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PROGRESS REPORT

on

THE AMMONIUM CARBONATE PRESSURE LEACHING OF
URANIUM ORES PROPOSED AS FEED TO
THE PILOT PLANT AT GRAND JUNCTION, COLORADO

to

DIVISION OF RAW MATERIALS
U. S. ATOMIC ENERGY COMMISSION

by

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THE AMMONIUM CARBONATE PRESSURE LEACHING OF
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C. M. Wheeler, B. G. Langston, and F. M. Stephens, Jr.

An integrated plant has been constructed to evaluate the amenability of three ores to an ammonium carbonate pressure leach for extraction of the uranium. The continuous leaching system consists of five towers which are operated under pressure.

Operation of the plant with Black Limestone ore as a feed has given extractions ranging from 92 to 93 per cent of the uranium. To obtain these extractions, a temperature of 225 F, a pressure of 90 psi, a retention time of about 3 hours, and a leach-solution concentration of 10 per cent ammonium carbonate and 2 per cent ammonium bicarbonate were required.

A continuous precipitation tower operating at a feed rate of 10 gallons per hour of pregnant liquor gave a precipitate that assayed 82 per cent of U_3O_8 , which represented a recovery of over 99 per cent of the uranium in the pregnant liquor.

INTRODUCTION

This is Progress Report BMI-282, the first of a series covering the operation of the pressure-leaching towers for the extraction of uranium by an ammonium carbonate leach. This program was authorized by Contract No. AT(49-6)-921. Three ores, designated Mineral Joe, Cal Uranium, and Black Limestone, were furnished Battelle for this study by the Division of Raw Materials of the Atomic Energy Commission.

Because the basic conditions for extracting the uranium from this type of ore were developed by small-scale autoclave tests run on Black Limestone ore, the initial tests in the pressure-leaching towers were made employing Black Limestone ore as a feed.

This report discusses the data obtained from tests run to show the effects of such variables as the amount of air and carbon dioxide passed

through the pulp, temperature, pressure, and concentration of ammonium carbonate and ammonium bicarbonate in the leach solution on the extraction of uranium. In addition, as part of an expanded program to evaluate a countercurrent decantation system for separation of the pregnant liquor from the solids and recovery of the uranium from the pregnant liquor, a precipitation tower was constructed. The results of preliminary tests in the precipitation tower are also discussed in this report.

SUMMARY

This is the first report covering a research program authorized by the Division of Raw Materials of the Atomic Energy Commission to evaluate on a continuous basis the amenability of uranium-bearing ores to an ammonium carbonate pressure leach. This report discusses the data obtained from the initial tests made to determine the feasibility of employing pressure-leaching towers for the extraction of uranium from the Black Limestone ore.

Data obtained from preliminary tests showed that, with minus 100-mesh ore pulped at 50 per cent solids in a leach solution containing 100 grams of ammonium carbonate and 20 grams of ammonium bicarbonate per liter, and a temperature of 210 to 230 F, at a pressure of about 100 psi, about 92 per cent of the uranium was extracted from the Black Limestone ore. Although the air was varied in these tests over a range of 1500 to 6000 cubic centimeters per minute, at the operating pressure, a flow rate of 3000 cubic centimeters appeared sufficient for the oxidation of the uranium and was chosen as a constant when investigating other variables. The feed rate was maintained at 30 pounds per hour (dry solids basis), which produced a leaching time of about 6.25 hours. However, assays made on samples from individual towers showed that about 91 per cent of the uranium was extracted during the first 3 hours of leaching time, and an additional 3 hours of leaching time increased the extraction of uranium only to about 92 per cent.

Precipitation of uranium from ammonium carbonate pregnant liquors by steam stripping has been carried out on a continuous basis. The data obtained from this work show that over 99 per cent of the uranium can be precipitated and recovered in a product assaying 77 to 82 per cent U_3O_8 . The barren solution from this process will contain uranium in an amount less than 0.005 gram per liter of solution.

DESIGN OF PRESSURE-LEACHING PLANT

Figure 1 is a picture of the pressure-leaching towers. The plant is composed of five towers 10 feet high with an inside diameter of 4 inches.

**FIGURE 1. PRESSURE-LEACHING TOWERS FOR
AMMONIUM CARBONATE LEACHING
OF URANIUM ORES**

The volume of a single tower is 0.87 cubic foot, giving a total volume of 4.35 cubic feet in the five units. The towers are connected by 1/2-inch transfer pipes. These pipes are arranged so that the pulp is pumped from the bottom to the top of the first tower and then through the transfer pipe to the bottom of the next tower.

A double-valve sampling system is attached to the bottom and top of each tower to permit selective sampling of each unit. In addition, to prevent flashing of the ammonia during sampling, bombs are employed, so that the sample of slurry may be cooled to room temperature before being exposed to the atmosphere.

To provide air, oxygen, or carbon dioxide, each tower is equipped with a gas inlet both at the bottom and at the 5-foot level.

The feed to the plant is a slurry, generally at a pulp density of about 50 per cent solids. The total volume of the towers is 33 gallons of slurry, or about 190 pounds of ore (dry solids basis).

