PRECIPITATION OF MOLYBDENUM FROM ION EXCHANGE FEEDS BY
NEUTRALIZATION IN THE PRESENCE OF IRON

By

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November 15, 1956

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ABSTRACT

The removal of molybdenum from acid leach liquors by neutralization in the presence of iron has been evaluated as a method of decreasing the concentration of molybdenum to a tolerable level in ion exchange feeds. Such variables as acid concentration, iron to molybdenum ratio, temperature, and concentration of silicate and aluminum in the leach liquor were examined in order to develop the optimum conditions for the precipitation of molybdenum.

The precipitation procedure was tested on leach liquors from Ambrosia Lake District ore and from several lignite ores. Leaching tests made on lignite ores indicate that iron and molybdenum can be precipitated during the leaching by suitable control of the acidity.

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INTRODUCTION

Molybdate is known (1, 2, 3) to be a serious interference in the recovery of uranium from acid leach liquors by ion exchange. Molybdenum is strongly adsorbed by anion exchange resins along with the uranium during the loading cycle, but is not removed from the resin in the normal elution procedure for uranium. This behavior results in an accumulation of molybdenum on the resin which leads to a decrease in the adsorption rate of uranium and ultimately to a decrease in the resin capacity.

Formerly, a periodic regeneration of the resin with 6 per cent sodium hydroxide was used to remove the molybdenum (2); more recently, it has been shown that a solution containing 0.5 per cent sodium hydroxide and 0.1 molar chloride or nitrate will effectively elute the molybdenum from the resin (3). Nevertheless, because of the effect of molybdenum on the rate of adsorption of uranium, a more satisfactory solution to the problem would be the removal of the molybdenum from the liquor before ion exchange.

Since it is known that at the Union Miniere du Haut-Katanga in the Belgian Congo the neutralization of acid leach liquors to a pH of 2.8 resulted in the precipitation of ferric iron and molybdenum, an investigation of this method of molybdenum removal was initiated. The purpose of this investigation was to study some of the factors which effect the precipitation of molybdenum with ferric iron and to apply the information toward the development of methods for the removal of molybdenum from acid leach liquors prior to the recovery of uranium by ion exchange.

SUMMARY

The removal of molybdenum from acid liquors by neutralization in the presence of ferric iron is governed by a number of interrelated variables. As the acidity of a solution containing molybdenum and iron is decreased, increasing amounts of molybdenum and iron are precipitated. If the molar ratio of iron to molybdenum is less than 8 to 1, some molybdenum remains in solution even at pH 3.6. However, very excellent precipitation can be made at somewhat lower molar ratios. Also, as the concentration of iron is increased, quantitative removal of molybdenum is achieved at lower pH's. Increasing the temperature of the solution results in more complete removal of molybdenum and iron at any particular acid and iron concentration.

The removal of molybdenum by this technique is more difficult if the molybdenum has been complexed in solution by silicate to form molybdosilicic acid or by aluminum to form some type of aluminum-molybdenum complex. Each of these obstacles can be greatly diminished by increasing the temperature at which the precipitation is made. Also, a high concentration of aluminum increases the amount of calcium carbonate required for neutralization and tends to retard the precipitation of the iron and molybdenum.

No definite composition can be assigned to the iron-molybdenum precipitate since its composition varies with acidity and the iron to molybdenum ratio.

Some uranium is removed from solution during the precipitation of iron and molybdenum. The amount of uranium coprecipitated increases with the iron content of the solution and the pH at which the precipitation is made, but is relatively independent of the uranium concentration. Increasing the temperature at which the precipitation is made decreases the amount of uranium removed from solution. The uranium in the iron-molybdenum precipitate can be almost completely recovered by an acid repulp of the precipitate with only small amounts of iron and molybdenum being redissolved at the proper conditions of acidity.

Cyclic tests involving leaching, precipitation of molybdenum, and repulp of the precipitate in the succeeding leach pulp subsequent to the strong acid leach were made. During a test of seven such cycles on leach liquor from a sample of ore from the Ambrosia Lake District, the ferric iron concentration increased from 0.5 to 2.1 grams per liter and the molybdenum concentration increased from 0.047 to 0.083 grams per liter. The precipitate at the end of the seventh cycle contained only 0.2 per cent of the total amount of uranium in the ore.

The molybdenum concentration of leach liquors from Edgemont, Farmington, and Northgate lignite was reduced to a level of 1 to 2 ppm by the precipitation technique. However, in leach liquors prepared from Bryco and Peter Kiewit lignite, the molybdenum concentration was reduced only to 10 to 20 ppm. A series of cyclic tests made on leach liquor prepared from Bryco lignite indicated that there is no iron and molybdenum buildup in the liquor, but a very substantial buildup of the aluminum concentration takes place. The amount of calcium carbonate required to neutralize the leach liquors increased from 380 to 650 lbs per ton of ash over four cycles, and therefore this type of process would not be practical for this ore because of excessive reagent costs.

The possibility of controlling the amounts of molybdenum present in acid leach filtrates through control of the leaching conditions was studied. Test work conducted on several lignite ore samples indicated that leach liquors relatively free of molybdenum can be produced through the use of a relatively high pH leach. A two-stage leaching procedure with close control of acidity and temperature at each stage is suggested as the best method of producing a low molybdenum pregnant solution from lignites.

APPARATUS AND REAGENTS

The following reagents were used in preparing the solutions used for the test work presented in this report.

Ammonium Molybdate - Baker & Adamson Reagent Grade
Uranyl Sulfate - Fisher Scientific Company
Ferric Sulfate (Crystals) - Fisher Scientific Company
Aluminum Sulfate - Baker & Adamson Reagent Grade
Sodium Metasilicate - Baker & Adamson Reagent Grade

All solutions were prepared using distilled water received from the Belmont Springs Water Company. Solutions of ammonium molybdate were stored in polyethylene bottles.

Measurements of pH were made using a battery operated Beckman Model N pH meter.

Precipitations were made in the following manner: calcium carbonate was added to the solution until precipitation began; this resulted in a drop in the pH; the final pH was then adjusted by addition of calcium carbonate until the pH of the solution remained constant for 10 to 15 minutes at the desired value.

For the purposes of this report, any precipitation which leaves only 0.001 gram of molybdenum per liter or less remaining in solution will be referred to as "a complete precipitation of molybdenum."

VARIABLES IN THE PRECIPITATION OF IRON AND MOLYBDENUMAcid Concentration

In order to test the effect of acid concentration or pH on the precipitation of molybdenum by ferric iron, a solution containing 0.05M ferric iron and 0.025M molybdenum was prepared. The pH of this solution was raised from 1.0 to 9.0 by the addition of lime. Samples were taken periodically over the entire pH range, filtered and analyzed for iron and molybdenum. Results of this test are shown in Table I.* These results show that increasing amounts of molybdenum and iron are precipitated as the pH is raised up to a value of 3.8; at this point all the iron is precipitated, but some molybdenum remains in solution. Maximum precipitation of the molybdenum is obtained in the pH range of 3.4 to 3.8. Raising the pH above this level resulted in some of the precipitated molybdenum being redissolved.

Iron to Molybdenum Ratio

When the pH of a solution containing 0.05M ferric iron and 0.025M molybdenum was raised to 3.4 to 3.8 about 99 per cent of the molybdenum was precipitated. In order to determine what molar ratio of ferric iron to molybdenum must be present in solution in order to effect complete precipitation of the molybdenum, precipitations were made at pH 3.6 from solutions containing ferric iron and molybdenum in various ratios. Results of these tests are presented below in Table II.

Table II. The Effect of the Molar Ratio of Iron to Molybdenum on the Precipitation of Molybdenum

<u>Molar Ratio,</u> <u>Fe/Mo</u>	<u>Head Solution</u> <u>Grams/Liter</u>		<u>Filtrate Assay</u> <u>Grams/Liter</u>	
	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>
1/4	1.40	9.60	0.23	2.54
1/2	1.40	4.80	0.015	0.06
1/1	1.40	2.40	0.008	0.02
2/1	1.40	1.20	0.005	0.009
4/1	1.40	0.60	0.005	0.002
8/1	1.40	0.30	0.003	0.001
16/1	1.40	0.15	0.004	0.001

* The large tables are presented at the end of the report.

