SEMI-PILOT OPERATION OF THE
AMMONIUM CARBONATE LEACHING PROCESS

By

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ABSTRACT

A process utilizing ammonium carbonate as a lixiviant for uranium and steam stripping as a means of recovery of the values has been tested. Some data are given on both leaching and precipitation aspects of the flowsheet.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	4
SUMMARY AND CONCLUSIONS	5
EQUIPMENT AND FLOWSHEET	6
SHAKEDOWN RUN (MONTICELLO STOCKPILE 6)	11
SECOND RUN (LA SAL ORE)	16
PRECIPITATION	22
APPENDIX: EFFECT OF VANADIUM ON URANIUM EXTRACTION DURING AMMONIUM CARBONATE LEACHING	25

INTRODUCTION

A process which involves leaching a uranium ore under pressure with ammonium carbonate and ammonium bicarbonate as lixiviants has been proposed for testing in the Grand Junction Pilot Plant by the Battelle Memorial Institute (BMI-282 and BMI-283).

Ore is prepared by conventional crushing and wet or dry grinding. The leaching step, however, departs from conventional practices in that it is accomplished by forcing the pulp through a large diameter pipe under pump pressure. The pipe, which is installed as a series of vertical columns, is of such a length as to give the desired retention time. The leached pulp is then discharged into a countercurrent decantation system to effect the recovery of a pregnant leach liquor. The recovery of values from the leach liquor is accomplished by removing the ammonia and carbon dioxide from the liquor by steaming, thereby causing the uranium to become insoluble and precipitate. The volatilized ammonia is recovered by conventional methods.

The results of the test work done at Battelle were promising enough so that the Raw Materials Division of the U. S. Atomic Energy Commission became interested in the possibility of erecting facilities at Grand Junction to evaluate the process on a pilot plant scale. At their request, the test equipment used at Battelle was moved to Winchester for the purpose of further study which would give the National Lead Company personnel an opportunity to become familiar with the process as well as to enable them to make suggestions for the pilot plant design work being done at Battelle.

The work discussed in this report was performed on two ores. A sample of Monticello Stockpile Number 6, designated as Sample 48-7 by the Winchester Laboratory, was used for the preliminary work. Since this work was designed primarily to shake down the equipment and train the operating personnel, no attempt was made to obtain complete metallurgical data. The second ore studied was a 7.5-ton sample of La Sal ore which was received from the Grand Junction Pilot Plant. This ore was designated as Sample 189-9 in the laboratory records.

SUMMARY AND CONCLUSIONS

The Battelle Memorial Institute's ammonium carbonate leaching process equipment has been set up and operated at the Winchester Laboratory. Most of the equipment, with the exception of the grinding circuit, was fabricated and initially operated at Battelle. At the request of the U. S. Atomic Energy Commission, this equipment was shipped to Winchester for further testing. The process, as proposed by Battelle, is somewhat unique in that leaching is carried out continuously and at elevated temperatures in vertical towers without agitation except for a small amount of air added primarily for oxidation. Two ores were tested; one (Stockpile Number 6 from Monticello) was found to be non-amenable to the process. Extractions were poor and the physical properties of the pulp were such that the towers became inoperable due to the accumulation of sand. Other ores, which were subjected to a routine ammonium carbonate laboratory amenability test, were also found to be non-amenable. (See Appendix A.) The second ore (La Sal) tested in the BMI equipment gave satisfactory extractions and little or no sand classified out in the towers. There were, however, other aspects which presented difficulties; one of these was the feed pump. The pump was a Milton Roy piston-type with double ball valves. Considerable wear was noticed on both piston and valves. This pump is a weak point in the equipment flowsheet which must be corrected to avoid an expensive maintenance problem. Another mechanical weakness was in the pressure let-down system. Here, serious erosion occurred as well as stoppage due to the deposition of sublimed ammonium salts.

The flowsheet incorporated conventional grinding and liquid-solid separation equipment.

Precipitation of uranium and recovery of ammonia is done by steaming the pregnant liquor. The steam requirement was found to be 3600 to 4000 pounds of steam per ton of ore. This would amount to a substantial cost item, but might be reduced by using more efficient equipment or by changing the flowsheet to reduce the volume of solution to the stripping unit.

As a result of the test work at the Winchester Laboratory, it can be said that the process is novel, but probably not economically attractive when compared to more conventional sodium carbonate methods in use.

EQUIPMENT AND FLOWSHEET

For purposes of discussion, the equipment used will be described under three sections: grinding, leaching, and precipitation. Except for the grinding circuit, the equipment was assembled from components received from Battelle.

Grinding

The circuit was designed to treat 1000 pounds of ore per day, but during the test work a maximum of about 750 pounds per day was ground.