The raw ore is ground to a designated particle size and pulped in a leach solution with the desired concentration of ammonium carbonate and ammonium bicarbonate. A continuously agitated mixing tank feeds the pulp to a piston-type positive-displacement pump which is capable of discharging the pulp against a pressure of 150 psi. The pump is equipped with double-ball check valves to insure a positive pressure seal when the pump is not in operation. The pump is connected to the bottom of the first tower by a 1/2-inch pipe and the pulp flows from the bottom to the top of each tower. The leached pulp overflows from the top of the last tower into a wet cyclone. At this point, the gases are separated from the pulp and are discharged through the pressure let-down valve. To prevent flashing of the ammonia during operation of the plant, the exhaust gases are cooled in a water-jacketed line. The pulp flows from the bottom of the cyclone into a receiver, where it is cooled to protect the discharge valve. From the receiver, the pulp is discharged intermittently through an air-operated valve by means of a level control instrument.

INSTRUMENTATION OF PRESSURE-LEACHING PLANT

The air to the plant is metered first through a master flowmeter and then individually to each tower. To measure the temperature, thermocouples are imbedded in the pulp at the bottom and top of each tower and the temperature is continuously recorded. An automatically controlled pressure let-down valve on the gas-discharge line maintains the desired pressure in the towers. The leached pulp is discharged out of the system by an air-operated valve in the following manner. The receiver acts as a surge tank in which a displacement-type ceramic float operates. This float is

attached to a rod which rises in the chamber as the pulp level rises, which, in turn, raises the float until, at a desired level, the push rod attached to the float triggers the electromagnetic solenoid that actuates a diaphragm-type valve to discharge the pulp. As the pulp level decreases in the surge tank, the float drops, thereby breaking the circuit to the solenoid, and closing the spring-loaded valve.

EXPERIMENTAL WORK

Because the preliminary small-scale leaching tests were made on the Todilto or Black Limestone ore (Battelle's designation, Ore 7), this ore was employed to establish the basic leaching conditions required in the plant. This initial report on the continuous leaching system presents only the data obtained from the leaching tests in which the Black Limestone ore was employed as feed. The following is the chemical analysis of the ore.

Assay, per cent										
<u>U</u>	<u>V</u>	<u>CaO</u>	<u>Al₂O₃</u>	<u>MgO</u>	<u>C</u>	<u>CO₂</u>	<u>SiO₂</u>	<u>Fe₂O₃</u>	<u>S</u>	<u>LOI</u>
0.27	0.02	49.9	1.19	0.62	10.4	37.4	9.13	0.64	0.13	38.9

Preliminary Test With the Pressure-Leaching Plant

The first test made in the continuous plant was a preliminary run to check for operating "bugs" and to provide operating experience for the personnel. The conditions employed were based primarily on the data obtained from small-scale ammonium carbonate pressure-leaching tests. Such factors, however, as air flow, pressure in the towers, and feed rate were chosen arbitrarily. The following leaching conditions were employed for the preliminary test: (1) minus 100-mesh ore was pulped at 50 per cent solids; (2) in a leaching solution containing 100 grams of commercial-grade ammonium carbonate plus 20 grams of ammonium bicarbonate per liter; (3) the leach temperature averaged between 215 and 220 F; (4) the pressure in the towers was maintained at 90 psi; (5) air was passed into the towers at a rate of 3000 cubic centimeters per minute (at operating pressure); and (6) the feed rate was 30 pounds per hour on a dry basis, which gave a total retention time in the towers of about 6 hours.

Under these conditions, the plant was operated continuously for a period of 15 hours. Samples of the leached pulp were obtained from each tower at hourly intervals and the extraction of uranium calculated from the assay of the residue.

Examination of the data obtained from this test showed that, although the amount of uranium solubilized increased as the feed progressed from the first to the last towers, the rate of increase remained practically the same during the entire 15-hour operating period. For simplicity and to avoid repetition of similar data, the following tabulation gives data typical of the results obtained during the 15-hour test.

<u>Tower Number</u>	<u>Elapsed Leaching Time, hr</u>	<u>Residue</u>	
		<u>Assay, U, %</u>	<u>Extraction, U, %</u>
2	1.25	0.031	88.5
3	2.50	0.024	91.2
4	3.75	0.023	91.5
5	5.00	0.021	92.3
Discharge	6.25	0.021	92.3

These data show that by the time the feed reached the third tower, a leaching time of about 2.5 hours, 91 per cent of the total uranium was extracted. In addition, the discharge from the system after being treated an additional 3.75 hours gave an extraction of only 92 per cent of the uranium. In other words, under these conditions, the feed rate could have been doubled, thereby reducing the total retention time in the towers to about 3 hours with the expectation of extracting about 92 per cent of the total uranium.

Discussion of Preliminary Test

For practical purposes, the continuous plant gave satisfactory mechanical performance during the 15-hour operating period. It was observed, however, that because of corrosion by ammonia, all control valves in the system should be iron or stainless steel. For example, for this test, the installation was equipped with stainless steel valves, with the exception of the air-control valves, which were brass-needle valves. Examination after the test showed that the valves were attacked by the ammonia. For this reason, the brass valves were replaced with stainless steel valves. During the first test, samples of pulp were removed from the towers, and, while still hot, exposed to the atmosphere. This appeared to cause a considerable loss of ammonia and carbon dioxide from the assay samples. Because the future work program included a study on the ammonia compounds present in the pregnant liquors, it was desirable to prevent any loss of the ammonia or carbon dioxide during sampling of the towers. For this

reason, sampling bombs were constructed so that a pulp sample could be removed from the system and cooled to, or below, room temperature before being exposed to the atmosphere.