These results show that an 8/1 molar ratio of ferric iron to molybdenum is sufficient to effect complete precipitation of the molybdenum at pH 3.6. However, very excellent precipitation can be made at somewhat lower ratios of iron to molybdenum. Ninety-nine per cent of the molybdenum was precipitated from a solution which contained an equimolar ratio of iron and molybdenum.

In order to study the effect of iron concentration on the pH at which the precipitation of molybdenum occurs, a series of tests were made on solutions containing 1.0 gram Mo per liter and from 2.0 to 20 grams of Fe^{+++} per liter. Precipitations were made in these solutions at pH values of 2.4, 2.6, 2.8, 3.0, 3.2, 3.4, and 3.6 by the addition of calcium carbonate to adjust the pH. Data from these tests are presented in Table III. It can be seen that as the concentration of iron in solution increases, the pH of complete molybdenum precipitation decreases. However, this effect is not too marked since a tenfold increase in iron concentration from 2.0 to 20 grams per liter resulted in a decrease in the pH required for complete precipitation from 3.6 to 3.0.

Temperature

In order to test the effect of temperature on the precipitation of molybdenum along with iron as the pH of an acid leach liquor is increased, a series of tests were made on solutions containing 1.0 gram Mo per liter and 5.0 grams Fe^{+++} per liter. Precipitations from these solutions were made at a number of pH values at 25, 50, 75 and 100°C. The results of these tests are presented in Table IV. A comparison of the results indicates that as the temperature increases, the pH at which complete molybdenum precipitation takes place decreases. It also appears that increasing the temperature causes more efficient precipitation of the molybdenum with iron.

Silicate Concentration

During the preliminary test work with iron and molybdenum solutions, considerable interference was encountered in precipitating the molybdenum because of the presence of dissolved silicate in the de-ionized water. It is well known that molybdenum and silicate combine in solution to form molybdosilicic acid. To evaluate the effect of the presence of silicate on the precipitation of molybdenum, a number of tests were performed. A solution containing 1.0 gram SiO_2 per liter as silicate, 1.0 gram Mo per liter, and 5.0 grams Fe^{+++} per liter was prepared by mixing the ferric iron and molybdenum prior to the addition of the silicate. From

this solution, all of the molybdenum was precipitated at a pH of 3.5. If, however, the solution was prepared by mixing the silicate and molybdenum, acidifying, and then adding the ferric iron, precipitation at a pH of 3.5 showed only 48 per cent of the molybdenum was removed. This would indicate that some of the molybdenum was complexed as molybdosilicic acid.

To test the effect of temperature on the molybdosilicic acid complex, a solution was prepared by mixing the molybdenum and silicate, acidifying, and adding ferric iron. Precipitations were made from this solution at ambient temperature, 50, 75 and 100°C by adjusting the pH to a value at which complete precipitation of the molybdenum could be expected. Results of these tests are presented below in Table V.

Table V. Effect of Temperature on Precipitation of Molybdenum Complexed as Molybdosilicic Acid

Head Solution Assay: SiO₂, 1.0 g/l; Mo, 1.0 g/l; Fe⁺⁺⁺ = 5.0 g/l.

T°C	pH	<u>Filtrate Assay</u>		<u>% Precipitated</u>	
		<u>Grams/Liter</u>			
		<u>Fe⁺⁺⁺</u>	<u>Mo</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>
Amb	3.7	0.001	0.52	99.9	48.0
50	3.1	0.010	0.36	99.8	64.0
75	3.0	0.023	0.16	99.5	84.0
100	2.7	0.008	0.004	99.9	99.6

These tests indicate that heating of the solution breaks down the complex ion and aids in the precipitation of molybdenum.

Aluminum Concentration

During the test work done on the application of this procedure for removing molybdenum from lignite leach liquors, it was found that the presence of substantial amounts of aluminum hindered the precipitation of molybdenum and iron. Therefore, in order to test this effect in pure solutions, a series of precipitations were made at pH values of 3.5, 3.8, and 4.1 from solutions containing 1.0 gram Mo per liter, 5.0 grams Fe⁺⁺⁺ per liter and various amounts of aluminum. The amounts of calcium carbonate used for precipitation were measured. The data are reported in Table VI.

These results indicate that the presence of aluminum in solution retards the precipitation of iron and molybdenum and increases the amount of calcium carbonate needed for neutralization. The larger the concentration of aluminum in solution, the greater the extent to which the precipitation is retarded and the larger the amount of calcium carbonate which is required in order to make the precipitation. Previous results indicated that when 5.0 grams of Fe^{+++} per liter is present in solution, complete precipitation of the molybdenum could be made at a pH of 3.4 with 12 grams CaCO_3 per liter of solution. However, when 4.0 grams Al_2O_3 per liter was present in this solution, 0.017 gram Mo per liter and 0.13 gram Fe^{+++} per liter remained in solution even at a pH of 3.5. By raising the pH to 4.1, it is possible to precipitate 99.8 per cent of the molybdenum and 99.9 per cent of the iron; but in so doing about 95 per cent of the aluminum is also precipitated and the calcium carbonate requirement is increased almost threefold to 33.0 grams CaCO_3 per liter of solution. This precipitation of aluminum along with the iron and molybdenum results in greater reagent costs for both neutralization of the liquor and repulping of the precipitate, and also presents the problem of a buildup of this constituent if a recycling procedure is used.

During this investigation involving the effect of aluminum, the possible existence of a molybdenum-aluminum complex was encountered. When aluminum and molybdenum were mixed in solution prior to the addition of the ferric iron, the molybdenum was only partially precipitated with the ferric iron; while when the iron and molybdenum were mixed in solution prior to the addition of aluminum, the molybdenum was completely precipitated with the ferric iron. This leads to the belief that molybdenum and iron form a complex ion in solution and that this formation must take place for the molybdenum to be precipitated with the ferric iron. If some of the molybdenum in solution complexes with some other ion or ions other than ferric ions, as in the presence of aluminum or silicate, then it would not be precipitated.

In order to test the effect of temperature on this possible aluminum-molybdenum complex, a solution was prepared by mixing the aluminum and molybdenum first and then adding ferric iron. The solution contained 1.0 gram Mo per liter, 18 grams Al_2O_3 per liter and 5.0 grams Fe^{+++} per liter. Precipitations were made at ambient temperature, 50 and 100°C. The results of these tests are presented below in Table VII.

Table VII. Effect of Temperature on Molybdenum-Aluminum Complex

Head Assay: Al_2O_3 , 18 g/l; Mo, 1.0 g/l; Fe^{+++} , 5.0 g/l

T°C	pH	<u>Filtrate Assay</u> - Grams/Liter			<u>% Precipitated</u>		
		Al_2O_3	Fe^{+++}	Mo	Al_2O_3	Fe^{+++}	Mo
A	4.1	0.60	0.004	0.64	96.7	99.9	36.0
50	3.6	0.20	0.006	0.028	98.9	99.9	97.2
100	3.0	0.40	0.007	0.007	97.8	99.9	99.3

It appears that increasing the temperature breaks down the aluminum-molybdenum complex and aids in the formation of the iron-molybdenum precipitate. This is indicated by the fact that at 100°C all but 0.7 per cent of the molybdenum was precipitated, in contrast to only 36 per cent of the molybdenum being precipitated at ambient temperature.

COMPOSITION OF THE PRECIPITATE

Raising the pH of a strongly acidic solution containing ferric iron and molybdenum results in the formation of a yellow precipitate. The pH at which the initial precipitation begins is dependent upon the ratio of the concentrations of iron and molybdenum in solution. The results presented below in Table VIII illustrate this point.