A portable bin, constructed with a slide in the bottom, was filled with ore which had been received in barrels. The bin was placed in position over a vibrating ore feeder and the slide opened. A small hopper between the ore bin and feeder provided feed during the period of time the barrel was being refilled. The vibrating feeder conveyed the ore at the desired rate to a mixing tank. This tank was constructed from a 10-inch length of eight-inch pipe with a steel plate welded on one end. Agitation was furnished by a six-inch paddle, driven at 240 rpm by a one-fourth horsepower "Ratiomotor". A valve regulated the amount of water to the mixing tank. The ore feed was conducted from the mixer to the ball mill by rubber hose. The hose was held rigidly to the mill at one end and to a nipple which turned in a ball bearing at the other. The bearing, in turn, was held by a shell brazed to the mixing tank. The pulp passed through a nipple welded to the mixing tank into the hose. The flow was by gravity as the mixer discharge was several inches above the rod mill.

The rod mill was constructed from a piece of 12-inch pipe with four, one-half inch by one-half inch lifters welded inside. Flanges were welded to each end and blind flanges about two inches greater in diameter were bolted to these. The mill rolled on the blind flanges. Two-inch pipe nipples in each end of the mill served as feed and discharge connections. The mill was turned at 65 rpm on rollers, chain-driven from a one-half horsepower "Ratiomotor". The rod charge was about 125 pounds of carbon steel rods of various diameters from one-quarter inch to one and one-half inches. The mill discharged by gravity into a holding tank having a conical bottom. The holding tank was 12 inches in diameter and three feet high. The pulp was pumped from the holding tank by a Denver diaphragm pump having an eight-inch Neoprene diaphragm and three-quarter-inch pipe fittings. The pulp flowed from the pump through one inch Uscolite pipe to a Sweco separator.

The Sweco separator (Model G-1D-5) was equipped with a 94-mesh stainless steel wire screen cloth having a wire opening of 0.0071 inches and a wire diameter size of 0.0035 inches. The screen was 18 inches in diameter. The separator power was furnished by a one-quarter horsepower, 115 volt, one phase, 60 cycle, 1200 rpm motor.

The plus 94-mesh material was recycled to the mixing tank ahead of the rod mill while the 94-mesh material was discharged into the well of a thickener by gravity. The thickener was 48 inches in diameter and had an 18-inch depth at the center and a 13-inch depth at the overflow. The rake was driven by a one-sixth horsepower motor at 0.4 rpm. Facilities for the addition of a flocculating agent and ammonium carbonate solutions were provided between the screen and the thickener.

Leaching

The thickened ore pulp was pumped from the thickener by a Denver pump having an eight-inch Neoprene diaphragm. Two tanks were provided for receiving the pulp, each being one-foot in diameter and 18-inches high. A launder was constructed above and between the tanks so that the tanks could be alternately filled. Agitation was furnished by a three-inch paddle driven at 1725 rpm by a one-sixth horsepower motor. Each tank had a half-inch diameter outlet which was connected so that either tank could supply the tower feed pump. Originally, a piston-type positive displacement Milton Roy pump, designated by the manufacturer as a MDL-25-26 Simplex pump, was used to convey the pulp from the conditioning tanks to the leaching towers. The pump was equipped with double-ball check valves to insure a positive seal and was capable of discharging against a pressure of 150 psi. The suction connection was one-half inch in diameter, and the discharge connection was three-eighths inch in diameter. The ball seats were constructed of 18-8 stainless steel and the ball valves of 440 stainless steel. Some difficulty with erosion of the valve seats was experienced which led to the testing of another pump. This pump was a Model 7502 Madden metering pump having a solution head of 316 stainless steel. The Milton Roy pump had been received with the other leaching equipment from Battelle Memorial Institute and had been used for an unknown length of time in their test work. We did not use either pump long enough to be able to evaluate their performances. The pulp, on leaving the pump, was introduced into leaching towers of which there were five connected in series. Each tower was 10 feet in height with an inside diameter of four inches; the material of construction was iron. The volume of each tower is 0.87 cubic foot, or an overall volume of 4.35 cubic feet in the five towers. Connection from one to the

other was by one-half inch iron pipe arranged so that the pulp was pumped into the bottom and out of the top of each successive tower. The lower five feet of each tower was jacketed for steam heating of the pulp. The towers were insulated, with the exception of the transfer pipes. A manifold for steam distribution was constructed at the five-foot level of the towers. Steam was fed from the manifold to the towers through one-half inch valves. By this arrangement, it was possible to control the steam in any tower. The condensate was collected from the bottom of the jacketed portion of the towers and discharged through a steam trap.

Each tower had facilities for the introduction of air at both the five-foot level and the tower bottom. However, during the test work, air was introduced only at either the first or second tower. Air was supplied at 200 psi and metered by a Brooks Rotameter (Type 1100), having a range of 1,000 to 13,000 cc per minute.