With these exceptions, it appeared practical to continue operating the plant without additional mechanical changes.

With a let-down pressure of 90 psi in the discharge tower, the feed tower operated under a pressure of about 130 psi. In discussing the pressure in this report, the pressure at the let-down valve or control point is used as a reference, recognizing that a differential of pressure of about 40 psi exists between it and the feed tower.

Another point worthy of discussion arose when an effort was made to account for the ammonia in the system by analytical procedures. In the preliminary test, weighed amounts of ammonium carbonate and ammonium bicarbonate were added to a weighed amount of water to give a solution containing 10 per cent ammonium carbonate and 2 per cent ammonium bicarbonate. On this basis, it would be expected that chemical analysis of the leach solution would approximate 100 grams of ammonium carbonate and 20 grams of ammonium bicarbonate per liter. However, chemical analysis of the solution prior to its addition to the pulping tank showed that the ammonium carbonate and ammonium bicarbonate concentrations were quite variable even before addition to the system. Therefore, a cursory petrographic examination was made of the ammonium carbonate and ammonium bicarbonate to determine their purity. It was observed that the ammonium bicarbonate was quite pure, with little, if any, ammonium carbonate present. On the other hand, the ammonium carbonate had none of the optical properties recorded in the literature for either ammonium carbonate, ammonium bicarbonate, or ammonium carbamate and was essentially a single phase. It is believed that the ammonium carbonate is what is referred to in the literature as "ammonium carbonate of commerce", which is the double salt $\text{NH}_4\text{NH}_2\text{CO}_2 \cdot \text{NH}_4\text{HCO}_3$, or ammonium bicarbonate-carbamate. Based on the experiences recorded in the literature, the amount of ammonium carbonate and ammonium bicarbonate formed by aqueous dissolution of the double salt is variable and is dependent on the degree of decomposition of the complex double salt. Therefore, in evaluating the tests, the chemical analysis of the solutions for ammonia, ammonium carbonate, and ammonium bicarbonate has been employed for comparison of the tests in which the ammonium carbonate and ammonium bicarbonate concentrations were varied.

A comparison of the chemical analysis of the leach solution for total ammonia with the calculated ammonia that should be present in a weighed amount of the ammonium carbonate and ammonium bicarbonate showed that less ammonia is available in the leach solution than is indicated by a calculation based on weighing the ammonium carbonate and ammonium bicarbonate. It is believed that this discrepancy is caused by the moisture content of the ammonium carbonate and ammonium bicarbonate. Chemical analysis

of the ammonia concentration of the leach solution appears to be the most accurate method for obtaining an ammonia balance in the system. However, to prevent complex description of the conditions employed in the test work, all leach-solution concentrations are expressed on the basis of the weight of ammonium carbonate and ammonium bicarbonate added to the feed to the towers.

Because of the complexity of differentiating between the carbonate and bicarbonate ions of the ammonium salt, the analytical procedures employed for these tests have been included in the Appendix of this report.

Because the ammonia in the soluble uranium complex decomposes and reports with the ammonia present as carbonate and bicarbonate, the calculation for carbonate and bicarbonate on the basis of the ammonia and carbon dioxide in the solutions is not exact. However, with solutions containing 2 grams of uranium per liter, the ammonia associated with the uranium is not sufficient to prohibit the use of the procedure for control purposes.

When treating ores such as Mineral Joe, where part of the ammonia will be present as ammonia sulfate, both the volatile ammonia and total ammonia contents of the solution must be known to determine the carbonate and bicarbonate concentrations of the solutions.

The Effect of Air Flow Through the Towers on the Extraction of Uranium by an Ammonium Carbonate Leach

Data obtained from the small-scale tests indicated that oxidation of the pulp during the leaching period was one of the most important factors affecting the extraction of uranium by an ammonium carbonate pressure-leaching process. For this reason, the second test in the continuous plant was made to determine the effect of varying the air flow through the towers on the extraction of uranium. This test was made under the conditions employed in Test 1, except that the air flow through the system was varied over a range of 1500 to 6000 cubic centimeters per minute. Table 1 presents the data obtained from this work and shows that, within the range investigated, about 92 per cent of the uranium was extracted under all three of the air-flow rates employed.

An analysis of the exhaust gas from the towers when operating at 1500 cubic centimeters per minute showed that they contained 17 per cent oxygen. In other words, even at the lowest flow rate studied, the amount of oxygen available for oxidation of the uranium was in excess of the amount required for oxidation of the uranium. Therefore, if air flow had an effect on the extraction of uranium in these tests, it should be attributed to improved agitation, rather than oxidation of the uranium. However, as previously discussed, in the range 1500 to 6000 cubic centimeters per minute, air flow had no effect on the extraction of uranium.

