClO_2$). The sludge samples invariably contained sufficient excess acid to produce an acidity (pH < 1.0) in the leach slurry which was low enough to dissolve the uranium values.

Efforts were made to employ a high pulp density during leaching, thereby providing a smaller slurry volume. It was found that the sludge could be leached at pulp densities as high as 33 per cent solids before crystallization of $MgSO_4$ was observed in the filtered liquor. Samples of sulfated sludge from Group "A"'s pilot plant test were leached at several different pulp densities for study of the effect of pulp density on the uranium concentration of the resulting insoluble

residue. It was found (Trials 1, 2, and 3, Table I) that at 25 per cent solids or less, better uranium solubilization was obtained than at 33 per cent solids. Other experiments in which the leaching time was varied showed that uranium solubilization was complete at the end of one hour (Trials 4, 5, and 6, Table I).

Samples of sludge from Group "B"'s laboratory investigations were leached for one hour at 90°C and a 33 per cent solids content (Trials 7 and 8, Table I). The uranium concentrations of the insoluble residues from these trials were similar to those obtained from the leaching of the Group "A" sludge under similar conditions.

TABLE I
LEACHING OF SULFATED SLUDGE

Trial No.	Sludge Sample	Wt of Sludge (g)	Vol Water (ml)	Leaching Conditions				Wt NaClO ₂ (g)	Acid-Insol Residue		Acid Filtrate				
				Time (hr)	Temp (°C)	pH	Solids (%)		Wt (g)	U (%)	Vol (ml)	U (g/l)	Mg (g/l)	SO ₄ (g/l)	Fe (g/l)
1	A 1	1000	2000	1.5	90	<0.5	33	2	148	0.16	2500	3.2	37.6	241	3.1
2	A 1	1000	3000	1.5	90	<0.5	25	2	140	0.058	3700	2.2	25.9	165	2.1
3	A 1	1000	4000	1.5	90	<0.5	20	2	137	0.059	4700	1.7	-	-	1.6
4	A 1	830	1660	3.0	90	0.4	33	2	117	0.14	2200	-	-	-	-
5	A-1	1000	2000	2.0	90	0.4	33	2	140	0.14	2625	2.7	35.1	224	3.3
6	A 1	1000	2000	1.0	90	0.4	33	2	144	0.13	2625	2.8	35.8	237	3.3
7	B 1	588	1175	1.0	90	0.2	33	1	26	0.19	1425	1.9	34.3	289	15.9
8	B-2	260	520	1.0	90	0.2	33	0.5	7.4	0.14	680	2.2	36.9	284	4.8

Not determined.

The leach liquors resulting from these tests were used in the uranium precipitation experiments which are reported in Section C of this report.

Uranium recoveries of 97 to 98 per cent were obtained during leaching, although in a number of experiments the acid-insoluble residues contained as much as 0.13 to 0.19 per cent uranium. It is expected that this small uranium loss could be reduced further in additional test work.

The solubility of the fluorides present in the sulfated sludge samples was found to be negligible (<0.5 g/l fluoride).

2. Carbonate Leach

A brief study was made of the feasibility of using a sodium carbonate leach to solubilize the uranium values present in sulfated sludge. It was thought that such a technique would provide a leach solution that was essentially free of impurities and that therefore would provide a purer uranium concentrate on precipitation. However, when samples of laboratory-produced sludge were leached in this manner (Table II), the high concentration of magnesium consumed large quantities of carbonate in excess of that required for neutralization of the excess sulfuric acid. A 0.7 to 1 weight ratio of sodium carbonate to sulfated sludge was required before satisfactory uranium recovery was obtained. Therefore, this line of investigation was discontinued and subsequent studies regarding the recovery of uranium from leach liquors were restricted to those obtained by the water leach technique.

TABLE II

CARBONATE LEACHING OF URANIUM FROM SULFATED SLUDGE*

Time (hr)	Trial ** 1			Trial 2		
	U in Residue† (%)	Filtrate		U in Residue (%)	Filtrate	
		Na ₂ CO ₃ (g/l)	U (g/l)		Na ₂ CO ₃ (g/l)	U (g/l)
1	0.068	20.6	-	0.16	17.5	-
2	0.058	20.1	-	0.15	18.0	-
3	0.046	16.4	-	0.16	18.6	-
4	0.050	12.7	1.8	0.15	13.8	1.7

* Sludge for each trial was prepared by roasting 333 g MgF₂ (2.3% U) and 318 ml 96% H₂SO₄ at 450° F. The volume of H₂O was 1000 ml.

The weight of Na₂CO₃ was 500 g. The temperature was 90° C.

** 5 g K₂Cr₂O₇ used in Trial 1.

† Residues were repulp washed with a 2% Na₂CO₃ solution at 80° C.

C. Recovery of Uranium from Leach Liquors

1. Ammonia Precipitation (Ammonium Diuranate-Type Product)

The results of an experiment in which the pH of a synthetic leach liquor was increased stepwise with ammonium hydroxide (Table III) showed that the uranium values contained in the liquor were completely precipitated at pH 6.0.

TABLE III

THE EFFECT OF pH ON THE PRECIPITATION OF URANIUM FROM SYNTHETIC SULFATED SLUDGE LEACH LIQUORS*

pH	Soluble U Conc. (g/l)
1	3.92
3	3.82
4	3.63
5	2.70
6	0.006
7	0.004

* The analysis of the stock solution (pH 1.0) was:

U (g/l) 3.92

Mg (g/l) 55.

SO₄ (g/l) 263.

Fe (g/l) 4.40

Precipitant: NH₃OH

Temperature: 60° to 70°C

A series of laboratory experiments was conducted to study the effect of the components of sulfated sludge (i.e., the concentrations of Fe and MgSO₄) on the precipitation of uranium from dilute sulfuric acid by ammonium hydroxide. It was found (Table IV) that neither iron nor magnesium sulfate interfered with the completeness of uranium precipitation but that iron quantitatively coprecipitated, adulterating the uranium cake. This ammonium diuranate cake was also contaminated with 5 to 10 per cent sulfate.