Samples could be removed from either the top or bottom of the towers through valves.

Thermocouple wells were located at the bottom and top of each tower.

The leached pulp flowed out of the top of the last tower into a wet cyclone. The cyclone had an overall height of 25 inches with the lower five inches being conical. The diameter was six inches. The purpose of the cyclone was to effect a separation of gas and pulp; hence, an outlet was provided at the top for gas, and the pulp flowed out of the bottom into a receiving tank. Two baffles were installed in the upper third of the cyclone to prevent pulp carry-over with the gas.

The receiving tank was constructed of a piece of four-inch flanged iron pipe which was 35 inches long. The lower flange had an attached conical section which was five inches long and tapered to a half-inch opening at the bottom. A ceramic float controlled the level of the pulp within the desired limits by using a "Magnetrol" liquid level control (Model A-150). The "Magnetrol" triggered an Asco solenoid (Catalog Number 83141) which, in turn, actuated an air-operated Bendix Westinghouse diaphragm valve. Air from this valve actuated a 500 series, half-inch cast iron Saunders type Hills-McCanna neoprene diaphragm valve. The Westinghouse valve was operated at 20 psi.

The flow of gas from the system was controlled by a Bristol pressure controller (Model Number 93) with a Helix range of zero to 300 psi. The valve was operated by five pounds of air

pressure. The Bristol valve controlled the pressure in the towers by holding the total pressure as desired and intermittently bleeding gas through the discharge valve. The discharge valve was a Hammel Dahl (Type 7705), one-half inch in size and with a diaphragm control operating under a maximum diaphragm pressure of 50 psi.

Precipitation Unit

The precipitation unit consisted of a tower, one foot in diameter and seven feet high. The upper half of the tower was equipped with seven baffle plates each having four radial slots. The bottom half of the precipitator was provided with discharge ports at one-foot intervals so that the stripped liquor and precipitate might be maintained at any level from one to four feet. Facilities were provided at the bottom to admit air and/or steam. Wells for the insertion of thermometers were provided at suitable intervals over the seven-foot height. The exterior wall of the tower was insulated with magnesite. Two condensers, each being a three-inch jacketed pipe filled with berl saddles, were attached in series to the side of the tower and connected to the gas discharge line which came out of the tower top. The condensate was collected from the bottom of the second condenser.

FIGURE 1

Pilot Plant Flowsheet Used at Winchester

SHAKEDOWN RUNMonticello Stockpile Number 6

The ore was a calcareous gray sandstone which contained carbonates, iron oxides, and hydrocarbons. The uranium was present mostly as carnotite in a matrix of clay. The chemical analysis is shown in Table I.

Table IChemical AnalysisMonticello Stockpile Number 6Sample 48-7

<u>Element</u>	<u>Per Cent</u>
U ₃ O ₈	0.257
CaO	6.39
V ₂ O ₅	1.66
MgO	3.82
Fe	1.99
SiO ₂	66.0
Total Sulfur	0.42
Sulfide Sulfur	0.085

Initially, an attempt was made to grind the ore in the open-circuit rod mill and after the addition of leaching reagents, the conditioned pulp was fed directly to the towers. Sanding occurred almost immediately in the first tower of the series as indicated by a pressure buildup at the tower feed pump. Flushing of the columns showed heavy sand at the bottom of the first tower.

The next approach was to install a small drag classifier and a four-foot thickener in closed circuit with the rod mill. The thickener underflow was pumped to the conditioning tanks where the leaching reagents were introduced. Composite tower feed resulting from this grind and tower discharge screen analyses are shown in Table II. The composite samples cover a 24-hour period of operation.

The data from Table II indicate the loss of the coarser particles in the leaching system and point to an eventual plugging of the towers. It was obvious that a more efficient method for the separation of the coarse particles would have to be employed. This was accomplished by installing a Sweco screen in place of the classifier. A typical screen analysis of the pulp feed and pulp discharge using this procedure is shown in Table III.

Table II

Screen Analyses of Composite Tower Feed and
Tower Discharge Samples for
Two 24-Hour Periods

<u>Sample</u>	<u>Screen Size</u>					
	<u>+65</u>	<u>-65 +100</u>	<u>-100 +150</u>	<u>-150 +200</u>	<u>-200 +270</u>	<u>-270</u>
Feed	2.09	7.00	13.81	11.39	6.13	59.58
Discharge	1.29	4.03	11.02	13.19	5.85	64.62
Feed	1.91	7.72	14.92	10.24	6.12	59.09
Discharge	1.12	5.13	12.26	12.50	7.29	61.7

Note: Results in weight, per cent.