Table VIII. Effect of the Molar Ratio of Iron to Molybdenum on the pH of Initial Precipitation

Molar Ratio Fe/Mo	Grams/Liter		pH at which ppt begins	Molar Ratio Fe/Mo	Grams/Liter		pH at which ppt begins
	Fe	Mo			Fe	Mo	
1/4	1.40	9.60	1.00	1/4	2.79	19.2	0.90
1/2	1.40	4.80	1.05	1/2	2.79	9.60	0.90
1/1	1.40	2.40	1.15	1/1	2.79	4.80	1.10
2/1	1.40	1.20	1.50	2/1	2.79	2.40	1.20
4/1	1.40	0.60	2.10	4/1	2.79	1.20	1.70
8/1	1.40	0.30	2.80	8/1	2.79	0.60	2.80

These results show that as the ratio of iron to molybdenum in solution increases, the pH at which the precipitation begins increases. It should also be noted that at an 8/1 ratio of iron to molybdenum, precipitation does not take place until a pH of 2.8 is reached, this is the pH at which ferric iron would normally begin to precipitate.

Precipitations were made at several pH values from solutions which contained a 4/1, 2/1, and 1/1 molar ratio of molybdenum to iron. These precipitates were dried at 110°C and analyzed for iron and molybdenum. Results of these tests are reported in Table IX. These results indicate that no definite composition can be assigned to the precipitate. The higher the ratio of molybdenum to iron present in solution, the higher the ratio of molybdenum to iron present in the precipitate for any given pH value. Likewise, the higher the pH at which precipitation is made, the lower the ratio of molybdenum to iron present in the precipitate. These facts indicate that perhaps more than one type of compound is being formed. The lower ratios of molybdenum to iron present in the precipitates made at pH values of 3.0 and 3.5 may be due to the precipitation of iron as ferric hydroxide. A brown color is imparted to the precipitates at these pH values and this brownish color becomes more pronounced as the ratio of molybdenum to iron in solution decreases; this fact would seem to indicate that at least some of the iron was being precipitated as ferric hydroxide.

RECOVERY OF COPRECIPITATED URANIUM

The precipitation of iron and molybdenum from a uranium pregnant acid leach liquor results in some of the uranium being coprecipitated. In order to determine how much uranium would be removed from solution and some of the factors which affect this coprecipitation, a series of tests were made on solutions containing iron, molybdenum, and uranium. Precipitations were made from solutions which contained 1.0 gram U_3O_8 per liter, 1.0 gram Mo per liter, and various amounts of iron at pH values of 2.8, 3.2 and 3.6. The results of these tests are presented in Table X. These results indicate that the amount of uranium coprecipitated is dependent on both the iron concentration and the pH. The higher the iron concentration in solution, the greater the amount of uranium which will be removed during precipitation. Also, the higher the pH at which precipitation is made, the greater the amount of uranium removed. The effect of pH is not simply a function of the amount of iron precipitated. In a solution containing 10 grams of Fe^{+++} per liter at a pH of 2.8, 95 per cent of the iron is precipitated and 3.9 per cent of the U_3O_8 is removed. While at a pH of 3.6, 99.9 per cent of the iron is precipitated and 17.2 per cent of the U_3O_8 is removed.

To test the effect of temperature on the coprecipitation of uranium with iron and molybdenum, precipitations were made at ambient temperature, 50, 75, and 100°C from solution containing 1.0 gram U_3O_8 per liter, 1.0 gram of Mo per liter, and 5.0 grams of Fe^{+++} per liter. The solutions were raised to a pH necessary to insure the precipitation of the molybdenum. Results of these tests are presented below in Table XI.

Table XI. Effect of Temperature on the Coprecipitation of Uranium

Head Assay: U_3O_8 , 1.0 g/l; Mo, 1.0 g/l; Fe^{+++} 5.0 g/l

T°C	pH	<u>Filtrate Assay</u> <u>Grams/Liter</u>			<u>Precipitate</u> <u>% U_3O_8</u>	<u>% U_3O_8 Removed</u>
		<u>U_3O_8</u>	<u>Fe^{+++}</u>	<u>Mo</u>		
A	3.6	0.85	0.007	0.001	0.65	13.8
50	3.1	0.92	0.004	0.001	0.29	7.0
75	2.9	0.95	0.015	0.001	0.089	2.1
100	2.7	0.98	0.045	0.002	0.036	0.9

These results show that as the temperature at which the precipitate is made increases, the amount of uranium removed with the precipitate decreases. When the precipitation was made at 100°C, less than 1 per cent of the total amount of uranium was coprecipitated.

To test the effect of the uranium concentration on its coprecipitation from solution with iron and molybdenum, precipitations were made from solutions containing 1.0 gram of Mo per liter, 5.0 grams of Fe^{+++} per liter, and various amounts of uranium at a pH of 3.6 and at ambient temperature. Results of these tests are presented in Table XII, below.

Table XII. Effect of Uranium Concentration on the Amount of Uranium Coprecipitated

Head Assay: Mo, 1 g/l; Fe^{+++} , 5.0 g/l

<u>Head Assay</u> <u>g U_3O_8/l</u>	<u>Filtrate Assay</u> <u>g U_3O_8/l</u>	<u>Precipitate</u> <u>% U_3O_8</u>	<u>% U_3O_8 Removed</u>
1.58	1.32	0.86	14.3
1.00	0.85	0.65	13.8
0.50	0.42	0.29	14.2
0.24	0.20	0.23	19.1

These results indicate that there is no significant difference in the percentage of uranium removed as the concentration of U_3O_8 in solution is varied.

As has already been shown, uranium is removed from solution with the precipitation of iron and molybdenum. To test the effectiveness of an acid repulp in recovering the uranium from the precipitate, a series of precipitations were made from solutions containing 1.0 gram U_3O_8 per liter, 1.0 gram Mo per liter, and 5.0 grams Fe^{+++} per liter at both ambient temperature and $100^\circ C$. The resulting precipitates were then repulped for one hour at a predetermined pH through the addition of dilute sulfuric acid. These repulps were made over a range of pH values at both ambient temperature and $100^\circ C$. Four possible combinations of precipitation and repulp were studied: (1) precipitation at ambient temperature and repulp at ambient temperature, (2) precipitation at ambient temperature and repulp at $100^\circ C$, (3) precipitation at $100^\circ C$ and repulp at ambient temperature, and (4) precipitation at $100^\circ C$ and repulp at $100^\circ C$. The results of these tests are reported in Table XIII. These results indicate that the uranium can be successfully recovered from the precipitate by an acid repulp. Nearly complete rejection of molybdenum was accomplished with a loss of 0.1 to 0.25 per cent of the uranium in the feed liquor.

REMOVAL OF MOLYBDENUM FROM AMBROSIA LAKE LEACH LIQUORS

Molybdenum Precipitation and Ion Exchange - Batch Tests

The neutralization of acid leach liquor from Ambrosia Lake Sample 331-1 with calcium carbonate to a pH of 3.6 results in almost complete removal of the molybdenum from the liquor. Analysis of the leach liquor after precipitation indicated that only 0.001 gram Mo per liter, 0.03 gram Fe^{+++} per liter, and 10.0 grams $SO_4^{=}$ per liter remain in solution so that a liquor which is readily amenable to ion exchange is obtained.

To illustrate the advantage of precipitating the iron and molybdenum prior to ion exchange, batch adsorption tests were made on leach liquor prepared from ore Sample 331-1. The leach liquor was split into three batches, the first batch (A) was adjusted to a pH of 1.5; the second batch (B) was neutralized to a pH of 3.6 with calcium carbonate to remove the iron and molybdenum, and then was adjusted to a pH of 1.5 with sulfuric acid; and the third batch (C) was also neutralized to a pH of 3.6 with calcium carbonate to remove the iron and molybdenum and the pH was adjusted to 3.2 to prevent any further hydrolysis. Partial chemical analysis of the three batches of liquor are presented on the following page.