TABLE IV

THE EFFECT OF IRON AND MAGNESIUM SULFATE CONCENTRATIONS
ON THE PRECIPITATION* OF URANIUM FROM SULFURIC ACID
SOLUTION AS AMMONIUM DIURANATE

Trial No.	Stock Solution**					Ammonium Diuranate Cake†				Filtrate		
	Vol (ml)	U (g/l)	SO ₄ (g/l)	Fe (g/l)	Fe/U	Wt (g)	U (%)	SO ₄ (%)	Fe (%)	Vol (ml)	U (g/l)	Fe (g/l)
Effect of Iron												
1	1000	5.1	38.3	3.2	0.6	12.4	38.7	6.46	23.8	1240	0.022	0.008
2	1000	4.9	18.5	1.6	0.3	9.0	51.1	5.01	16.7	1265	0.0005	0.003
3	1000	5.1	21.0	0.4	0.08	7.7	61.8	7.93	4.8	1265	0.001	0.005
Effect of Iron and MgSO ₄												
4	1000	4.2	223	2.5	0.6	10.7	37.9	9.76	23.0	1220	0.002	0.01
5	1000	4.7	211	1.4	0.3	8.8	51.1	5.40	15.0	1325	0.005	0.008
6	1000	4.2	199	0.8	0.2	7.0	59.8	6.30	9.6	1200	0.002	0.008

* Precipitation pH: 6.2, precipitation temperature: 60° to 70°C, precipitant: 28 per cent NH₄OH

** pH of stock solution: 1.0

† Ammonium diuranate cakes were washed on the filter with 200 ml water

Samples of filtered liquors obtained by leaching the sulfated sludge samples obtained from both Group "A" and Group "B" were precipitated with ammonium hydroxide at pH 6.2 and at 60° to 70°C (Table V). The ammonium diuranate cake obtained from treatment of the Group "A" material assayed 26 to 29 per cent uranium and 28 to 34 per cent iron. These investigators indicated that the iron content of sludge resulting from a production operation would be expected to be lower than that resulting from pilot plant tests, due to a higher ratio of material volume to reactor surface area in production-scale equipment.

TABLE V

**PRECIPITATION* OF URANIUM (AS AMMONIUM DIURANATE)
FROM SULFATED SLUDGE LEACH LIQUORS**

Trial No.	Leach Filtrate Used	Leach Filtrate			Ammonium Diuranate Cake**						Diuranate Filtrate	
		Vol (ml)	U (g/l)	Fe (g/l)	Wt (g)	U (%)	Mg (%)	Fe (%)	SO ₄ (%)	F (%)	Vol (ml)	U (g/l)
1	A-1 (Trial 1) [†]	2450	3.2	3.1	26.8	28.9	0.75	33.7	8.2	<0.03	4000	0.006
2	A-1 (Trial 2) [†]	3650	2.2	2.1	30.0	26.5	1.94	28.3	12.4	0.33	4300	0.007
3	A-1 (Trial 3) [†]	4650	1.7	1.6	27.2	29.0	0.95	31.4	5.5	0.55	5300	0.033
4	B-1 (Trial 7) [†]	675	1.9	15.9	11.0	6.7	0.87	47.9	12.7	—	1200	0.17
5	B-2 (Trial 8) [†]	640	2.2	4.8	7.0	17.5	0.55	42.5	4.2	—	1200	0.009

* Precipitation temperature: 60° to 70°C, precipitation pH: 6.2

** Washing conditions: Ammonium diuranate cakes were repulp washed with water at ambient temperatures.

† Refers to the trial (Table I) in which the filtrate was produced.

The ammonium diuranate cake obtained by treatment of the Group "B" material contained only 6.7 to 17.5 per cent uranium depending on the sample, and its iron content exceeded 40 per cent. This is probably not representative of what could be expected from a large-scale operation.

Since essentially none of the components of the sulfated sludge (with the exception of iron and uranium) precipitate at pH 6.2, the quality of the uranium concentrate obtained has been found to be dependent largely on the amount of iron picked up (1) by the slag during grinding and (2) by corrosion during the roasting of slag with sulfuric acid. The effect of iron upon the uranium concentration is shown by the calculated relationship between the Fe/U weight ratio (in the sludge, leach liquor, or diuranate cake) and the iron and uranium concentrations of a pure mixture of $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and $\text{Fe}(\text{OH})_3$ (Fig 1). These theoretical values have been found to compare favorably with the results of the laboratory experiments.