Table III

Screen Analyses of Ore Pulp Tower Feed and
Tower Discharge

<u>Sample</u>	<u>Screen Size</u>				
	<u>+65</u>	<u>-65 +100</u>	<u>-100 +150</u>	<u>-150 +200</u>	<u>-200</u>
Feed	0.04	2.28	13.38	12.01	72.29
Discharge	0.02	1.93	11.63	11.79	74.63

Note: Results in weight, per cent.

An improvement in the feed is shown by the data although the possibility of sanding after an extended operation is still present.

The pressure in the leaching towers was controlled by the Bristol valve in the pressure let-down system. This valve was set at 90 psi which meant that the pressure at the discharge end of the towers was maintained at 90 psi. However, the pressure on the pump at the feed end was about 120 psi due mainly to the hydrostatic head. In this report, a reference to pressure means the pressure at the let-down system as the pulp and gas were being discharged.

During the initial work on 48-6 ore, the air which was used as the oxidant was fed at 3000 ml per minute at 120 psi to the bottom of the Number One tower. Sanding in the bottom of the Number One tower resulted in a gradual pressure buildup on the feed pump and necessitated constant adjustment and increase in

the air pressure. Failure to adjust the air pressure resulted in the pulp backing up into and clogging the air line. Since there was a possibility that the admission of air to the bottom of the Number One tower was a contributing factor to the sanding phenomenon, a run was made in which the air was fed to the bottom of the Number Two tower. Sanding in the Number One tower again caused a shutdown after three days of operation. The air was therefore changed back to the Number One tower.

The remainder of the test work was done using 3000 cc of air per minute at 140 psi, with the plant to be shut down for cleaning when the pressure at the feed pump reached this point. Continuous operation for as long as five days was maintained.

The reagents were added to the conditioning tanks in the solid form with the concentration being 10 per cent ammonium carbonate and two per cent ammonium bicarbonate. However, an analysis of the reagents, which were of technical grade and purchased locally, showed that the ammonium carbonate salt contained more ammonium bicarbonate than ammonium carbonate and could be considered a carbamate. An analysis of the ammonium bicarbonate salt indicated that the ammonia and carbon dioxide were present in nearly stoichiometric amounts. The analytical data are shown in Table IV.

Table IV

Chemical Analysis of Ammonium Leaching Reagents

	<u>Theoretical %</u>		<u>Actual %</u>	
	<u>NH₃</u>	<u>CO₂</u>	<u>NH₃</u>	<u>CO₂</u>
NH ₄ HCO ₃ ·NH ₂ CO ₂ NH ₄	32.5	56.0	28.2	55.7
NH ₄ HCO ₃	21.6	55.7	21.6	55.8

The equation for a water solution of ammonium carbamate reagent would be as follows:

If 100 grams of the ammonium carbamate compound were dissolved in water to make a 10 per cent (NH₄)₂CO₃ solution, the solution would actually contain 61 grams per liter of (NH₄)₂CO₃ and 50 grams of NH₄HCO₃ per liter.

If the ammonium salt available here were dissolved in water in an attempt to obtain a solution of the same concentration (10

per cent $(\text{NH}_4)_2\text{CO}_3$, the solution would have 37.4 grams $(\text{NH}_4)_2\text{CO}_3$ and 69.6 grams of NH_4HCO_3 per liter.

The decomposition of the ammonium carbonate salts was readily evident by the strong odor of NH_3 present when a barrel was opened. The analytical results shown in Table IV were obtained on a salt sample from a freshly opened barrel. It is suspected that the results might vary from barrel to barrel or from one sample to a later sample from the same barrel.

As a result of the above data, further reagent addition was limited to 10 per cent ammonium carbonate which contained more than enough bicarbonate for leaching. The reagent was added as a solid during the test work for the sake of convenience. Cutting down on the bicarbonate concentration would have required the addition of anhydrous ammonia to the solution.

The nature of the test work on the 48-7 ore was such that little metallurgical data were collected. Since an extraction of about 10 per cent was indicated, the amenability of 48-7 ore to ammonium carbonate leaching was further investigated in the laboratory using the one-gallon autoclave. The ore was pulverized to minus 65-mesh (75 per cent minus 200-mesh) and one kilogram charges were used in the test work. The ore was leached at 50 per cent solids and 100° to 110°C . Five tests were run; oxygen was used as the oxidant in four of the tests, and air was used as the oxidant in the fifth test.

The test data in Table V indicate that under the test conditions, the important variable is the concentration of the lixivants.

Table V

Pressure Leaching of Ore in the Laboratory Autoclave

Oxygen Pressure psi	Leach Time, Hours	Grams/Liter		% U_3O_8 Ext'n
		$(\text{NH}_4)_2\text{CO}_3$	NH_4HCO_3	
250	4	100	20	16.0
300	4	200	---	36.9
700 ^{1/}	4	200	100	68.8
245	4	200	100	68.2
245	6	200	100	67.6

^{1/} Air pressure.