Batch	pH	Grams/liter					
		U_3O_8	Fe^{+++}	Fe^{++}	Mo	$SO_4^{=}$	Al_2O_3
A	1.5	0.66	0.32	0.034	0.076	14	0.17
B	1.5	0.63	0.015	0.032	0.001	10	0.15
C	3.2	0.63	0.015	0.032	0.001	10	0.15

One thousand ml of each batch of liquor was contacted with 10 ml of fresh IRA-400 resin in the sulfate form. Samples were taken at 1, 2, 4, 8, 16, 32, 64, 128 and 256 minutes. The amount of uranium adsorbed was plotted against the contact time and the three curves obtained are presented in Figure 1. These curves show that the adsorption of uranium from this liquor is more rapid at a pH of 3.2 than at a pH of 1.5. Also, the uranium adsorption is more rapid from the liquor from which the iron and molybdenum have been removed than from the liquor at the same pH which contains iron and molybdenum.

Saturation loadings on IRA-400 resin for the three batches of liquor were obtained by column ion exchange. The retention times were 3 minutes for exhaustion and 10 minutes for elution. The eluant used was 1.0M sodium chloride adjusted to a pH of 1.0 with hydrochloric acid. Elution was complete in 10 bed volumes. The loadings based on the eluate assay are presented below:

<u>Batch</u>	<u>g U_3O_8/1 WSR</u>
A Containing Mo, pH 1.5	56.3
B Mo Removed, pH 1.5	71.1
C Mo Removed, pH 3.2	89.5

Considerably higher loadings were obtained when the ion exchange was made at a pH of 3.2, as compared to the loadings obtained when the ion exchange was made at 1.5. The removal of molybdenum from the leach liquor, also led to higher saturation loadings when compared to the liquor at the same pH containing molybdenum.

Cyclic Leaching and Molybdenum Precipitation

A series of cyclic leaching and precipitation tests was made on ore Sample 331-1. The ore was leached with 175 lbs H_2SO_4 and 10 lbs MnO_2 per ton of ore. The resulting leach liquor was neutral-

Figure 1. Adsorption of uranium from Ambrosia Lake District Leach Liquor (Sample 331-1)

- A. pH adjusted to 1.5
- B. Neutralized to pH 3.6 and pH adjusted to 1.5
- C. Neutralized to pH 3.6 and pH adjusted to 3.2

ized to a pH of 3.6 with calcium carbonate to precipitate molybdenum and iron. Previous test work had shown that about 2 per cent of the uranium is removed from the liquor during this precipitation. Therefore, in an attempt to recover this precipitated uranium, the precipitate was re-pulped in the next acid leach pulp, subsequent to the leaching. This procedure has the advantage that in addition to the recovery of uranium, the pH of the liquor is higher than it would ordinarily be and therefore requires less calcium carbonate for neutralization. In these tests the iron precipitate was not washed, in order to keep the uranium concentration of the pregnant liquor as high as possible, and therefore the amount of uranium held by the precipitate was larger than the 2 per cent normally coprecipitated. Since this precipitate was recycled to the next acid leach pulp, washing was not necessary.

Seven leaching and neutralization tests were made. The overall calcium carbonate consumption was only about 25 lbs per ton of ore. The uranium extraction varied from 91.4 to 96.0 per cent. Due to the recycling of the neutralization precipitate there is an increase in the iron and molybdenum content of the acid leach filtrates. The iron concentration increased from 0.5 to 2.13 grams per liter while the molybdenum concentration increased from 0.047 to 0.083 gram per liter. In order to prevent an accumulation of these constituents, it would be necessary to either bleed the circuit periodically or to discard the precipitate from the system at certain intervals. In these tests, after seven cycles, the iron precipitate weighed only 9.5 grams and assayed 0.2 per cent U_3O_8 . The amount of uranium which would be lost, if it were decided to discard the precipitate at this point, would amount to only 0.2 per cent of the total amount of uranium in the ore treated. Data for the seven cycles are presented in Table XIV.

REMOVAL OF MOLYBDENUM FROM LIGNITE LEACH LIQUORS

Neutralization of Leach Liquors from Several Lignites

Precipitation tests for the removal of molybdenum were made on leach liquors prepared from the following ashed samples:

<u>Sample No.</u>	<u>Description</u>
185-8	A. S. & R. Co. Edgemont Lignite
185-16	Bryco Mining Co. Hilltop
185-18	Peter Kiewit Ore
185-19	Farmington Lignite Section 27
185-21	Northgate Lignite Smith No. 1

Molybdenum can be successfully removed from liquors prepared from ore Samples 185-8, 185-19 and 185-21, with only 1 to 2 ppm remaining in solution. However, on leach liquors prepared from ore samples 185-16 and 185-18, between 10 and 20 ppm of molybdenum remained in solution. The precipitate from 185-8 leach liquor was difficult to filter and contained 20 per cent of the uranium in the liquor. This is probably due to the large amount of ferric iron present in the liquor. The precipitate from the other liquors all filtered readily and contained 12 per cent or less of the uranium originally in the liquor. Chemical assays in grams per liter of the liquors before and after precipitation are presented in Table XV.

Molybdenum Removal and Ion Exchange

Ion exchange amenability tests were made on liquors prepared from ore Samples 185-16 and 185-18. Since the removal of molybdenum from these liquors by precipitation is not complete, a charcoal scavenger column was employed prior to the ion exchange columns in order to remove the small amounts of molybdenum remaining in the liquors.

Bryco Hilltop Sample 185-16

Minus 10-mesh muffle roasted ore was leached at 50 per cent solids for six hours at 75°C with 677 lbs of H_2SO_4 per ton of ash. After leaching, the pulp was diluted to approximately 30 per cent solids and flocculated with Separan. The diluted pulp was filtered and washed with hot water to a final volume of four liters per kilogram of ash. Uranium extraction, based on the residue assay, was 85 per cent.

The leach liquor was oxidized with potassium permanganate to an emf of -540 mv. It was then heated to 50°C, and calcium carbonate was added until a pH of 3.5 was reached. Neutralization requirements were 400 lbs of $CaCO_3$ per ton of ash. The precipitate was filtered and water washed. Filtration characteristics were excellent. About 98 per cent of the molybdenum was removed by the precipitation. Practically all of the iron was precipitated and about 64 per cent of the sulfate was removed as shown below:

Precipitation of Molybdenum from 185-16 Leach Liquor

	pH	Emf(mv)	Grams/Liter					
			U ₃ O ₈	Mo	Fe ⁺⁺⁺	Fe ⁺⁺	SO ₄ ⁼	Al ₂ O ₃
Before neutralization	1.5	-420 ^{1/}	1.10	0.52	2.66	1.29	77.7	19.0
After neutralization	3.7	-540	1.04	0.012	0.01	0.07	28.0	7.5

^{1/} emf of the liquor before oxidation

The precipitate from the neutralization was repulped for the recovery of uranium. A pH of 3.2 was maintained for one hour by the addition of sulfuric acid. The precipitate before repulp assayed 0.074 per cent U₃O₈; and after the repulp, assayed 0.016 per cent U₃O₈. The amount of uranium remaining in the precipitate is equal to 1.2 per cent of the total amount in the liquor before precipitation. Analysis of the filtrate indicated that about 10 per cent of the molybdenum and iron was redissolved during the repulping.

Cyclic ion exchange test work was done on the treated liquor. The ion exchange system consisted of 3 columns of 25 ml of wet settled IRA-400 resin. Two columns were run to exhaustion while one was being eluted. The leach liquor was passed through a scavenger column containing 25 ml of wet settled Columbia activated charcoal prior to the ion exchange resin. This charcoal column removes the small amount of molybdenum remaining in the liquor after the precipitation. The leach liquor was adjusted to a pH of 3.0 with sulfuric acid. Retention times were 3 minutes for exhaustion and 10 minutes for elution. The eluant was 1.0M sodium chloride adjusted to a pH of 1.0 with sulfuric acid. Four complete cycles of exhaustion and elution of each column in the system were run. The average U₃O₈ loading was 92 grams U₃O₈ per liter of wet settled resin, with no apparent molybdenum poisoning. A total of approximately 20 liters of liquor were passed over the charcoal scavenger column. The effluents for this column assayed 0.004 gram Mo per liter. The ion exchange data is summarized in Table XVI.