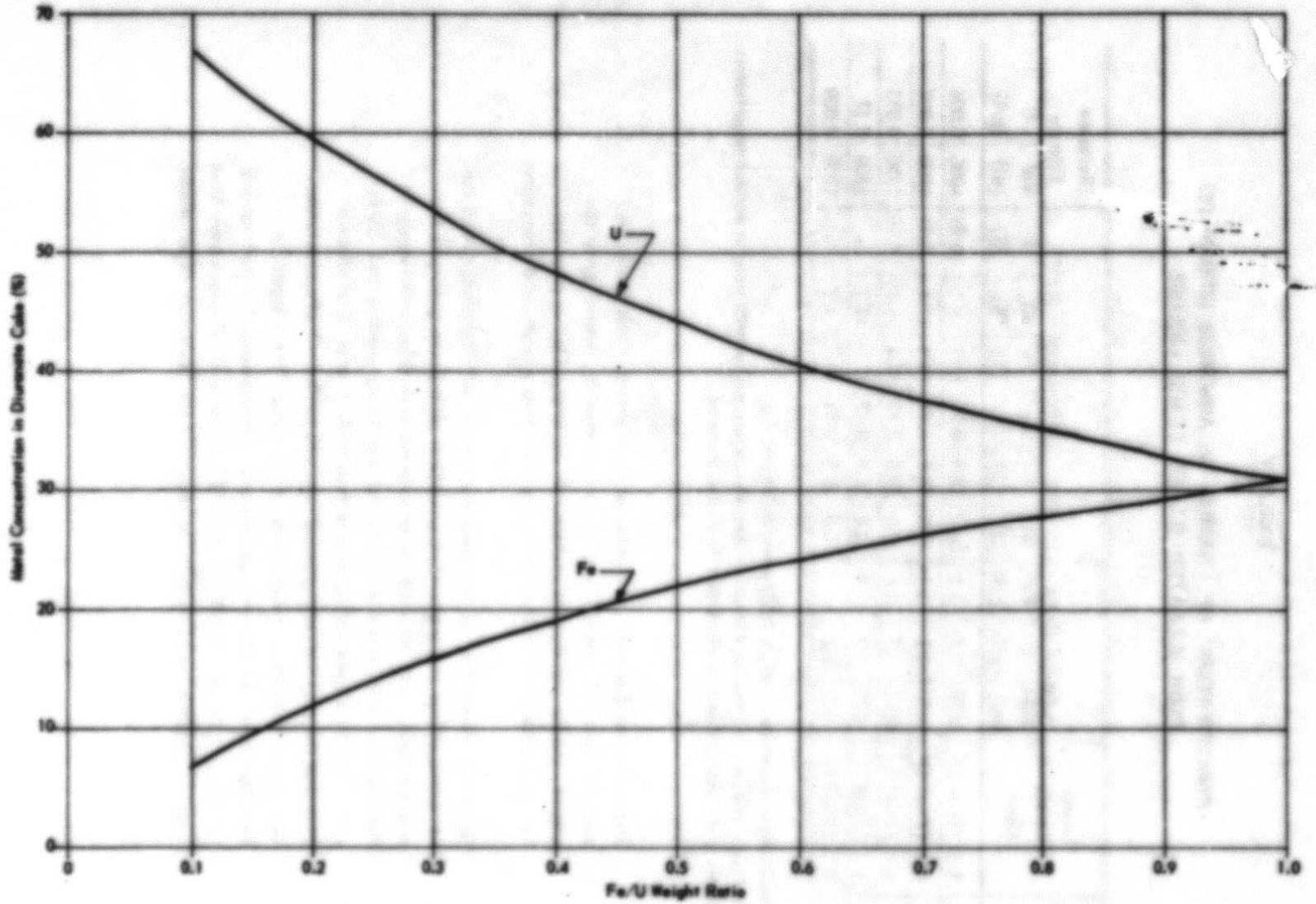


FIGURE 1 Calculated Relationship Between the Fe/U Weight Ratio and the Uranium Concentration of a Pure Mixture of $(\text{NH}_4)_2\text{U}_2\text{O}_7$ and $\text{Fe}(\text{OH})_3$

A schematic flowsheet for the recovery of uranium from sulfated sludge by the ammonia precipitation process is shown in Figure 2. The figures in this flowsheet were based on the following assumptions:

- (a) The sulfated sludge was assumed to result from an HF recovery operation which was 80 per cent efficient and in which a 60 per cent excess of sulfuric acid was used.
- (b) The sulfated sludge sample was assumed to contain 1.2 per cent uranium (3 per cent uranium in the original MgF_2 slag) and a Fe/U weight ratio of 0.5/1.
- (c) The analyses of the product and discard streams from the processing of this material were estimated from the experimental data.
- (d) Processing conditions were established on the basis of the results of the experimental studies.
- (e) Consumption of reagents generally was based on the results of the experimental studies, except for the requirements of ammonium hydroxide which were calculated as the stoichiometric quantity required for complete neutralization of the free sulfuric acid in the sulfated sludge.

2. Phosphate Precipitation (Uranous Phosphate Product)

A study was conducted in the laboratory to investigate the feasibility of recovering uranium from sulfated sludge leach liquors by precipitation as uranous phosphate. The use of this technique has been reported by a number of investigators in connection with the hydrometallurgical processing of several uranium ores.³ The process consists of adjusting the leach liquor to pH 1.5, reducing the solution to +200 to +300 mv (platinum vs. saturated calomel electrode), and precipitating the uranium by the addition of orthophosphoric acid. The resulting uranous phosphate cake is then treated with sodium hydroxide solution to convert the uranium to uranous hydroxide, thereby solubilizing the contained phosphate as Na_2PO_4 .

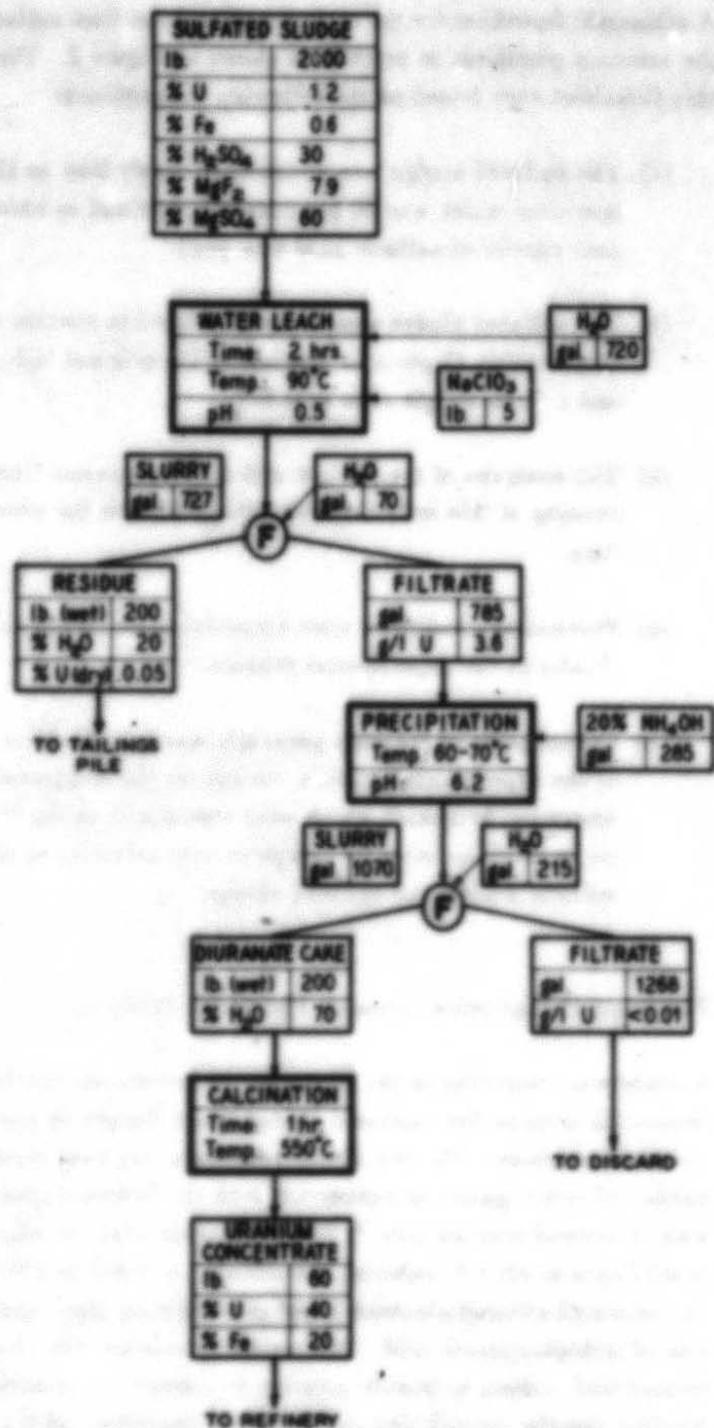


FIGURE 2 Recovery of Uranium from Sulfated Sludge by the Ammonium Hydroxide Precipitation Process (Schematic Flowsheet)

(a) Synthetic Leach Liquors

A series of experiments was conducted using synthetic leach liquors to study the effects of the variables involved in this phosphate precipitation technique. A stock $MgSO_4 - UO_2SO_4$ solution having the following composition was prepared: U, 4.7 g/l; Mg, 60.9 g/l; SO_4 , 257.0 g/l; pH, adjusted to 1.0 with H_2SO_4 .