Since the uranium extraction failed to reach a satisfactory figure, five additional tests were run using sodium carbonate as the leaching reagent.

The leaching was done using one kilogram charges as in the ammonium carbonate leach. The sodium carbonate concentration was five per cent; the sodium bicarbonate was two per cent. The first test was run in the autoclave for four hours with the ore pulped at 30 per cent solids, a temperature of 100° to 110°C and an air pressure of 100 psi. The air was bled from the autoclave at the rate of two cubic feet per minute. The resulting extraction was 95.2 per cent of the contained uranium values.

The remaining four tests were run at 40 per cent solids at atmospheric pressure. The test work was done in jacketed reaction flasks with the pulp temperature maintained at 80°C. Air was bubbled through the pulp for oxidizing purposes.

The test data given in Table VI show that after 48 hours an extraction of 95.2 per cent of the uranium was obtained.

Table VI

Atmospheric Leaching of Ore Using
Five Per Cent Sodium Carbonate and Two
Per Cent Sodium Bicarbonate

<u>Time, Hours</u>	<u>% U₃O₈ Extraction</u>
24	91.5
48	95.2
72	95.2
96	96.7

Most of the ores giving low extractions contain vanadium and it is possible that vanadium may interfere under the conditions used in ammonium carbonate systems. This is the subject of a current laboratory investigation. A preliminary report on this investigation is presented as Appendix A.

SECOND RUNLa Sal Ore

After the initial shakedown run, the process was operated using a sample of La Sal ore (Sample 189-9). This ore handled nicely in the towers for a period of about two weeks, six days of which were on a continuous basis. A total of 4,462 pounds of ore was leached. The chemical analysis is shown in Table VII.

Table VIIChemical Analysis

La Sal Ore
Sample 189-9

<u>Element</u>	<u>Per Cent</u>
U ₃ O ₈	0.69
V ₂ O ₅	0.02
MgO	1.84
CaO	8.53
Fe	1.86
SiO ₂	61.4
Total Sulfur	0.34
Sulfide Sulfur	0.038

The ore was ground at 60 per cent solids and screened at about 30 per cent solids.

The La Sal ore presented a problem in that it was impossible to obtain a clear overflow from the thickening operation which followed the screening. It was found that it was necessary to add ammonium carbonate and Separan 2610 to the thickener feed.

The thickener underflow, at about 40 per cent solids, was pumped to conditioners where the reagent addition was made. Ammonium carbonate was added in an amount to give a solution concentration of 10 per cent.

The La Sal ore pulp was of such a consistency at 50 per cent solids that the tower feed pump could not handle it. Therefore, leaching was carried out at 40 per cent solids with the pulp pumped at an average rate of 22 pounds of ore per hour. This flow rate gave a retention time in the towers of about 8.5 hours.

Oxidation was effected by introducing air, at a rate of 3000 cc per minute and a pressure of 140 psi, into the bottom of the Number One tower. The excess air was bled from the towers through the gas discharge system.

The temperature of the leach was maintained between 100° and 107°C. At this retention time and flow rate, it was possible to raise the temperature of the ore pulp to 100°C in the upper portion of the Number One column.

The pressure in the towers was considered as being 90 psi as the Bristol Regulator was set to maintain that pressure by opening or closing the valve in the pressure let-down system. The air swept a small amount of ammonia out of the system with it, but no effort was made to recover this ammonia.

Samples were withdrawn from the bottom of Towers two, three, four, and five, and a fifth sample was taken of the pulp discharge. The samples were considered to be representative of the top of the preceding tower. Samples were taken every two hours, filtered, and the residues washed with water and assayed for U₃O₈.

The data presented in Table VIII have been averaged for each shift during the period.

These data show excellent extractions and, in some cases, indicate the possibility of either increasing the feed rate or removing one tower from the circuit.

There was, however, a serious difficulty experienced during the test work. The gas discharge line required flushing with water at least once a day to remove white salts which formed in the pipe. Operation of the system longer than 24 hours resulted in a total plugging of the pipe and a subsequent rise in pressure in the leach circuit.

Chemical analyses of the white salt from the pipe indicated that it was ammonium bicarbonate. The conditions in the gas discharge line favored the formation of a salt because the gas consists of carbon dioxide and ammonia vapor from the leaching reagents, the excess of air used as an oxidant, and water vapor from the heated ore pulp.

It was felt that an increase in pressure would keep more ammonia and carbon dioxide in solution and reduce the problem of salting. However, because of the available equipment, the most attractive approach was to maintain the pressure and temperature relationships by lowering the leaching temperature. The effect of lowering the temperature is shown in Table IX. The data, as in Table VIII, are taken from a three-day run with the samples averaged for each shift.