TABLE 1. THE EFFECT OF AIR FLOW THROUGH THE TOWERS DURING THE LEACHING PERIOD ON THE EXTRACTION OF URANIUM BY AN AMMONIUM CARBONATE PRESSURE LEACH

Tower	Elapsed Leaching Time, hr	Residue	
		Assay, U, %	Extraction, U, %
<u>Air Flow, 1500 cc per Minute</u>			
2	1.25	0.034	87.5
3	2.50	0.024	91.2
4	3.75	0.023	91.5
5	5.00	0.021	92.3
Discharge	6.25	0.020	92.6
<u>Air Flow, 3000 cc per Minute</u>			
2	1.25	0.032	88.0
3	2.50	0.027	90.0
4	3.75	0.025	90.7
5	5.00	0.025	90.7
Discharge	6.25	0.022	91.9
<u>Air Flow, 6000 cc per Minute</u>			
2	1.25	0.033	87.8
3	2.50	0.027	90.0
4	3.75	0.025	90.7
5	5.00	0.022	91.9
Discharge	6.25	0.023	91.5

On the other hand, because the partial pressure of oxygen in the system is believed to be an important factor affecting the rate of oxidation of the uranium, tests were run after enriching the air with tank oxygen and increasing the total pressure in the towers. This work is discussed in the following section of this report.

The Effect of Adding Oxygen to the Air to Increase the
Partial Pressure of Oxygen in the Towers
on the Extraction of Uranium

In a further effort to increase the extraction of uranium over the 93 per cent obtained when air was employed as the oxidizing agent, a test was made on the effect of increasing the partial pressure of oxygen in the towers by enriching the air to the towers with tank oxygen. This test was made under conditions similar to those employed in the tests that extracted 92 to 93 per cent of the uranium where only air was used as the oxidizing agent, except that tank oxygen was added to the air in an amount calculated to increase the oxygen content of the air to 30 per cent. The results of this test showed that, under these conditions, about 92 per cent of the uranium was extracted. This is about the same amount as was extracted when air alone was employed as the oxidizing agent. In other words, under the conditions employed, addition of this amount of oxygen did not materially increase the extraction of uranium by an ammonium carbonate pressure leach.

It is possible that additional experimental work would show that an oxygen partial pressure could be established that would increase the extraction of uranium over the 93 per cent obtained in the plant to date. However, small-scale tests made in the autoclave showed that, with a chemical oxidizer, the maximum extraction readily obtainable was about 95 per cent. For this reason, it is questionable whether additional work is warranted at this time to obtain an increase in extraction of 2 or 3 per cent of the uranium.

The Effect of Ammonium Carbonate Concentration in the
Leach Solution on the Extraction of Uranium

Data obtained from the small-scale tests indicated that a leach solution containing 100 grams of ammonium carbonate and 20 grams of ammonium bicarbonate per liter was required for optimum extraction of uranium by pressure leach. However, to determine the effect of ammonium carbonate concentration on the extraction of uranium when operating on a continuous basis, a series of tests was run maintaining the amount of ammonium bicarbonate added to the leach solution constant and varying the amount of ammonium carbonate. Because the actual concentration of

ammonium carbonate and ammonium bicarbonate is dependent on the degree of decomposition of the "ammonium carbonate of commerce", chemical analysis of the leach solution for ammonium carbonate and ammonium bicarbonate has been used to evaluate these tests. Except for the ammonium carbonate concentration in the leach solutions, all other conditions were similar to those maintained in the preliminary test. Tables 2, 3, 4, and 5 present the data obtained from this work and show that, under the conditions employed, about 92 per cent of the uranium was extracted with a leach solution containing 80 grams of ammonium carbonate and 10 grams of ammonium bicarbonate per liter. Concentrations in excess of this amount did not materially increase the extraction of uranium. In addition, these tables show the concentration of carbon dioxide and ammonium compounds contained in the pregnant liquor during the tests. These data show, in general, that the amounts of ammonia, carbon dioxide, and ammonium carbonate remain fairly constant from the start to the end of the leaching period. The variations in ammonium carbonate that do occur are believed to be the result of a temperature variation in individual towers which decomposes the ammonium carbonate to give free ammonia and carbon dioxide. The free ammonia and carbon dioxide then pass to the next tower, where the temperature is favorable for reformation of the ammonium carbonate. However, as shown in these tables, most of the ammonium bicarbonate in the system is destroyed almost immediately after heat and pressure are applied to the pulp.

The Effect of Adding Carbon Dioxide to the Towers During the Leaching Period on the Extraction of Uranium

Assays made on the pregnant liquor from Test 3 showed that, under the conditions employed, there was practically no ammonium bicarbonate in the leach solution shortly after the pulp enters the pressurized leaching system. For this reason, tests were run to determine whether the addition of carbon dioxide to the leach solution would maintain the ammonium bicarbonate concentration at a level that would increase the extraction of uranium over the 92 per cent obtained in the previous tests. These tests were made by varying the ammonium carbonate concentration in the leach solution and maintaining a constant carbon dioxide flow rate. The data obtained from this work showed that the addition of carbon dioxide during the leaching period did stabilize the bicarbonate ion concentration. Table 6 presents, for comparison, the conditions observed in the pilot plant with and without the addition of carbon dioxide during the leaching period.

These data show that, without the addition of carbon dioxide, about 92 per cent of the uranium was extracted. However, when carbon dioxide was added, the extraction of uranium dropped to about 88 per cent. Apparently, the addition of carbon dioxide, although stabilizing the bicarbonate concentration, reduced the partial pressure of oxygen in the towers sufficiently to prevent maximum oxidation of the uranium, thereby decreasing the extraction of uranium from the ore.