Effect of pH - A series of experiments was carried out in which NaOH was used to adjust the pH of the solution to values of 1.0, 1.5, and 2.0 (Trials 1, 2, and 3, Table VI). The solutions then were reduced with powdered aluminum to +320 mv at 60°C. The slurry was filtered in order to remove unreacted aluminum, and the reduced filtrate was precipitated with H_3PO_4 (85%) at ambient temperature. The precipitated liquor was agitated for 30 minutes and then filtered. The cake was repulped with hot water, filtered again, and rewashed on the filter with hot water. As can be seen in Trials 1, 2, and 3 in Table VI, little effect was noted due to pH variations. There was good reason to suspect that the high soluble-uranium values noted in Trials 2 and 3 could be attributed to faulty filtration.

Solution Potential - The results of attempts to determine the lower limits of the reduction potential necessary for complete uranium recovery are shown in Trials 4 and 5, Table VI. On the basis of these data, it was concluded that reduction potentials between +200 and +300 mv are required for acceptable uranium precipitation.

Phosphoric Acid Requirements - Investigation of the quantity of H_3PO_4 necessary for complete precipitation of the uranium values (Trials 6, 7, and 8, Table VI) revealed that at least a 1 to 1 weight ratio of 85 per cent H_3PO_4 to uranium was required.

Precipitation Time - Trials 9 and 10 in Table VI show the effect of the holding time of the precipitated slurry (prior to filtration) on the completeness of uranium precipitation. No

significant effect could be noted in the range studied (10 to 20 minutes). It should be pointed out, however, that filtration rates were slower at the shorter hold times.

TABLE VI

PRECIPITATION OF URANIUM AS URANOUS PHOSPHATE
FROM UO_2SO_4 - $MgSO_4$ SOLUTIONS

Trial* No.	Reduction** pH	Solution Potential† (mv)	Vol†† 85% H_3PO_4 (ml)	Precipitation Time‡ (min)	Uranous Phosphate Cake‡‡					Filtrate			
					wt (g)	U (%)	Mg (%)	SO_4 (%)	PO_4 (%)	Vol (ml)	U (g/l)	Mg (g/l)	SO_4 (g/l)
Effect of pH													
1	1.0	+320	5	30	12.6	27.2	5.3	26.1	21.9	600	0.032	61.1	190
2	1.5	+320	5	30	10.5	34.9	3.8	16.9	26.9	560	0.16	64.6	312
3	2.0	+320	5	30	-	32.0	5.1	22.0	22.1	575	0.19	64.6	279
Effect of Solution Potential													
4	1.5	+100	5	30	5.6	44.3	1.7	9.1	33.5	610	1.5	66.6	273
5	1.5	+200	5	30	7.3	49.4	0.9	3.7	36.9	580	0.034	67.0	277
Effect of H_3PO_4													
6	1.5	+420	1	30	4.7	54.8	0.3	7.5	23.8	840	0.59	51.1	204
7	1.5	+420	2	30	6.7	-	0.5	5.3	30.4	740	0.052	53.6	210
8	1.5	+420	3	30	7.5	47.6	0.7	4.2	33.1	650	0.041	62.2	249
Effect of Precipitation Time													
9	1.5	+420	5	10	8.4	41.0	0.4	7.1	32.2	550	0.029	62.4	245
10	1.5	+420	5	20	7.8	46.0	0.5	2.7	35.0	575	0.037	63.3	247

* Volume of stock solution: 750 ml, assay of stock solution: U 4.7 g/l, Mg 60.9 g/l, SO_4 , 257.0 g/l

** Reduction temp: 60° - 70°C, Reducing agent: powdered aluminum

† Platinum vs. saturated calomel electrode.

†† pH readjusted to reduction pH after H_3PO_4 addition

‡ Precipitation temp: 25° - 30°C

‡‡ Uranous phosphate cakes were repulp washed with 250 ml water at 80°C

Effect of Iron - The addition of iron to the stock solutions in Fe/U weight ratios of 0.05, 0.1, 0.2, and 0.4 did not affect the completeness of uranium precipitation, nor did the iron contaminate the resulting uranium concentrate (Table VII).

TABLE VII

THE EFFECT OF IRON TO URANIUM WEIGHT RATIO ON THE PRECIPITATION OF URANIUM AS URANOUS PHOSPHATE FROM $UO_2SO_4 - MgSO_4$ SOLUTIONS

Trial* No.	Fe/U Wt Ratio**	Uranous Phosphate Cake						Filtrate			
		Wt (g)	U (%)	Mg (%)	SO ₄ (%)	PO ₄ (%)	Fe (%)	Vol (ml)	U (g/l)	Mg (g/l)	SO ₄ (g/l)
1	0.05	7.7	45.8	0.56	2.98	38.0	0.05	650	0.013	61.5	253
2	0.10	7.8	44.8	0.60	3.98	37.2	0.06	610	0.019	64.1	267
3	0.20	7.5	47.9	0.25	1.29	39.3	0.08	675	0.021	56.0	238
4	0.40	7.1	48.0	<0.10	0.11	36.5	0.01	660	0.017	58.8	236

- * Stock solution 750 ml, assay of stock solution: U, 4.7 g/l; Mg, 60.9 g/l, SO₄, 257.0 g/l
- ** Fe₂(SO₄)₃ was added to the stock solution to give the desired Fe/U weight ratio. Reduction temp: 60° - 70°C; Reduction pH: 1.5; Reducing agent: powdered aluminum, Solution potential: +300 to +400 mv (Pt vs saturated calomel electrode); Vol 85% H₃PO₄: 5 ml; Precipitation temp: 25° to 30°C; pH readjusted to 1.5 after H₃PO₄ addition; Precipitation time: 30 min; Uranous phosphate cakes were repulp washed with 250 ml water at 80°C.

(b) Sulfated Sludge Leach Liquors

Samples of filtered liquors resulting from the leaching of sulfated sludge samples from Group "A" and Group "B" were (1) adjusted to pH 1.5, (2) reduced at 70°C with powdered aluminum to a potential in excess of +250 mv, and (3) precipitated with 85 per cent H₃PO₄. The resulting cakes were repulped with 10 per cent NaOH for one hour at 90°C to convert the uranium in the uranous phosphate to uranous hydroxide.

The uranous phosphate cake obtained in these runs was very gelatinous and contained about 80 per cent moisture. Prior to treatment with NaOH, this cake had to be washed thoroughly to remove occluded $MgSO_4$, as any magnesium present would precipitate under these highly alkaline conditions. It can be seen in Table VIII that the uranous hydroxide product from those runs in which the uranous phosphate cake was not repulp washed (or washed on the filter after repulping) contained a higher concentration of magnesium and a correspondingly lower uranium assay than did those which were carefully washed. In the case where the uranous phosphate cake was both repulp washed and washed during subsequent filtration of the repulped slurry (Trial 5), a uranous hydroxide cake assaying 66.7 per cent uranium, 3.9 per cent phosphate, and only 2.3 per cent magnesium was obtained.