Table XVI
Cyclic Ion Exchange of 185-16 Lignite
Leach Liquor

<u>Column Number</u>	<u>Cycle</u>	<u>Bed Volumes to</u>		<u>Loading^{1/}</u> <u>g U₃O₈/l WSR</u>
		<u>Breakthrough</u>	<u>Elution</u>	
1	1	174 ^{2/}	13	88.7
2	1	99	13	88.1
3	1	93	13	92.2
1	2	107	13	95.7
2	2	85	13	94.2
3	2	94	13	90.5
1	3	98	13	96.8
2	3	89	13	89.9
3	3	92	13 ^{3/}	89.6
1	4	98	10 ^{3/}	94.4
2	4	85	10	95.8
3	4	96	10	91.4

- 1/ Loadings calculated from eluate assays.
2/ Initial startup. Two fresh columns on exhaustion.
3/ Eluant on the 4th cycle was 1.0M NaCl acidified with HCl to a pH of 1.0.

Peter Kiewit Sample 185-18

Minus 10-mesh roasted ore was leached at 50 per cent solids for six hours at 75°C with 1100 lbs of H₂SO₄ per ton of ash. After leaching, the pulp was diluted to approximately 30 per cent solids and flocculated with Separan. The diluted pulp was filtered and washed with hot water to a final volume of four liters per kilogram of ash. The uranium extraction, based on the residue assay, was 88 per cent.

The leach liquor was oxidized with potassium permanganate to an emf of -540 mv. It was then heated to 55°C and calcium carbonate was added to a pH of 3.7. This neutralization produced a precipitate which removed about 98 per cent of the molybdenum and iron, 56 per cent of the sulfate, and 12 per cent of the uranium. This uranium, however, can be recovered by a repulp of the precipitate.

Precipitation of Molybdenum from 185-18 Leach Liquor

	pH	Emf(mv)	U ₃ O ₈	Mo	Fe ⁺⁺⁺	Fe ⁺⁺	SO ₄ ⁼	Al ₂ O ₃
Before neutralization	1.5	-460 ^{1/}	0.98	0.42	7.70	0.77	90.0	18.5
After neutralization	3.9	-360	0.86	0.01	0.02	0.10	39.0	8.8

^{1/} emf of liquor before oxidation

The precipitate from the neutralization was repulped for one hour with 552 grams of H₂SO₄ (94 lbs per ton of ash) to a terminal pH of 3.3. The precipitate assayed 0.10 per cent U₃O₈ before repulp and 0.02 per cent U₃O₈ after repulp. The amount of uranium remaining in the precipitate is equal to 2.5 per cent of the total amount of uranium in the liquor before precipitation. The filtrate from the repulp showed that about 10 per cent of the molybdenum and iron was redissolved during the repulping. The filtration characteristics were very poor.

Cyclic ion exchange test work was done on the treated liquor. The ion exchange system was the same as that used on the 185-16 leach liquor. The leach liquor was adjusted to a pH of 3.0 with sulfuric acid. The retention time was 3 minutes for exhaustion and 10 minutes for elution. The eluant was 1.0M sodium chloride acidified with hydrochloric acid to a pH of 1.0. A total of 26.6 liters or 1064 bed volumes were treated in the charcoal scavenger column. The molybdenum assays of the effluents ranged from 0.002 to 0.003 gram per liter. This molybdenum concentration had no apparent effect on the resin capacity.

Uranium loadings were approximately 90 g of U₃O₈/1 WSR. The ion exchange data is summarized in Table XVII.

Table XVII
Cyclic Ion Exchange of 185-18 Lignite Leach Liquor

Column Number	Cycle	Bed Volumes to		Loading g U ₃ O ₈ /1 WSR
		Breakthrough	Elution	
1	1	196	10	92.5
2	1	110	10	91.3
3	1	110	10	86.3
1	2	110	10	87.8
2	2	110	10	85.6
3	2	110	10	87.1
1	3	110	10	91.5
2	3	110	10	90.7
3	3	130	10	91.1

Effect of Recycling Repulp Solution

Since good results were obtained when cyclic ion exchange tests were conducted on lignite leach liquor from which the molybdenum had been precipitated, it now remained to determine the effect of recycling the filtrate, resulting from an acid repulp of the precipitate, back to the next acid leach. This is made necessary in order to recover the uranium which was removed with the precipitate. Ore sample 185-16 was used for these tests. The following procedure was used:

Leaching Conditions. Minus 10-mesh ash was leached for 6 hours at 75°C and 50 per cent solids with 700 lbs H_2SO_4 per ton of ash. In tests 2, 3 and 4, repulp solution was used in the leach and to dilute the pulp after leaching.

Precipitation. The leach liquor was heated to 50°C and calcium carbonate was added until the desired pH was reached. The precipitate was filtered and the filtrate was ion exchanged.

Repulp. The precipitates were repulped for one hour with the addition of sulfuric acid. The filtrates from these repulps were recycled to the next acid leach. The residues were discarded.

Ion Exchange. The liquor after precipitation was adjusted to a pH of 3.0 with sulfuric acid. Prior to ion exchange, the liquor was passed through a molybdenum scavenger column containing activated charcoal in order to remove any molybdenum remaining in the liquor. For each leaching test, one saturation loading on IRA-400 resin was obtained. Retention times were 3 minutes on exhaustion and 10 minutes on elution. The eluant used was 1.0M sodium chloride acidified to a pH of 1.0 with hydrochloric acid. Complete test data are summarized in Table XVIII.

The test data show that there is no increase of iron and molybdenum in the acid leach filtrate due to the recycling procedure. This may be due to the fact that partial precipitation of these elements takes place during the leaching. The terminal pH increased with each leaching cycle, and this increase in pH would aid in the precipitation of iron and molybdenum. The ion exchange data shows no apparent effect because of the recycling of the repulp filtrates. The uranium saturation loadings increased with each successive cycle, and this was probably due to the increase in uranium concentration of the feed liquor over the first three cycles. However, there was a very substantial buildup of aluminum in the acid leach filtrates. Apparently, the precipitated aluminum was partially redissolved during the repulping operation and was returned to the next acid leach. The aluminum in the acid leach filtrates increased

from 19.5 grams Al_2O_3 per liter in the first cycle to 53.0 grams Al_2O_3 per liter in the fourth cycle. In the repulp filtrates, the Al_2O_3 increased from 16.1 to 65.0 grams per liter over the four cycles. The calcium carbonate necessary to neutralize the leach liquors increased from 380 to 650 lbs per ton of ash and the sulfuric acid used in the repulping step increased from 158 to 310 lbs per ton of ash over the four cycles. This increase in reagent consumption can be attributed to the buildup of aluminum in the system. It would appear, therefore, that a process of this type involving the recycling of a repulp filtrate would be impractical for this ore because of excessive reagent costs.

Precipitation of Molybdenum During Leaching

In all of the test work previously discussed, the molybdenum and iron had been precipitated by the addition of calcium carbonate to a clear solution. The possibility of controlling the amount of molybdenum present in an acid leach liquor through control of the leaching conditions has been studied. It should be noted that although the work done on this aspect of the problem was on a very limited scale, the results obtained indicated that probably the most practical way of precipitating molybdenum in this manner would be through proper controlling of acid leaching conditions.

Leaching tests were made on roasted ore, Sample 185-19, at 70, 80, 90, and 98°C to determine what effect increasing the leaching temperature would have on the amount of molybdenum found in the filtrates. In order to give a terminal pH of about 1.5, 550 lbs of H_2SO_4 per ton of ash was used. Results of these tests are presented in Table XIX. The tests show that increasing the leaching temperature has no effect on the uranium extractions; however, the amounts of molybdenum and iron present in the filtrates decrease as the temperature increases. This decrease in molybdenum and iron concentration can be attributed to the fact that increasing the temperature causes precipitation of iron and molybdenum.