TABLE 2. METALLURGICAL DATA FROM SECTION 1 OF TEST 3

The Effect of Ammonium Carbonate Concentration
in the Leaching Solution on the Extraction of
Uranium by a Pressure Leach

Test Conditions: Feed	Black Limestone
Average Feed Rate	33 Lb/Hr (Dry Solids Basis)
Oxidizing-Air Rate, Average	3000 CC/Minute
Pressure Maintained in System	90 PSI
Total Operating Time	8 Hours
Average Leach Temperature	240 F

Concentration of Ammonia Compounds in the Leaching Solution

Assay, grams per liter				
Total Ammonia	Free Ammonia	Total Carbon Dioxide	Ammonium Carbonate	Ammonium Bicarbonate
16.3	0	27.8	44.9	3.2

Tower	Elapsed Leaching Time, hr	Average Extraction of Uranium,		Average Concentration of Ammonia Compounds in the Pregnant Liquor, Assay, grams per liter				
		Residue		Total	Free	Total		
		Assay, U, %	Extraction, U, %	NH ₃	NH ₃	CO ₂	(NH ₄) ₂ CO ₃	NH ₄ HCO ₃
2	1.25	0.071	73.7	15.9	0	22.3	41.4	5.9
3	2.50	0.052	80.8	14.1	1.37	16.8	36.6	0
4	3.75	0.039	85.6	16.5	0	22.6	46.3	4.5
5	5.00	0.044	83.8	16.6	0	22.0	44.8	2.5
Discharge	6.25	0.043	84.1					

TABLE 3. METALLURGICAL DATA FROM SECTION 2 OF TEST 3

The Effect of Ammonium Carbonate Concentration
in the Leaching Solution on the Extraction of
Uranium by a Pressure Leach

Test Conditions:	Feed	Black Limestone
	Average Feed Rate	33 Lb /Hr (Dry Solids Basis)
	Oxidizing-Air Rate, Average	3000 CC/Minute
	Pressure Maintained in System	90 PSI
	Total Operating Time	8 Hours
	Average Leach Temperature	240 F

Concentration of Ammonia Compounds in the Leaching Solution

Assay, grams per liter				
<u>Total</u>	<u>Free</u>	<u>Total</u>	<u>Ammonium</u>	<u>Ammonium</u>
<u>Ammonia</u>	<u>Ammonia</u>	<u>Carbon Dioxide</u>	<u>Carbonate</u>	<u>Bicarbonate</u>
28.3	0	45.3	61.3	34.7

Tower	Elapsed Leaching Time, hr	Average Extraction of Uranium, Residue		Average Concentration of Ammonia Compounds in the Pregnant Liquor, Assay, grams per liter				
		Assay, U, %	Extraction, U, %	Total NH ₃	Free NH ₃	Total CO ₂	(NH ₄) ₂ CO ₃	NH ₄ HCO ₃
2	1.25	0.053	80.4	26.5	0	35.0	73.4	2.5
3	2.50	0.056	79.3	25.6	4.8	26.9	58.3	0
4	3.75	0.041	85.0	25.7	0	37.0	63.7	13.9
5	5.00	0.032	88.2	24.0	0	32.6	63.9	5.8
Discharge	6.25	0.032	88.2					

TABLE 4. METALLURGICAL DATA FROM SECTION 3 OF TEST 3

The Effect of Ammonium Carbonate Concentration
in the Leaching Solution on the Extraction of
Uranium by a Pressure Leach

Test Conditions: Feed	Black Limestone
Average Feed Rate	33 Lb/Hr (Dry Solids Basis)
Oxidizing-Air Rate, Average	3000 CC/Minute
Pressure Maintained in System	90 PSI
Total Operating Time	8 Hours
Average Leach Temperature	240 F

Concentration of Ammonia Compounds in the Leaching Solution

Assay, grams per liter				
Total Ammonia	Free Ammonia	Total Carbon Dioxide	Ammonium Carbonate	Ammonium Bicarbonate
30.6	0	42.3	80.2	10.0

Tower	Elapsed Leaching Time, hr	Average Extraction of Uranium, Residue		Average Concentration of Ammonia Compounds in the Pregnant Liquor, Assay, grams per liter				
		Assay, U, %	Extraction, U, %	Total NH ₃	Free NH ₃	Total CO ₂	(NH ₄) ₂ CO ₃	NH ₄ HCO ₃
2	1.25	0.034	87.5	29.9	0	39.8	82.0	3.8
3	2.50	0.024	91.2	30.5	2.6	35.9	78.4	0
4	3.75	0.023	91.5	30.7	2.6	36.2	79.0	0
5	5.00	0.021	92.3	26.0	7.1	24.4	53.2	0
Discharge	6.25	0.020	92.6					

TABLE 5. METALLURGICAL DATA FROM SECTION 4 OF TEST 3

The Effect of Ammonium Carbonate Concentration
in the Leaching Solution on the Extraction of
Uranium by a Pressure Leach

Test Conditions: Feed	Black Limestone
Average Feed Rate	33 Lb/Hr (Dry Solids Basis)
Oxidizing-Air Rate, Average	3000 CC/Minute
Pressure Maintained in System	90 PSI
Total Operating Time	8 Hours
Average Leach Temperature	240 F