18

Table VIII

Uranium Extractions Achieved with an Ammonium Carbonate
Pressure Leach Over a Three-Day Period

Tower 2 Residue % U ₃ O ₈		Tower 3 Residue % U ₃ O ₈		Tower 4 Residue % U ₃ O ₈		Tower 5 Residue % U ₃ O ₈		Discharge Residue % U ₃ O ₈	
<u>Assay</u>	<u>% Ext'n</u>	<u>Assay</u>	<u>% Ext'n</u>	<u>Assay</u>	<u>% Ext'n</u>	<u>Assay</u>	<u>% Ext'n</u>	<u>Assay</u>	<u>% Ext'n</u>
<u>First Day</u>									
0.32	52.5	0.12	83.7	0.061	91.2	0.059	91.5	0.031	95.6
0.26	62.3	0.18	74.0	0.085	87.8	0.021	97.0	0.020	97.1
0.30	56.6	0.16	76.9	0.073	89.4	0.039	96.8	0.021	96.7
<u>Second Day</u>									
0.48	30.4	0.27	60.9	0.088	87.1	0.051	92.6	0.024	96.5
0.23	66.6	0.015	78.3	0.085	87.7	0.046	93.4	0.021	96.7
0.17	75.4	0.71	89.7	0.029	95.8	0.020	97.1	0.018	97.4
<u>Third Day</u>									
0.51	26.0	0.13	81.2	0.069	91.0	0.028	95.9	0.014	98.0
0.31	45.0	0.13	81.2	0.047	93.2	0.024	96.5	0.014	98.0

Table IX

Effect of Lowering the Leaching Temperature on the Extraction of
Uranium with the Ammonium Carbonate Pressure Leach

Average Temp °C	Tower 2 Residue % U ₃ O ₈		Tower 3 Residue % U ₃ O ₈		Tower 4 Residue % U ₃ O ₈		Tower 5 Residue % U ₃ O ₈		Discharge Residue % U ₃ O ₈	
	<u>Assay</u>	<u>% Ext'n</u>	<u>Assay</u>	<u>% Ext'n</u>	<u>Assay</u>	<u>% Ext'n</u>	<u>Assay</u>	<u>% Ext'n</u>	<u>Assay</u>	<u>% Ext'n</u>
<u>First Day</u>										
68	--	--	0.23	66.6	0.17	75.4	0.1	85.5	0.086	87.5
73	0.38	45.0	0.17	75.4	0.12	82.7	0.082	88.1	0.090	87.0
67	0.40	42.1	0.22	68.1	0.15	78.2	0.11	84.1	0.096	86.1
<u>Second Day</u>										
73	--	--	0.35	49.4	0.19	72.5	0.13	81.2	0.095	86.2
73	0.55	20.0	0.29	58.0	0.14	79.8	0.082	88.1	0.097	86.0
69	0.45	36.2	0.33	58.2	0.23	66.8	0.16	76.9	0.17	75.4
<u>Third Day</u>										
75	--	--	0.21	69.6	0.16	76.9	0.096	86.1	0.077	88.8
74	0.56	19.0	0.30	56.6	0.16	76.9	0.09	87.0	0.076	89.0

The data demonstrate that there is a sharp drop in the rate of dissolution of the uranium values when the leaching temperature is lowered from about 107° to about 70°C.

The test work, however, served its purpose in that no further difficulty was experienced with salting in the lines. At the completion of the test, the pipes were dismantled and there were no visual indications of white salts.

A pressure let-down system designed to effect a heat exchange would probably allow the leaching operation to be performed at or about 107°C without causing sublimation in the pressure let-down equipment.

During the test work on La Sal ore, there were no operational difficulties experienced from sand deposition in the bottom of the towers.

The addition of a flocculent to the ore pulp plus the leaching reagents appeared to produce a viscous slurry which held the coarser particles in suspension. Table X shows the average size distribution of the tower feed and the tower discharge over a five-day operating period.

Table X

Composite Screen Analyses of La Sal Ore Before and
After Leaching Over a Five-Day Period

<u>Day</u>	<u>Mesh Size</u>				
	<u>+65</u>	<u>-65 +100</u>	<u>-100 +150</u>	<u>-150 +200</u>	<u>-200</u>
<u>Tower Feed</u>					
1	0.03	1.53	18.48	15.20	64.76
2	0.08	2.08	19.89	15.06	62.89
3	0.07	2.70	15.21	12.12	69.90
4	0.01	2.24	13.31	12.00	72.44
5	0.09	1.20	12.16	12.38	74.17
<u>Tower Discharge</u>					
1	0.05	0.81	12.56	13.26	73.32
2	0.05	1.65	13.98	12.71	71.61
3	0.10	2.11	18.14	13.42	66.23
4	0.07	3.61	18.9	12.23	65.19
5	0.02	1.62	10.32	14.02	74.02

Note: Results in weight, per cent.