On occasion, uranium losses in the filtrate from the phosphate precipitation were higher than was desirable. It is expected that further work will indicate that a high recovery can be obtained consistently.

(c) Process Flowsheet

Figure 3 is a schematic flowsheet for the recovery of uranium from sulfated sludge leach liquors by precipitation as uranous phosphate. The figures in this flowsheet were based on the same assumptions used in the preparation of Figure 2 except that the sodium hydroxide requirements for caustic treatment were estimated at an NaOH:U weight ratio of 1.1.

3. Phosphate Precipitation (Uranyl Ammonium Phosphate Product)

A study was conducted in the laboratory to investigate the feasibility of recovering uranium from sulfated sludge leach liquors by (1) precipitation of the uranium as uranyl ammonium phosphate and (2) treatment of the uranyl ammonium phosphate with NaOH to solubilize the phosphate, volatilize the ammonia, and convert the uranium to a sodium diuranate type compound. This technique has been employed previously in the recovery of uranium from C-Oxide and MgF_2 slag.^{2,4}

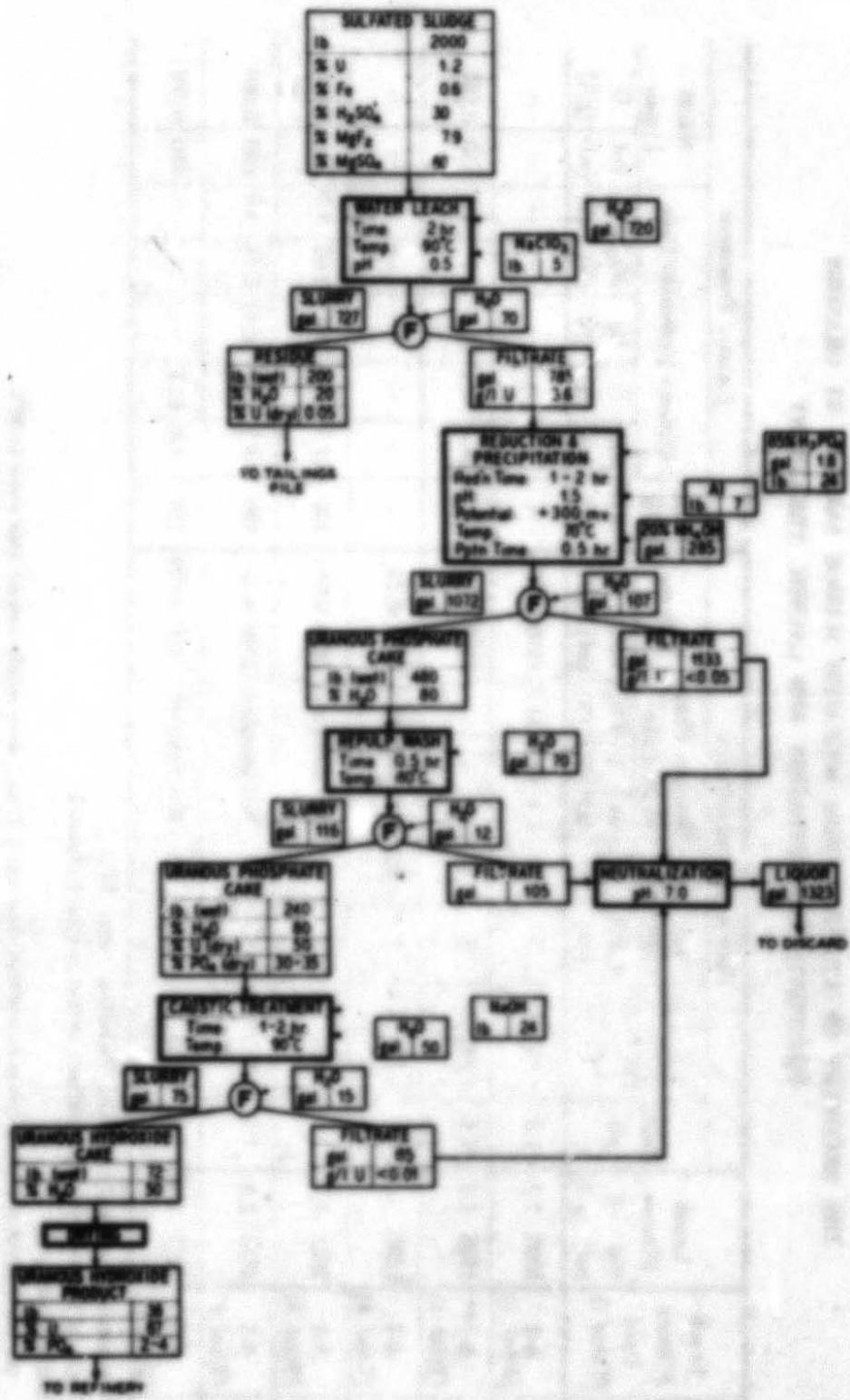


FIGURE 3 Recovery of Uranium from Sulfated Sludge by the Uranous Phosphate Precipitation Process (Schematic Flow-sheet)

TABLE VIII

**THE RECOVERY OF URANIUM FROM SULFATED SLUDGE SAMPLES BY URANOUS
PHOSPHATE PRECIPITATION AND CAUSTIC TREATMENT**

Trial No.	Leach Filtrate Used (Table I)	Leach Filtrate Vol U (ml) (g/l)	Phosphate Precipitation										Caustic Treatment									
			Red'n pH	Soln. Pot. * (mv)	Wt Al (g)	Vol 85% H ₃ PO ₄ (ml)	Pptn Time (min)	Uranous Phosphate Cake†			Filtrate		Vol 10% NaOH (ml)	Uranous Hydroxide Cake					NaOH Liquor			
								Wt (g)	U (%)	PO ₄ (%)	Vol (ml)	U (g/l)		Wt (g)	U (%)	Mg (%)	SO ₄ (%)	PO ₄ (%)	Vol (ml)	U (g/l)		
1	A-1 (Trial 1)	1000 3.2	1.5	+330	2	5	30	5.3	47.8	34.7	1310	0.053	-	-	-	-	-	-	-	-	-	-
2	A-1** (Trial 1)	2500 3.2	1.5	+290	5	5	15	-	-	-	3150	0.12	500	24.2	30.1	18.7	2.7	2.3	830	0.007		
3††	A-1 (Trial 4)	2200 -	0.3	+270	3.4	5	30	9.5	51.6	31.5	3575	0.23	-	-	-	-	-	-	-	-	-	
4	A-1 (Trial 5)	2525 2.7	1.5	+320	3.5	5	30	Not Sampled			2450	0.043	500	11.7	57.6	4.7	0.62	3.7	760	0.002		
5	A-1 (Trial 6)	2525 2.8	1.5	+350	3.5	5	30	Not Sampled			2300	0.12	500	9.7	66.7	2.32	0.71	3.9	660	0.001		
6	B-1 (Trial 7)	675 1.9	1.5	+370	2	2	30	Not Sampled			750	0.028	150	3.0	41.8	-	-	-	280	0.002		

* Pt vs saturated calomel electrode. Reduction temp: 70°C

** Liquor for this trial prepared similarly to that in Trial 1, Table I.

† Washing Conditions:

- (a) All uranous phosphate cakes except that obtained in Trial 2 were repulp washed with water at 80°C.
- (b) All uranous phosphate cakes except those obtained in Trials 2 and 4 were washed on the filter after repulp washing.
- (c) Uranous hydroxide cakes were washed on the filter with water at ambient temperatures.