A series of leaching tests were made at 98°C on several lignite ore samples in order to test the effect of leaching pH on the molybdenum to be found in the filtrates. Leaching tests were made on roasted ore samples 185-19, -21, and -25. The amounts of acid used were varied in order to produce terminal leach pH values which would cover a range from 0.0 to 2.5. The data presented in Tables XX, XXI and XXII show that the higher the pH of the leach, the lower the concentration of molybdenum in the filtrate. These results indicate that a leach liquor relatively free of molybdenum and ferric iron can be produced by leaching lignite ash at a relatively high pH and at elevated temperature.

A two-stage leaching circuit is suggested as a method of rejecting molybdenum and ferric iron from pregnant solutions in treating high molybdenum ores without resorting to the use of an excessive amount of reagents for neutralization. One stage would be a neutralizing leach made at a pH sufficiently high to precipitate the iron and molybdenum and render the liquor amenable to ion exchange; the second stage would be a strong acid leach necessary to obtain optimum uranium extraction.

LITERATURE CITED

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Table I. Effect of pH on the Precipitation of MolybdenumHead Solution: Mo, 2.40 g/l; Fe⁺⁺⁺, 2.79 g/l

pH	Filtrate Assay Grams/Liter		% Precipitated	
	Mo	Fe ⁺⁺⁺	Mo	Fe ⁺⁺⁺
1.5	1.04	2.43	56.7	12.9
2.0	0.66	2.26	72.5	19.0
2.5	0.46	2.08	80.1	25.4
3.0	0.042	0.11	98.2	96.0
3.2	0.016	0.03	99.3	98.9
3.4	0.012	0.014	99.5	99.5
3.6	0.009	0.004	99.6	99.9
3.8	0.010	<0.001	99.6	>99.9
4.0	0.024		99.0	
4.5	0.078		96.7	
5.0	0.11		95.4	
6.0	0.57		76.4	
7.0	0.96		60.0	
8.0	1.32		45.0	
9.0	1.60		33.3	

Table III

Effect of Iron Concentration on the pH at which Molybdenum is Precipitated

2.0g Fe ⁺⁺⁺ /l					5.0g Fe ⁺⁺⁺ /l				
pH	Filtrate Assay, g/l		% Precipitated		pH	Filtrate Assay, g/l		% Precipitated	
	Fe ⁺⁺⁺	Mo	Fe ⁺⁺⁺	Mo		Fe ⁺⁺⁺	Mo	Fe ⁺⁺⁺	Mo
2.4	1.25	0.250	37.5	75.0	2.4	1.84	0.185	63.2	81.5
2.6	1.05	0.153	47.5	84.7	2.6	1.11	0.117	77.8	88.3
2.8	0.45	0.066	77.5	93.4	2.8	0.41	0.071	91.8	92.9
3.0	0.13	0.027	93.5	97.3	3.0	0.16	0.029	96.8	97.1
3.2	0.041	0.012	97.9	98.8	3.2	0.038	0.007	99.2	99.3
3.4	0.016	0.006	99.2	99.4	3.4	0.007	0.001	99.9	99.9
3.6	0.002	0.002	99.9	99.8	3.6	0.003	0.001	>99.9	99.9

10.0g Fe ⁺⁺⁺ /l					20.0g Fe ⁺⁺⁺ /l				
pH	Filtrate Assay, g/l		% Precipitated		pH	Filtrate Assay, g/l		% Precipitated	
	Fe ⁺⁺⁺	Mo	Fe ⁺⁺⁺	Mo		Fe ⁺⁺⁺	Mo	Fe ⁺⁺⁺	Mo
2.4	1.79	0.151	82.1	84.9	2.4	1.04	0.069	94.8	93.1
2.6	0.50	0.057	95.0	94.3	2.6	0.46	0.033	97.7	96.7
2.8	0.17	0.022	98.3	97.8	2.8	0.13	0.012	99.4	98.8
3.0	0.073	0.009	99.3	99.1	3.0	0.037	0.001	99.8	99.9
3.2	0.017	0.001	99.8	99.9	3.2	0.009	<0.001	>99.9	>99.9
3.4	0.008	<0.001	>99.9	>99.9	3.4	0.005	<0.001	>99.9	>99.9
3.6	0.003	<0.001	>99.9	>99.9					

Table IV. Effect of Temperature on the Precipitation of Molybdenum

pH	<u>Filtrate Assay</u> <u>g/l at 25°C</u>		<u>Filtrate Assay</u> <u>g/l at 50°C</u>		<u>Filtrate Assay</u> <u>g/l at 75°C</u>		<u>Filtrate Assay</u> <u>g/l at 100°C</u>	
	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>
1.6							4.65	0.62
1.8							3.50	0.17
2.0					2.64	0.17	0.390	0.005
2.2			1.50	0.065	1.22	0.045	0.061	0.003
2.4	1.84	0.185	0.39	0.035	0.22	0.004	0.034	0.001
2.6	1.11	0.117	0.13	0.009	0.071	0.001	0.012	< 0.001
2.8	0.41	0.071	0.043	0.003	0.015	< 0.001		
3.0	0.16	0.029	0.015	< .001	0.006	< 0.001		
3.2	0.038	0.007	0.004	< .001				
3.4	0.007	0.001						
3.6	0.003	0.001						

Table VI. Effect of Aluminum On The Precipitation of MolybdenumTest I Head Assay: Al_2O_3 , 4.0 g/l; Mo, 1.0 g/l; Fe^{+++} , 5.0 g/l

pH	<u>Filtrate Assay</u> <u>Grams/Liter</u>			<u>% Precipitated</u>			<u>CaCO₃ Consumption</u> <u>Grams/Liter of</u> <u>Solution</u>
	<u>Al₂O₃</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	<u>Al₂O₃</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	
3.5	3.6	0.13	0.017	10	97.4	98.3	22
3.8	2.6	0.045	0.007	35	99.1	99.3	28
4.1	0.2	0.003	0.002	95	>99.9	99.8	33

Test II Head Assay: Al_2O_3 , 18 g/l; Mo, 1.0 g/l; Fe^{+++} , 5.0 g/l

pH	<u>Filtrate Assay</u> <u>Grams/Liter</u>			<u>% Precipitated</u>			<u>CaCO₃ Consumption</u> <u>Grams/Liter of</u> <u>Solution</u>
	<u>Al₂O₃</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	<u>Al₂O₃</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	
3.5	16.0	1.84	0.23	11.1	62.2	77.0	40
3.8	9.6	0.10	0.018	46.7	98.0	98.2	58
4.1	0.3	0.004	<0.001	98.3	>99.9	99.9	72

Test III Head Assay: Al_2O_3 , 30 g/l; Mo, 1.0 g/l; Fe^{+++} , 5.0 g/l

pH	<u>Filtrate Assay</u> <u>Grams/Liter</u>			<u>% Precipitated</u>			<u>CaCO₃ Consumption</u> <u>Grams/Liter of</u> <u>Solution</u>
	<u>Al₂O₃</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	<u>Al₂O₃</u>	<u>Fe⁺⁺⁺</u>	<u>Mo</u>	
3.5	27.0	4.29	0.81	10.0	14.2	19	87
3.8	11.5	0.089	0.013	61.7	98.2	98.7	127
4.1	0.03	0.003	0.002	99.9	>99.9	99.8	144

Table IX. Composition of Precipitates

Test I Molar Ratio Mo/Fe = 4/1

<u>pH</u>	<u>Analysis of Precipitate in %</u>			<u>Molar Ratio Mo/Fe</u>
	<u>Mo</u>	<u>Fe</u>	<u>L.O.I. at 450°C</u>	
1.70	48.1	8.11	10.9	3.45
2.05	47.6	9.25	10.3	2.99
3.00	50.7	12.5	6.2	2.36
3.50	50.6	13.5	6.9	2.18