Pulp samples were taken from the bottom of each of the five towers at the end of 12 days of operation and screen analyses were made of these products. The data are shown in Table XI.

Table XI

Screen Analyses of La Sal Ore Pulp
Taken from Tower Bottoms

<u>Tower</u>	<u>Mesh Size</u>				
	<u>+65</u>	<u>-65 +100</u>	<u>-100 +150</u>	<u>-150 +200</u>	<u>-200</u>
1	0.01	2.74	13.68	15.91	67.66
2	0.04	2.28	13.94	16.83	66.91
3	0.04	2.54	13.18	15.09	69.15
4	0.06	2.83	13.20	15.64	68.27
5	0.01	1.76	11.71	15.87	70.65

Note: Results in weight, per cent.

Since the size distribution indicates that about the same material is present in each tower and is not different than the feed, it may be said that the La Sal ore sample tested is much more amenable to the process from the standpoint of material handling than was the sample from the Monticello Stockpile.

PRECIPITATION

The initial test work was done in a batch operation. A known volume of liquor was introduced into the tower and then steam, at eight psi, was fed into the liquor through the tower bottom. Air was not used in these tests. When the temperature of the solution reached 100°C, the time measurement was started. Three tests were run under the above conditions with varying retention times.

The per cent precipitation of the uranium was calculated from the assay of the solution removed from the tower at the completion of the test, while the ammonia recovery was calculated from the assay of the ammonia in the condensate. The data are shown in Table XII.

Table XII

Batch Recovery of Uranium and Ammonia From an
Ammonium Carbonate Leach Liquor

<u>Time, Minutes</u>	<u>Solution Volume, Liters</u>			<u>% Recovery</u>	
	<u>Start</u>	<u>Barren</u>	<u>Condensate</u>	<u>U₃O₈</u>	<u>NH₃</u>
45	18.93	25.1	18.0	99.9	83.8
105	18.93	30.3	35.0	99.9	83.5
165	18.93	36.0	46.4	99.2	89.4

Feed: 2.88 grams U₃O₈ per liter; 24.8 grams NH₃ per liter

The data show excellent uranium recoveries and fair ammonia recoveries. It is to be noticed that better than a threefold increase in the contact time resulted in only a five per cent increase in ammonia recovery. An indication of the steam losses is shown by the large increase in the solution volumes at the completion of the test.

The possibility of avoiding the increases in solution volumes, by using a steam heated coil and an air sweep instead of live steam, was investigated. Because of the tower construction, it was necessary to remove the baffles before the coil could be used. The test work consisted of introducing a measured amount of liquor into the tower and heating the solution by means of the coil using 10 psi of steam. When a temperature of 100°C was reached, 3000 cc of air per minute was introduced at the bottom of the tower. The test data are shown in Table XIII.

Table XIIIUranium and Ammonia Recovery from an Ammonium Carbonate Leach Liquor by Using a Heating Coil and Air Sweep

<u>Time, Minutes</u>	<u>Solution Volume, Liters</u>			<u>% Recovery</u>	
	<u>Start</u>	<u>Barren</u>	<u>Condensate</u>	<u>U₃O₈</u>	<u>NH₃</u>
45	18.93	2.84	16.1	99.9	89.8
115	37.86	3.85	18.0	99.9	96.8

Feed: 2.88 grams U₃O₈ per liter; 29.9 grams NH₃ per liter.

It can be seen that the uranium recovery is just as good as when live steam is used and the ammonia recovery is higher than it is with live steam. There remained, however, the problem of steam consumption, which while not measured, must have been large, as indicated by the change in solution volumes.

A test series was run designed to obtain data on steam consumption. The pregnant liquor was fed into the top of the tower at a predetermined rate and varying amounts of air and steam were fed into the tower bottom. The steam consumption was calculated from the difference in the volume of the original liquor and the total volume of the condensate and the barren liquor. The data are shown in Table XIV.

Table XIVSteam Consumption While Recovering Uranium and Ammonia From Ammonium Carbonate Leach Liquors

<u>Steam psi</u>	<u>Air Liter/ Minute</u>	<u>Steam Lb/Ton Ore</u>	<u>Grams NH₃</u>	
			<u>Input</u>	<u>Recovered</u>
2.5	10	3980	287	255.8
2.5	3	3620	299	268.3
5.0	10	3820	321	269.5
5.0	5	3640	326	265.9
5.0	3	3600	313	244.6

Note: Dilution = 3.5 ton H₂O per ton of ore.

The data indicate that the steam consumption is about two pounds per pound of ore regardless of the steam and air pressure.

The ammonia shown as being recovered was that found in the condensate. It does not include the loss in the barren solution or the vaporized ammonia remaining in the tower at the end of the run. The scale of the test work and the design of the recovery equipment were such that total ammonia recovery was impossible.