Concentration of Ammonia Compounds in the Leaching Solution

Assay, grams per liter				
<u>Total</u> <u>Ammonia</u>	<u>Free</u> <u>Ammonia</u>	<u>Total</u> <u>Carbon Dioxide</u>	<u>Ammonium</u> <u>Carbonate</u>	<u>Ammonium</u> <u>Bicarbonate</u>
46.2	--	74.8	98.0	54.0

Tower	Elapsed Leaching Time, hr	Average Extraction of Uranium, Residue		Average Concentration of Ammonia Compounds in the Pregnant Liquor, Assay, grams per liter				
		Assay, U, %	Extraction, U, %	Total NH ₃	Free NH ₃	Total CO ₂	(NH ₄) ₂ CO ₃	NH ₄ HCO ₃
2	1.25	0.025	90.7	38.0	7.4	39	86	0
3	2.50	0.025	90.7	40.0	5.0	45	97	0
4	3.75	0.023	91.5	40.0	10.2	38	83	0
5	5.00	0.021	92.3	39.0	9.0	38	84	0
Discharge	6.25	0.021	92.3					

TABLE 6. THE EFFECT OF ADDING CARBON DIOXIDE DURING
THE LEACHING PERIOD ON THE EXTRACTION OF
URANIUM BY A PRESSURE LEACH

Test Conditions: Feed	Black Limestone Ore
Average Feed Rate	34 Lb/Hr (Dry Solids Basis)
Oxidizing-Air Flow	3000 CC/Minute
Pressure Maintained in Towers	90 PSI
Total Operating Time	8 Hours
Leach Temperature	240 F

Concentration of Ammonia Compound in the Leaching Solution								
<u>Assay, grams per liter</u>								
	<u>Total Ammonia</u>	<u>Free Ammonia</u>	<u>Total CO₂</u>	<u>Ammonium Carbonate</u>	<u>Ammonium Bicarbonate</u>			
	30.5	0	44.1	78.3	9.9			

Tower	Elapsed Leaching Time, hr	Average Extraction of Uranium, Residue		Average Concentration of Ammonia Compounds in the Pregnant Liquor, Assay, grams per liter				
		Assay, U, %	Extraction, U, %	Total	Free	Total	(NH ₄) ₂ CO ₃	NH ₄ HCO ₃
				NH ₃	NH ₃	CO ₂		
<u>No Carbon Dioxide Added</u>								
2	1.25	0.034	87.5	29.9	0	39.8	81.6	3.8
3	2.50	0.024	91.2	30.5	2.5	35.9	78.1	0
4	3.75	0.024	91.2	30.4	2.7	32.6	77.5	0
5	5.00	0.021	92.3	27.0	7.6	24.4	53.2	0
Discharge	6.25	0.021	92.3					
<u>Carbon Dioxide Added at the Rate of 1 Cubic Foot per Hour</u>								
2	1.25	0.041	84.8	28.7	0	40.4	74.0	11.6
3	2.50	0.039	85.6	29.1	0	40.9	75.1	11.6
4	3.75	0.037	86.3	28.7	0	40.0	74.5	10.5
5	5.00	0.032	88.2	26.8	1.6	32.6	71.0	0
Discharge	6.25	0.033	88.0					

The Effect of Adding a Mixture of Carbon Dioxide and Oxygen
to the Air in the Towers on the Extraction of Uranium

Although addition of carbon dioxide to the system stabilized the bicarbonate concentration of the leach solution, the extraction of uranium was not improved over that obtained when air alone was added to the system. Therefore, a series of tests was run to determine whether increasing the partial pressure of oxygen in the system would improve the extraction of uranium. In this test, sufficient oxygen was added to the air to increase the oxygen content of the air to 30 per cent, while 500 cubic centimeters of carbon dioxide per minute was added to the towers. In this test, 90 per cent of the uranium was extracted from the Black Limestone ore. Although this extraction is an improvement over the 88 per cent extraction obtained with air and carbon dioxide, it is not a significant improvement, considering that, with air alone, 93 per cent of the uranium was extracted readily.

The Effect of Leaching Temperature on the
Extraction of Uranium by a Pressure Leach

The small-scale leaching tests showed that a leaching temperature of 225 to 250 F was optimum for the extraction of uranium by an ammonium carbonate leach. However, examination of the data obtained from the first three tests in the continuous plant indicated that leaching temperatures in excess of 225 F might be detrimental to the extraction of uranium by this process. For this reason, a series of tests was made in which the leaching temperature was varied over a range of 180 to 250 F, while maintaining the other variables at values comparable to the previous tests. The data obtained from this work are presented in Table 7, which indicates that, under the conditions employed, optimum extraction of uranium was obtained at a leach temperature of about 220 F. For example, these data show that, as the leaching temperature was increased from 180 F to about 220 F, the extraction of uranium was increased to about 92 per cent. If, however, a leaching temperature of 250 F were employed, the extraction of uranium decreased to about 89 per cent. It is believed that, in the ammonium carbonate pressure-leaching system, temperature has two effects on the extraction of uranium: (1) in the range 180 to 220 F, temperature affects the rate of reaction between the ammonium carbonate and the uranium minerals; and (2) with the knowledge that ammonium uranyl carbonate decomposes at 212 F under atmospheric pressure, it is believed that, in the pressure-leaching system, temperatures above 220 F probably decompose the ammonium uranyl carbonate formed by reaction of the ammonium carbonate with the uranium minerals in the ore. At temperatures above 220 F, higher operating pressures should prevent decomposition of ammonium uranyl carbonate, ultimately resulting in extraction of nearly all of the uranium.