†† In trial 3, the reduction was conducted in the leach slurry.

(a) Synthetic Leach Liquors

A series of experiments was conducted using synthetic leach liquors to study the effect of the variables involved in the precipitation of uranyl ammonium phosphate (UA⁺). A stock $MgSO_4 - UO_2SO_4$ solution was prepared which has the following composition. U, 4.4 g/l; Mg, 52 g/l; SO_4 , 246 g/l; pH, 0.5.

Effect of pH and PO_4 :U Weight Ratio - A series of experiments was carried out in which solutions containing PO_4 :U weight ratios of 0.5, 1.0, and 1.5 were adjusted to pH 1.5, 2.0, and 2.5 with NH_4OH (Table IX). The precipitated liquors were agitated for 30 minutes and filtered, and the resulting cakes were washed on the filter. It was found that a PO_4 :U weight ratio of approximately 1:1 and a precipitation pH of at least 2.0 were necessary to insure quantitative precipitation of the uranium. It was observed that filtration characteristics of the precipitated slurries were greatly improved by the use of a flocculating agent (Cyanamid S 3000).

Effect of Iron - A series of experiments was conducted in which iron was added (as $Fe_2(SO_4)_3$) to synthetic leach solutions to produce Fe:U weight ratios of approximately 0.25, 0.50, and 1.0 (Table X). Quantities of H_3PO_4 used were sufficient to produce a PO_4 :U weight ratio of 1:1 plus the calculated requirements for the formation of $FePO_4$. It was found that for solutions containing iron, precipitation must be carried out at a slightly higher pH (2.5) to insure quantitative precipitation of the uranium. It was also found that the iron present in the leach solutions coprecipitated (presumably as $FePO_4$) with the uranium.

Effect of Caustic Treatment - Samples of phosphate cakes that had been precipitated from solutions containing no iron and from solutions containing a Fe:U weight ratio of 0.5 were slurried with 5 per cent solutions of NaOH. It was found (Table XI) that treatment of the phosphate cake obtained from liquors containing no iron produced a soda salt product which assayed about 64 per cent uranium and 6.6 per cent phosphate, whereas, treatment of phosphate cake obtained from liquors having Fe:U weight ratio of 0.5 produced a soda salt product which assayed about 37 per cent uranium, 10 per cent phosphate, and 18 per cent iron. It was

observed that uranium losses in the caustic filtrates were higher in the cases where iron was present in the UAP.

TABLE IX

PRECIPITATION OF URANIUM AS URANYL AMMONIUM PHOSPHATE FROM $UO_2SO_4 - MgSO_4$ SOLUTIONS

Trial [*] No.	H_3PO_4 (ml)	PO_4 :U Weight Ratio	28% NH_4OH (ml)	Precip. ^{**} pH	Filtrate			Cake [†]				
					Vol (ml)	U (g/l)	PO_4 (g/l)	Wt (g)	U (%)	PO_4 (%)	Mg (%)	SO_4 (%)
1	4.7	1.5	45	1.5	1180	0.59	3.4	-	55.8	23.5	0.51	2.01
2	4.7	1.5	53	2.0	1190	0.012	3.2	-	58.5	24.7	0.17	0.11
3	4.7	1.5	58	2.5	1300	0.004	3.5	-	58.4	25.3	0.2	0.11
4	3.2	1.0	40	1.5	1270	3.6	-	-	56.9	-	-	-
5	3.2	1.0	50	2.0	1280	0.042	2.9	8.3	58.0	24.3	0.14	0.08
6	3.2	1.0	56	2.5	1330	0.022	1.8	8.4	58.0	24.6	0.25	0.30
7	1.6	0.5	41	1.5	1260	3.1	0.6	-	52.0	-	-	-
8	1.6	0.5	51	2.0	1260	1.6	0.3	5.6	52.9	21.4	0.19	0.07
9	1.6	0.5	57	2.5	1270	0.046	0.2	9.4	52.8	22.2	0.24	0.09

* Vol stock solution used: 1000 ml. Assay of stock solution: U, 4.4 g/l; Mg, 52 g/l; SO_4 , 246 g/l; pH, 0.5.

** Precipitation temp: 40°C. Precipitation time: 30 min.

† Precipitated cakes washed with 200 ml H_2O .

TABLE X

THE EFFECT OF IRON ON THE PRECIPITATION OF URANYL AMMONIUM PHOSPHATE FROM UO_2SO_4 - $MgSO_4$ SOLUTIONS

Trial ^a No.	H_2PO_4 (ml)	$PO_4:U$ Weight Ratio	$Fe:U^{**}$ Weight Ratio	28S NH_4OH (ml)	Precip. [†] pH	Filtrate				Cake ^{††}					
						Vol (ml)	U (g/l)	PO_4 (g/l)	Fe (g/l)	Wt (g)	U (%)	PO_4 (%)	Mg (%)	SO_4 (%)	Fe (%)
1	4.8	1	0.25	51	2.0	1180	0.75	3.6	-	8.6	46.0	30.6	0.30	1.99	6.0
2	6.4	1	0.50	54	2.0	1200	0.54	4.0	-	11.4	37.1	34.9	0.21	1.95	10.7
3	9.6	1	1.0	65	2.0	1200	0.75	3.9	-	20.5	20.0	42.7	0.47	4.84	16.4
4	6.4	1	0.5	63	2.5	1270	0.028	1.9	0.05	16.8	32.2	38.7	0.12	1.65	11.2

^a Stock solution for each trial was 1000 ml. Assay of the stock solution: U, 4.4 g/l; Mg, 52 g/l; SO_4 , 246 g/l; pH 0.5.

^{**} Fe was added to stock solution as $Fe_2(SO_4)_3$.

[†] Precipitation temp: 40°C. Precipitation time: 30 min.

^{††} Precipitated cakes washed with 200 ml H_2O .

[‡] $PO_4:U$ ratio employed was a 1:1 ratio plus the calculated phosphate requirements for the formation of $FePO_4$.