Test II Molar Ratio Mo/Fe = 2/1

<u>pH</u>	<u>Analysis of Precipitate in %</u>			<u>Molar Ratio Mo/Fe</u>
	<u>Mo</u>	<u>Fe</u>	<u>L.O.I. at 450°C</u>	
1.75	45.6	12.0	8.15	2.21
2.00	46.7	13.3	6.33	2.04
3.00	46.9	15.1	6.22	1.81
3.50	47.6	15.6	4.35	1.77

Test III Molar Ratio Mo/Fe = 1/1

<u>pH</u>	<u>Analysis of Precipitate in %</u>			<u>Molar Ratio Mo/Fe</u>
	<u>Mo</u>	<u>Fe</u>	<u>L.O.I. at 450°C</u>	
1.8	43.9	12.9	9.95	1.98
2.2	43.3	15.5	7.04	1.62
3.0	41.2	21.2	4.72	1.13
3.5	38.9	23.2	6.85	0.98

Table X.Coprecipitation of Uranium During Precipitation of
Iron and MolybdenumTest I U_3O_8 , 1.0 g/l; Mo, 1.0 g/l; Fe^{+++} , 1.5 g/l

pH	<u>Filtrate Assay</u> <u>Grams/Liter</u>			<u>Precipitate</u>		% U_3O_8 Precipitated
	U_3O_8	Fe^{+++}	Mo	$\text{U}_3\text{O}_8\%$	Wt. (g)	
2.8	0.99	1.21	0.36	0.26	1.0	0.52
3.2	0.97	0.163	0.048	0.16	8.9	2.83
3.6	0.94	0.008	0.003	0.33	8.9	5.88

Test II U_3O_8 , 1.0 g/l; Mo, 1.0 g/l; Fe^{+++} , 5.0 g/l

pH	<u>Filtrate Assay</u> <u>Grams/Liter</u>			<u>Precipitate</u>		% U_3O_8 Precipitated
	U_3O_8	Fe^{+++}	Mo	$\text{U}_3\text{O}_8\%$	Wt (g)	
2.8	0.99	1.42	0.18	0.057	4.4	0.5
3.2	0.94	0.046	0.006	0.30	10.0	6.0
3.6	0.85	0.007	0.001	0.65	10.6	13.8

Test III U_3O_8 , 1.0 g/l; Mo, 1.0 g/l; Fe^{+++} , 10.0 g/l

pH	<u>Filtrate Assay</u> <u>Grams/Liter</u>			<u>Precipitate</u>		% U_3O_8 Precipitated
	U_3O_8	Fe^{+++}	Mo	$\text{U}_3\text{O}_8\%$	Wt (g)	
2.8	0.95	0.50	0.050	0.07	28.0	3.92
3.2	0.86	0.025	0.002	0.20	30.8	12.3
3.6	0.82	0.005	0.001	0.27	31.8	17.2

Table XIII. Recovery of Uranium from Iron-Molybdenum Precipitates
By An Acid Repulp

Head Solution Assay: U_3O_8 , 1.0 g/l; Mo, 1.0 g/l; Fe^{+++} , 5.0 g/l

Precipitation					Repulp					Residue		
T°C	pH	Filtrate Assay Grams/Liter			T°C	pH	Filtrate Assay Grams/Liter			Wt (g)	%U ₃ O ₈	%U ₃ O ₈ of Head
		U ₃ O ₈	Fe ⁺⁺⁺	Mo			U ₃ O ₈	Fe ⁺⁺⁺	Mo			
A	3.5	0.82	0.025	0.003	A	3.0	0.16	0.047	0.003	13.0	0.047	1.2
A	3.6	0.82	0.010	0.002	A	2.5	0.17	0.54	0.036	12.4	0.010	0.25
A	3.6	0.78	0.009	0.002	A	2.0	0.22	4.05	0.62	8.6	0.0013	0.02
A	3.6	0.77	0.006	0.001	A	1.5	0.24	4.95	0.98	8.0	0.0010	0.02
A	3.6	0.82	0.012	0.002	100	2.3	0.19	0.039	0.002	12.2	0.007	0.17
A	3.6	0.83	0.004	0.001	100	2.0	0.17	0.38	0.007	11.5	0.006	0.14
A	3.6	0.81	0.008	0.001	100	1.5	0.19	2.12	0.073	10.6	0.005	0.11
A	3.6	0.80	0.008	0.001	100	1.0	0.20	4.95	0.99	5.6	0.001	0.01
100	2.6	0.98	0.020	0.002	A	3.0	0.025	0.009	0.001	13.8	0.040	1.1
100	2.6	0.99	0.015	0.002	A	2.5	0.006	0.070	0.001	13.2	0.020	0.53
100	2.7	0.97	0.008	0.001	A	2.0	0.030	0.370	0.003	12.6	0.020	0.50
100	2.6	0.97	0.013	0.001	A	1.5	0.025	1.64	0.14	12.0	0.020	0.48
100	2.6	0.98	0.012	0.001	A	1.0	0.015	4.34	0.86	8.1	0.012	0.19
100	2.6	0.97	0.016	0.001	100	2.3	0.022	0.014	0.001	13.6	0.007	0.19
100	2.6	0.99	0.040	0.002	100	2.0	0.010	0.259	0.004	12.6	0.0038	0.10
100	2.6	0.98	0.013	0.001	100	1.5	0.012	3.25	0.34	8.5	0.0041	0.08
100	2.6	0.98	0.012	0.001	100	1.0	0.027	5.00	1.00	5.8	0.0029	0.03

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Table XIV

Precipitation of Molybdenum from Ambrosia Lake District Ores

Sample 331-1

Test Number	Leaching ^{1/} Conditions Lb/Ton		Terminal ^{2/} Conditions		Terminal ^{2/} Conditions		Residue Assay % U ₃ O ₈	% U ₃ O ₈ Ext'n	Liquor Before CaCO ₃					Liquor After CaCO ₃					CaCO ₃ Lb/Ton
	H ₂ SO ₄	MnO ₂	pH	Emf(mv)	pH	Emf(mv)			Grams/Liter					Grams/Liter					
									pH	U ₃ O ₈	Mo	Fe	SO ₄	pH	U ₃ O ₈	Mo	Fe	SO ₄	
1	165	20	1.7	-	-	-	0.010	93.6	1.8	0.37	0.047	0.42	-	3.7	0.34	0.002	0.035	6.13	40
2	155	20	1.9	-	2.2	-	0.012	91.8	2.6	0.38	0.078	0.76	6.60	3.9	0.35	<0.001	0.019	4.21	12
3	175	10	1.4	-	1.9	-	0.013	91.4	2.2	0.41	0.053	1.47	7.80	3.6	0.39	0.001	0.033	5.10	22
4	175	10	1.3	-595	2.2	-550	0.013	91.4	2.3	0.38	0.056	1.19	8.40	3.6	0.38	<0.001	0.046	4.72	22
5	175	10	1.3	-535	2.3	-500	0.012	91.9	2.4	0.38	0.038	1.52	8.42	3.6	0.36	<0.001	0.057	6.90	21
6	175	10	1.1	-520	1.9	-500	0.006	96.0	2.1	0.41	0.070	1.87	9.52	3.6	0.38	0.001	0.105	4.78	27
7	175	10	1.1	-520	2.0	-490	0.009	94.0	2.3	0.44	0.083	2.13	9.05	3.5	0.40	0.002	0.170	4.95	28

1/ Five hundred grams of minus 10-mesh ore were ground for 10 minutes at 67 per cent solids, then leached at 50 per cent solids for 4 hours at ambient temperature.

2/ Terminal conditions of acid leach.

3/ Terminal conditions after repulping the neutralization precipitate in acid leach pulp for 30 minutes.