TABLE 7. THE EFFECT OF LEACHING TEMPERATURE ON THE
EXTRACTION OF URANIUM BY AN AMMONIUM
CARBONATE PRESSURE LEACH

Tower	Elapsed Leaching Time, hr	Residue	
		Assay, U, %	Extraction, U, %
<u>Leaching Temperature, 180 F</u>			
2	1.25	0.037	86.3
3	2.50	0.035	87.1
4	3.75	0.030	88.9
5	5.00	0.031	88.5
Discharge	6.25	0.032	88.2
<u>Leaching Temperature, 220 F</u>			
2	1.25	0.040	85.2
3	2.50	0.028	89.6
4	3.75	0.027	90.0
5	5.00	0.026	90.4
Discharge	6.25	0.021	92.3
<u>Leaching Temperature, 245 F</u>			
2	1.25	0.037	86.3
3	2.50	0.033	87.8
4	3.75	0.031	88.5
5	5.00	0.031	88.5
Discharge	6.25	0.029	89.3

Discussion of Tests on the Black Limestone Ore

Based on the operation of the pressure-leaching vessels for periods of 72 to 96 hours on a continuous basis and for a total time of about 300 hours, the leaching vessels gave very satisfactory performance from a mechanical standpoint.

From a technical standpoint, the test program has demonstrated that the ammonium carbonate pressure leach is capable of extracting 93 per cent of the uranium from the Black Limestone ore.

A small-scale test in the autoclave employing a chemical oxidizing agent gave an extraction of 95 per cent of the uranium. On the basis that this extraction represents the maximum extraction of uranium obtainable by an ammonium carbonate leach, it appears that further tests are not warranted, at this time, to increase the extraction of uranium from 93 per cent to 95 per cent.

The tests where oxygen and carbon dioxide were added to the system along with the air have demonstrated the effect of oxygen partial pressure on the amount of uranium extracted by the process. However, with either gas, the extractions were not improved over that obtained with air alone.

PRECIPITATION OF URANIUM FROM AMMONIUM CARBONATE PREGNANT LIQUOR WITH STEAM

In conjunction with the pressure-leaching unit, a small steam-stripping tower for the continuous precipitation of uranium by steam stripping has been constructed at Battelle. This precipitation unit consists of a tower 1 foot in diameter and 7 feet high. The upper half of the tower is equipped with baffle plates. The bottom half of the precipitator is provided with discharge ports at 1-foot intervals so that the stripped liquor and precipitate may be maintained at any level from 1 to 3 feet.

The operation of the steam precipitator is as follows: Steam enters through the bottom of the unit and the pregnant liquor is fed into the top. A bed of stripped liquor is built up to the desired operating level and, by adjusting the feed rate and steam input, ammonia is driven out of the pregnant liquor. This decreases the pH of the solution to a level optimum for the precipitation of uranium. The exhaust steam carrying the ammonia vapors passes through a water-cooled condenser and the ammonia is absorbed in water as ammonium hydroxide.

Data obtained from small-scale precipitation tests showed that uranium starts to precipitate from ammonium carbonate leach liquors at a pH

of about 8.9 and precipitation is accelerated as the pH of the solution is decreased to about 7.0, which appears to be the optimum point for maximum precipitation. A pH lower than 7.0 causes the precipitated uranium to redissolve in the barren solution.

A cursory test was made to determine the effect of pH on the precipitation of uranium in the continuous precipitator. This test was made by obtaining samples of the stripped liquor in the unit as the pH was decreased from about 9.0 to 7.0. The following tabulation presents the data obtained from this work:

Solution pH	Assay, U, gpl(a)	Assay, NH ₃ , gpl	Precipitation of Uranium, %
9.1 (Start)	1.9	15.0	0
8.6	0.033	0.5	98.7
8.1	0.003	0.5	99.8
7.5	0.001	0.5	99.9
7.0	0.001	0.5	99.9

(a) Feed assayed 1.9 grams of uranium and 15.0 grams of ammonia per liter.

This tabulation shows that the optimum pH for the precipitation of uranium on a large scale is in the pH range 7 to 8, at which point more than 99 per cent of the uranium is precipitated by the steaming process.

Having established the conditions required for optimum precipitation of uranium in the continuous unit, a second test was made on a somewhat larger scale to obtain additional operating data. This test was made by operating the precipitator continually for a period of about 9 hours. During this period, ammonium carbonate pregnant liquor, which assayed 2.0 grams of uranium per liter, was employed as feed. The feed rate was maintained at about 32 liters per hour, and the stripped liquor was discharged at a pH of 7.0 to 7.5. The results of this test showed that the stripped liquor assayed 0.005 gram of uranium per liter over a 9-hour period. More than 99 per cent of the uranium was precipitated and recovered in a product assaying 82 per cent U₃O₈ and 11 per cent vanadium pentoxide. In this test, no attempt was made to obtain a balance on the ammonia recovery; however, future work is planned to obtain data that will show how much of the ammonia can be recovered in a form which, after recarbonation, would be suitable as a leach solution for fresh ore.