TABLE XI

CAUSTIC TREATMENT OF URANYL AMMONIUM PHOSPHATE OBTAINED FROM SYNTHETIC SULFATED SLUDGE LEACH LIQUORS

Trial* No.	Precipitation									Caustic Treatment [‡]								
	H ₂ PO ₄ (ml)	PO ₄ :U Wt Ratio	Fe:U [†] Wt Ratio	28% NH ₄ OH (ml)	Ppta ^{††} pH	Filtrate				Vol ^{‡‡} 75% NaOH (ml)	Cake						Filtrate	
						Vol (ml)	U (g/l)	PO ₄ (g/l)	Fe (g/l)		Wt (g)	U (%)	PO ₄ (%)	Fe (%)	SO ₄ (%)	Mg (%)	Vol (ml)	U (g/l)
1	3.2	1.0	0	54	2.5	1300	0.005	1.7	-	88	7.6	64.7	6.7	-	0.31	0.30	225	0.041
2	3.2	1.0	0	55	2.5	1325	0.005	1.7	-	88	7.6	63.5	6.5	-	0.21	0.18	250	0.045
3	6.4	**	0.5	65	2.5	1280	0.024	1.7	0.04	188	13.5	33.9	12.9	17.0	0.12	3.99	400	0.92
4	6.4	**	0.5	68	2.5	1270	0.032	1.8	0.05	188	11.2	41.0	8.2	19.1	0.13	0.33	370	0.11

* Stock solution for each trial: 1000 ml. Assay of stock solution: U, 4.4 g/l; Mg, 52 g/l; SO₄, 246 g/l, pH, 0.5.

** PO₄:U ratio employed was a 1:1 ratio plus the calculated phosphate requirements for the formation FePO₄.

† Fe added to stock solution as Fe₂(SO₄)₃.

†† Precipitation temp: 40°C; Precipitation time: 30 min; Precipitated cakes washed with 200 ml H₂O

‡ Caustic treatment temp: 30°C. Caustic treatment time: 30 min. Cakes from caustic treatment washed with ~150 ml H₂O

‡‡ Vol of NaOH was sufficient to produce a 1:1 wt ratio of NaOH:U plus the calculated requirements for converting the PO₄ present as FePO₄ to the more soluble form, Na₂PO₄.

(b) Sulfated Sludge Leach Liquors

A composite sample of sulfated sludge from Group "A" (A-2) was water leached and filtered to produce a leach liquor for a precipitation test. This liquor contained 1.5 g/l uranium, 0.3 g/l iron, 3.9 g/l nickel, 22 g/l magnesium, and 187 g/l sulfate. The filtered liquor was precipitated at pH 2.5 with NH_4OH and H_3PO_4 . The resulting precipitated cake assayed 39.6 per cent uranium, 6.1 per cent iron, 30.3 per cent phosphate, and 0.3 per cent nickel.

(c) Process Flowsheet

A schematic flowsheet for the recovery of uranium from sulfated sludge leach liquors by precipitation as uranyl ammonium phosphate has been included in Figure 4. The figures in this flowsheet were based on the same assumptions used in the preparation of Figure 4.

(d) Peroxide Precipitation (Peruranic Acid Product)

A number of investigators have used hydrogen peroxide for the precipitation of uranium in various applications. This procedure offers the advantage of producing a uranium concentrate (peruranic acid) of high purity, as the precipitation is effected at a sufficiently high acidity (pH 2.0 to 3.0) to preclude the separation of other metals. Carbide and Carbon (Y-12) has precipitated peruranic acid from nitric acid liquors of sufficient purity for fluorination. The Vitro Rare Metals Company experimented with this technique in connection with the processing of wastes having a high fluoride content and found that the fluoride did not precipitate appreciably at the low pH.⁵

The duPont Company studied the use of peroxide precipitation during their investigation of uranium recovery from a sulfated sludge resulting from the reaction of MgF_2 slag and sulfuric acid and found it to be the most satisfactory method for recovering uranium from sulfated sludge leach liquors.⁶ However, duPont maintained high uranium concentrations in the leach liquors by leaching other high-grade scrap materials simultaneously with the sulfated sludge.