Table XV

Precipitation of Molybdenum from Lignite Leach Liquors by Neutralization with Calcium Carbonate

<u>Lignite Ore Sample</u>	<u>Liquor Before Neutralization</u>						<u>Liquor After Neutralization</u>						<u>% U₃O₈ of Feed Precipitated</u>
	<u>T°C</u>	<u>pH</u>	<u>Grams/Liter</u>		<u>Fe⁺⁺⁺</u>	<u>SO₄⁼</u>	<u>T°C</u>	<u>pH</u>	<u>Grams/Liter</u>		<u>Fe⁺⁺⁺</u>	<u>SO₄⁼</u>	
			<u>U₃O₈</u>	<u>Mo</u>					<u>U₃O₈</u>	<u>Mo</u>			
185-8	50	1.5	0.90	0.13	18.6	125	50	3.5	0.72	0.002	0.10	45	20.0
185-16	50	1.5	1.12	0.72	2.33	81	50	3.5	1.13	0.021	0.12	28	8.0
185-18	50	1.5	0.98	0.41	6.97	94	50	3.8	0.86	0.009	0.03	30	12.2
185-19	26	1.5	1.38	0.078	4.87	--	26	3.6	1.28	0.002	0.01	--	7.2
185-21	26	1.5	0.42	0.031	2.26	66	26	3.6	0.40	0.001	0.01	22	4.8

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Table XVIII

Effect of Recycling Repulp Filtrate (185-16 Leach Liquor)

Precipitation of Molybdenum with CaCO_3 at 50°C

Test No.	Liquor Before CaCO ₃							Liquor After CaCO ₃							CaCO ₃ lb/ton ash
	Vol(l)	pH	Grams/Liter					Vol(l)	pH	Grams/Liter					
			U ₃ O ₈	Mo.	Fe ⁺⁺⁺	SO ₄ ⁼	Al ₂ O ₃			U ₃ O ₈	Mo	Fe ⁺⁺⁺	SO ₄ ⁼	Al ₂ O ₃	
1	2.00	1.5	1.57	0.82	3.42	102	19.5	2.90	3.8	1.00	0.05	0.03	27.4	7.6	380
2	4.15	1.5	1.69	0.90	4.82	116	28.7	5.28	3.8	1.17	0.024	0.01	20.3	6.7	500
3	3.75	1.9	1.84	0.65	2.16	136	42.2	4.50	3.5	1.32	0.124	0.08	28.6	7.8	500
4 ^{1/}	4.25	2.1	1.71	0.61	2.87	116	53.0	5.60	3.3	1.16	0.049	0.01	20.0	8.2	650

Repulp of the Precipitate

Ion Exchange

Test No.	<u>Filtrate</u>					<u>H₂SO₄</u> lb/ton ash	<u>Residue</u>			<u>Bed Volumes To:</u>			<u>Loadings</u> g U ₃ O ₈ /l WSR
	Vol(l)	<u>Grams/liter</u>					<u>%U₃O₈</u>	<u>Wt(g)</u>	<u>%Loss</u> U ₃ O ₈	<u>Breakthrough</u>	<u>Saturation</u>	<u>Elution</u>	
		<u>U₃O₈</u>	<u>Mo</u>	<u>Fe⁺⁺⁺</u>	<u>Al₂O₃</u>								
1	1.60	0.13	0.33	1.62	16.1	158	.004	183	0.2	62	128	10	94.8
2	3.20	0.20	0.02	1.10	22.8	158	.024	510	1.7	60	128	10	97.2
3	3.50	0.27	0.51	2.37	35.2	248	.003	490	0.2	57	124	10	100
4	3.40	0.26	0.35	0.89	65.0	310	.012	856	1.5	58	140	10	103

^{1/} Neutralization was made at 100°C

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Table XIX. Effect of Leaching Temperature on 185-19 Roasted Ore

<u>Leaching Conditions</u> ^{1/}			<u>Terminal Conditions</u>		<u>Residue</u>	<u>Pregnant Liquor Assay</u> ^{2/}					
Lb H ₂ SO ₄	Temp °C	Ton of Ore	pH	Emf(mv)	<u>Assay</u> %U ₃ O ₈	%U ₃ O ₈ Extraction	U ₃ O ₈	Mo	<u>Grams/Liter</u> Fe ⁺⁺⁺ Fe ⁺⁺		SO ₄
550	70		1.45	-450	0.088	84.0	1.09	0.30	2.74	0.57	57
550	80		1.40	-430	0.080	84.3	1.09	0.036	0.73	0.44	49
550	90		1.60	-370	0.080	84.2	1.09	0.015	0.18	0.50	48
550	100		1.65	-370	0.080	84.0	1.09	0.013	0.17	0.37	43

^{1/} Minus 10-mesh ash from ore sample 185-19 was leached for 6 hours at 40 per cent solids.

^{2/} Solution to ore ratio - 4:1

Table XX, Effect of Leaching pH on 185-19 Roasted Ore

Leaching ^{1/} Conditions Lb/Ton Ash H ₂ SO ₄	Terminal Conditions		Residue Assay % U ₃ O ₈	% U ₃ O ₈ Ext'n	Pregnant Liquor Assay ^{2/} Grams/Liter			
	pH	Emf (mv)			U ₃ O ₈	Mo	Fe ⁺⁺⁺	Fe ⁺⁺
600	2.55	-365	0.071	86.9	1.24	0.008	0.06	0.35
700	2.00	-400	0.064	88.7	1.27	0.020	0.063	0.56
800	1.40	-430	0.046	92.1	1.33	0.036	1.63	0.63
900	1.10	-445	0.041	93.1	1.38	0.069	4.16	0.71
1000	0.70	-470	0.041	93.1	1.38	0.114	5.39	0.81

^{1/} Minus 10-mesh ash leached at 98°C and 40 per cent solids for 6 hours.

^{2/} At a 4:1 solution to ore ratio.

Note: Head assay U₃O₈ = 0.58%

Table XXI, Effect of Leaching pH on 185-21 Roasted Ore

Leaching ^{1/} Conditions Lb/Ton Ash H ₂ SO ₄	Terminal Conditions		Residue Assay % U ₃ O ₈	% U ₃ O ₈ Ext'n	Pregnant Liquor Assay ^{2/} Grams/Liter			
	pH	Emf (mv)			U ₃ O ₈	Mo	Fe ⁺⁺⁺	Fe ⁺⁺
170	2.00	-375	0.057	66.0	0.34	0.001	0.00	0.27
275	1.55	-400	0.040	79.2	0.36	0.003	0.10	0.48
500	1.05	-450	0.020	90.0	0.43	0.032	2.26	0.54
600	0.70	-465	0.017	91.7	0.43	0.065	4.71	0.47
700	0.40	-485	0.014	93.3	0.44	0.094	6.07	0.48
800	0.20	-510	0.013	93.9	0.44	0.173	10.5	0.56

^{1/} Minus 10-mesh ash leached at 98°C and 40 per cent solids for 6 hours.

^{2/} At a 4:1 solution to ore ratio.

Note: Head Assay U₃O₈ = 0.19%

Table XXII. Effect of Leaching pH on 185-25 Roasted Ore

Leaching ^{1/} Conditions Lb/Ton Ash H ₂ SO ₄	Terminal Conditions		Residue		Pregnant Liquor Assay ^{2/}			
			Assay	% U ₃ O ₈	Grams/Liter			
	pH	Emf (mv)	% U ₃ O ₈	Ext'n	U ₃ O ₈	Mo	Fe ⁺⁺⁺	Fe ⁺⁺
600	2.65	-375	0.064	89.8	1.56	0.006	0.04	0.33
670	2.30	-440	0.050	93.0	1.60	0.031	0.84	0.36
800	1.55	-470	0.040	94.0	1.62	0.140	3.77	0.37
1000	0.90	-515	0.032	95.3	1.65	0.630	13.4	0.41
1200	0.40	-530	0.032	95.7	1.65	1.17	18.0	0.46

^{1/} Minus 10-mesh ash leached at 98°C and 40 per cent solids for 6 hours.

^{2/} At a 4:1 solution to ore ratio.

Note: Head Assay U₃O₈ = 0.69%