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FUTURE WORK

The immediate future work will consist of experimental tests in the plant to determine the leaching conditions for maximum extraction of uranium by an ammonium carbonate pressure leach of the Mineral Joe ore. Following this work, tests are planned to obtain similar data on the Cal Uranium ore. Additional studies are planned to obtain more data on the precipitation of uranium by supplementing air for part of the steam and to obtain more data on the recovery of uranium and ammonia from this process.

The long-range future-work program consists of expanding the plant to a point where it will continuously produce a precipitate from the pregnant liquors. This will be done by integration of three thickeners for counter-current washing of the leached pulps with the steam precipitation unit and the additional ammonia-recovery unit.

The experimental work discussed in this report is based on data recorded in Battelle Laboratory Record Book No. 10233, pages 7 to 61, inclusive. This work was done during the period March 2, 1955, to April 8, 1955. In addition to the authors, the following personnel contributed to the operation of the continuous plant for ammonium carbonate leaching of the Black Limestone ore:

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APPENDIX

DETERMINATION OF COMBINED
AMMONIA-AMMONIUM SALTS

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DETERMINATION OF COMBINED
AMMONIA-AMMONIUM SALTS

Strong bases decompose ammonium salts, liberating ammonia. This may be distilled off into standard acid or a saturated solution of boric acid (neutral to methyl orange) and titrated with a standard acid.

The procedure is presented in Scott's "Standard Methods of Chemical Analysis" under "Nitrogen" ("Volumetric Methods for the Determination of Ammonia", pages 638, 639, and 648).

Volatile Ammonia. Determined by distillation of the ammonia into an excess of standard acid or 40 ml of saturated boric acid solution. With the exception that caustic soda is omitted in this determination, the details are the same as for total ammonia as stated in the next paragraph.

Total Ammonia. The combined and volatile ammonia content of the liquor is ascertained by its total ammonia content.

Ten to 25 ml of the sample are diluted to about 250 ml in a distilling flash with a potash connecting bulb; 20 ml of 5 per cent sodium hydroxide are added and about 150 ml of solution distilled into an excess of sulfuric acid. The excess is then titrated according to the standard procedure for ammonia.

Alternative. 40 ml of saturated boric acid solution may be used in place of the sulfuric acid; then the ammonia is titrated with methyl red indicator and standard 0.1 normal HCl.

Combined ammonia is the difference between the total and the volatile ammonia:

$$1 \text{ ml of } N \cdot H_2SO_4 = 0.01703 \text{ gram } NH_3$$

$$\text{or } HCl = 0.01703 \text{ gram } NH_3$$

$$1 \text{ ml of } N/10 \text{ HCl} = 0.001703 \text{ gram } NH_3 .$$

CALCULATIONS

Having determined the total ammonia, volatile ammonia, and carbon dioxide (by evolution and collection in a train), the following calculations may be made to show the amount of ammonium carbonate and ammonium bicarbonate present in the solution. Because the carbonate and bicarbonate ions can exist only within certain limits of the molar ratio of $\text{CO}_2:\text{NH}_3$, three alternative calculations are required. The following equation determines the molar ratio:

$$\text{Molar ratio} = \frac{0.387 \times \text{CO}_2}{\text{NH}_3} .$$

Equations and Relation of Molar Ratio to Existence
of Ammonium Carbonate, Ammonium Bicarbonate, Free
Ammonia, and Free Carbon Dioxide

Calculation of Ammonium Carbonate
and Ammonium Bicarbonate

If molar ratio of $\text{CO}_2:\text{NH}_3$ is over 1, the solution contains NH_4HCO_3 plus some free CO_2 . To determine the amount of each component present, calculate as follows:

A-3 and A-4

$$\text{g/l NH}_3 \times 4.58 = \text{g/l NH}_4\text{HCO}_3$$

$$\text{g/l CO}_2 - 2.59 \times \text{g/l NH}_3 = \text{g/l free CO}_2.$$

If the molar ratio of $\text{CO}_2:\text{NH}_3$ is between 0.5 and 1, the solution contains both $(\text{NH}_4)_2\text{CO}_3$ and NH_4HCO_3 . To determine the amount of each component, calculate as follows:

$$5.643 \times \text{g/l NH}_3 - 2.18 \times \text{g/l CO}_2 = \text{g/l } (\text{NH}_4)_2\text{CO}_3$$

$$3.592 \times \text{g/l CO}_2 - 4.648 \times \text{g/l NH}_3 = \text{g/l NH}_4\text{HCO}_3.$$

If the molar ratio $\text{CO}_2:\text{NH}_3$ is less than 0.5, the solution contains $(\text{NH}_4)_2\text{CO}_3$ plus free NH_3 . To determine the amount of each component, calculate as follows:

$$\text{g/l CO}_2 \times 2.18 = \text{g/l } (\text{NH}_4)_2\text{CO}_3$$

$$\text{g/l NH}_3 - 0.775 \times \text{g/l CO}_2 = \text{g/l free NH}_3.$$

CMW:BGL:FMS/ims