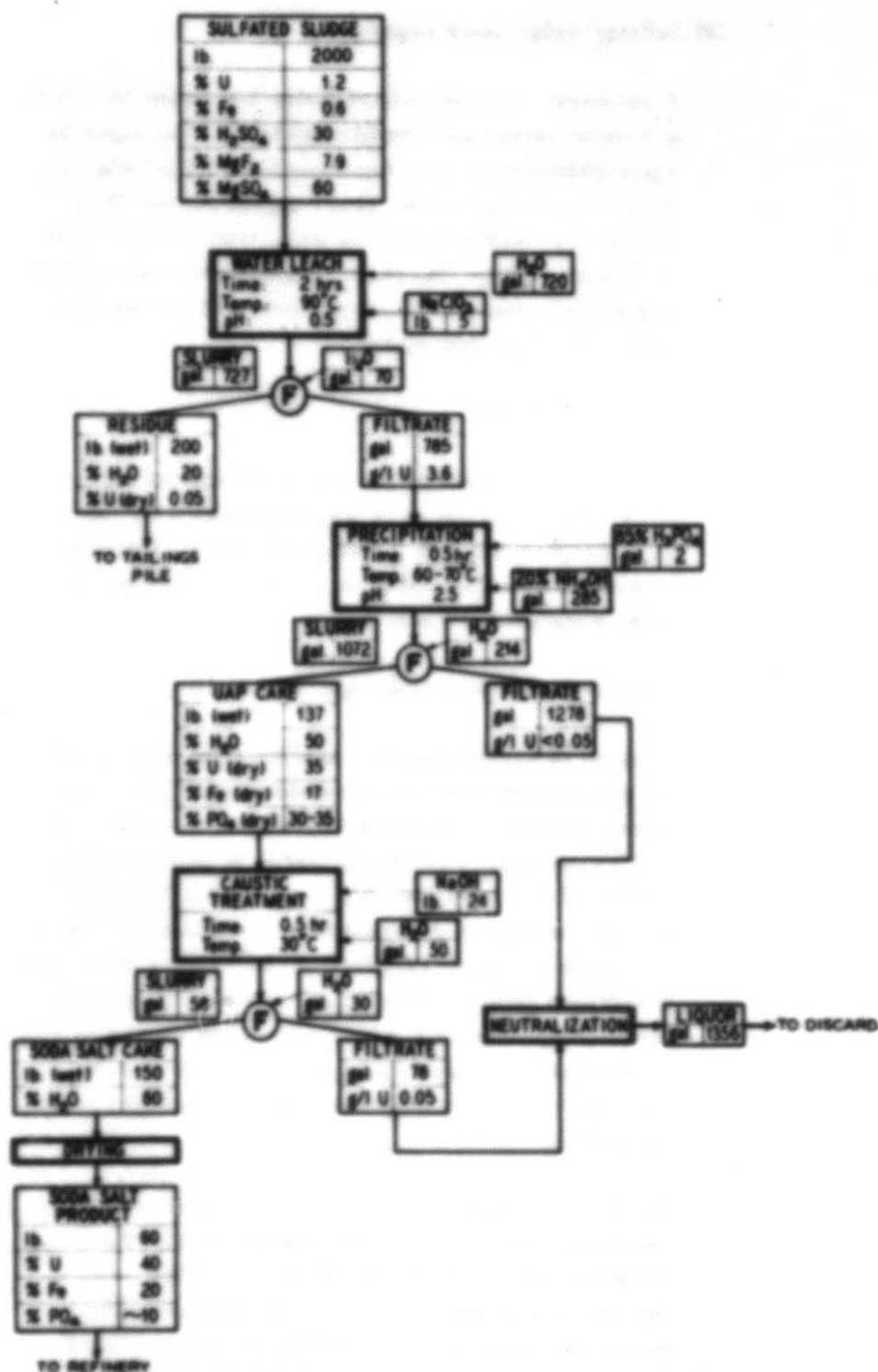


FIGURE 4 Recovery of Uranium from Sulfated Sludge by the Uranyl Ammonium Phosphate Precipitation Process (Schematic Flowsheet)

The reported disadvantages of peroxide precipitation include (1) slow quantitative precipitation, (2) the fineness of the precipitate, (3) the interference of high salt concentrations with precipitation, and (4) poor recovery in the presence of iron (due to decomposition of the peroxide).

Several attempts to recover the uranium present in synthetic sludge leach liquors by peroxide precipitation (Trials 1 and 2, Table XII) were made in the laboratory. Leach liquors containing 4 to 5 g/l U, 4 to 5 g/l Fe, and 230 to 280 g/l SO_4 were adjusted to pH 2.5 to 3.0 with NaOH, 30 per cent H_2O_2 was added, and the mixture was allowed to agitate for periods up to 44 hours. These trials were accompanied by substantial uranium losses in the resulting filtrates.

An attempt was made to make a preliminary precipitation of iron from the leach liquor (Trials 3 and 4, Table XII). Samples of liquor were adjusted to pH 3.0 to 4.0, using CaCO_3 at 90°C . After filtration, peroxide was added to the resulting liquor and the mixture was allowed to agitate for 18 hours. This technique was successful in recovering all of the uranium from the leach liquor in the form of a concentrate assaying 66 to 69 per cent uranium, but the residue obtained from the CaCO_3 treatment (the intermediate cake) contained an appreciable concentration of uranium even after exhaustive washing with water. An attempt was made to reduce this uranium loss by reducing the quantity of CaCO_3 used. This was successful in reducing the weight of the residue, but its uranium content was slightly higher. More peroxide was required in order to precipitate the uranium from the resulting liquor. This was probably due to the incomplete precipitation of iron at pH 3.0.

TABLE XII

**PRECIPITATION OF URANIUM FROM SYNTHETIC SULFATED
SLUDGE LEACH LIQUORS USING HYDROGEN PEROXIDE**

Trial No.	pH Adjustment							Peroxide Precipitation											
	Head Solution				Adjusted to pH	Reagent	Intermediate						Vol 30% H ₂ O ₂ (ml)	Pptn Time (hr)	Pptn Temp (°C)	UO ₂ Cake		Filtrate	
	Vol (ml)	U (g/l)	SO ₄ (g/l)	Fe (g/l)			Cake		Filtrate							Wt (g)	U (%)	Vol (ml)	U (g/l)
					Wt (g)	U (%)	Vol (ml)	U (g/l)	SO ₄ (g/l)	Fe (g/l)									
1	1000	5.3	277	~6	2.5	NaOH	4.5	20.1	1010	-	-	-	65	20	27	-	-	-	2.63*
2	1000	3.7	231	~4	3.0	NaOH	No						40	44	27	-	-	-	0.78*
3	2000	3.9	173	3.0	3.5 -	CaCO ₃	66.0	0.69	1590	3.9	142	0.013	40	18	40	4.0	68.9	1240	0.004
3a**					4.0								40	17	40	4.3	66.3	1240	0.010
4	1000	3.7	173	3.0	3.0	CaCO ₃	31.4	0.88	800	4.2	138	0.004	40	19	40	1.4	-	830	3.1
4a†													60	8	40	3.4	69.0	975	0.004

- * The supernatant liquor from the peroxide precipitation was not clear after centrifuging for one hour. Weights of cake were not determined.
 ** 3.7 g (NH₄)₂SO₄ was added to half of the intermediate filtrate from Trial 3 in order to increase the filterability of the peroxide precipitate.
 † The filtrate from the peroxide precipitation step in Trial 4 was treated with additional peroxide in Trial 4a.

CONCLUSIONS

Samples of sulfated sludge (resulting from the treatment of MgF_2 slag with H_2SO_4 for HF recovery) have been examined in the laboratory. It was found that 97 to 98 per cent of the uranium in these sludges could be solubilized by a water leach in the presence of an oxidant. The resulting leach liquors contained less than 0.5 g/l fluoride.

Recovery of uranium from the leach liquors was effected adequately by precipitation (1) as an ammonium diuranate type product at pH 6.0 by the addition of NH_4OH , (2) as uranous phosphate at pH 1.5 by the use of phosphoric acid and aluminum, or (3) as uranyl ammonium phosphate at pH 2.5 by the addition of phosphoric acid and NH_4OH . In the latter two cases, the uranium was converted subsequently to uranous hydroxide and sodium diuranate, respectively, by treatment with a caustic solution. Precipitation of the uranium contained in these leach liquors, either as an ammonium diuranate or a uranyl ammonium phosphate type compound, was accompanied by the coprecipitation of iron. This effected a significant product adulteration. However, iron coprecipitation was negligible when the uranium was precipitated as uranous phosphate from reduced leach liquors, as the solubility of ferrous phosphate is significantly higher than that of the oxidized form. The uranous phosphate cake assayed 45 to 55 per cent uranium and 30 to 35 per cent phosphate. Slurrying this cake with a solution of sodium hydroxide resulted in a uranium concentrate which assayed 67 per cent uranium and 4 per cent phosphate. In all three processes, the excess acidity present in sulfated sludge samples required large quantities of reagent for neutralization.

Precipitation of uranium from synthetic sludge leach liquors with hydrogen peroxide was not consistently successful in quantitatively recovering the uranium values.

ACKNOWLEDGMENTS

The authors would like to acknowledge the contributions made to this study by B. Geislers, E. Brown, A. B. Kreuzmann, and B. C. Doumas.

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