APPENDIX A

WIN-37
- 26 -

National Lead Company, Inc.

RAW MATERIALS DEVELOPMENT LABORATORY

February 9, 1956

SUBJECT Effect of Vanadium on Uranium Extraction During Ammonium
Carbonate Leaching

TO G. W. Clevenger

FROM D. R. George and H. I. Viklund

REFERENCE

Early in the investigation of the extraction of uranium from ore by ammonium carbonate leaching, it was established that for many ores the extraction of uranium by sodium or ammonium carbonate solutions are strictly comparable. On the other hand, many ores which yielded uranium extractions of 95 per cent or better when leached under standard test conditions at atmospheric or elevated pressures with sodium carbonate and bicarbonate solutions yielded much lower extractions when leached under standard test conditions with ammonium carbonate-bicarbonate solutions. It was thought, at first, that the low extractions were due to insufficient reagents since uranium extractions were improved by increasing the amount of ammonium carbonate and bicarbonate in the leaching solution. As additional data were accumulated, however, it became evident that consumption of reagents by non-amenable ores was not excessive and that the ores refractory to ammonium carbonate leaching were those containing appreciable amounts of vanadium. The extent of uranium extractions from vanadiferous and non-vanadiferous ores by sodium carbonate and ammonium carbonate leaching are shown in Table I.

The standard conditions during the leaching tests were as follows:

Sodium Carbonate

Grind - Minus 65-mesh

% Solids - 50

Solution Composition - 50 grams Na_2CO_3 and 20 grams NaHCO_3 /liter

Temperature - 110°C

Pressure - 100 psi - air bleed of two cubic feet per hour

Time - Four hours

Ammonium Carbonate

Grind - Minus 65-Mesh

% Solids - 50

Solution Composition - 100 grams $(\text{NH}_4)_2\text{CO}_3$ and 20 grams NH_4HCO_3 /liter

Temperature - 110°C

Pressure - 250 psi of oxygen or 700 psi of air - no bleed

Time - Four hours

Table I

Pressure Leaching Tests

<u>Ore</u>	<u>Sample Number</u>	<u>Assay, %</u>		<u>% U₃O₈ Extraction</u>	
		<u>U₃O₈</u>	<u>V₂O₅</u>	<u>Na₂CO₃</u>	<u>(NH₄)₂CO₃</u>
Hecla	325-1	0.443	0.02	95.1	96.5
Hecla	325-2	0.184	0.03	93.5	93.5
Four Corners	321-1	0.190	0.29	95.4	95.8
Four Corners	321-2	0.337	1.07	96.5	34.9
Ralston Creek	306-1	0.616	0.03	89.5	94.0
Midnight	305-1	0.208	0.01	84.6	84.1
White Canyon	324-11	0.248	0.41	89.4	79.7
Lukachukai	17-10	0.237	0.95	98.3	33.5
Mineral Joe	88-2	0.38	1.60	98.1	7.6
Utex	75-5	0.52	0.95	95.6	78.9
Stockpile 6	48-7	0.256	1.68	95.2	16.0
Stockpile 6	48-7	0.256	1.68	95.2	36.9 ^{1/}
Stockpile 6	48-7	0.256	1.68	95.2	68.8 ^{2/}
Stockpile 6	48-7	0.256	1.68	95.2	68.8 ^{3/}
Stockpile 6	48-7	0.256	1.68	95.2	67.6 ^{4/}

^{1/} Two hundred grams of (NH₄)₂CO₃ per liter - no bicarbonate.

^{2/} Two hundred grams of (NH₄)₂CO₃ + 100 grams of NH₄HCO₃ per liter - 700 psi of air pressure.

^{3/} Two hundred grams of (NH₄)₂CO₃ + 100 grams of NH₄HCO₃ per liter.

^{4/} Same as Footnote 3 but leached for six hours.

As is evident from Table I, the extraction of uranium by ammonium carbonate solutions varies inversely with the vanadium content of the ore. A series of tests was therefore made to determine the effect of added vanadium on the extraction of uranium with ammonium carbonate solutions from ores of low vanadium content. The leaching conditions were as previously described and vanadium was added as ammonium vanadate. The results of these tests are shown in Table II.

Table IIEffect of Added Vanadium on Uranium Extraction
with Ammonium Carbonate Solutions

<u>Vanadium Added Grams/Liter</u>	<u>Sample Number</u>	<u>% U₃O₈ Extraction</u>
0.0	321-1	95.8
2.0	321-1	80.0
10.0	321-1	75.8
0.0	306-1	94.0
0.5	306-1	89.3
2.0	306-1	87.2
5.0	306-1	86.3

The data in Table II show that while the addition of vanadium decreased the extraction of uranium, the effect was not the same for both ores, and the decrease in extraction was less than was anticipated for the amount of vanadium added. Further evaluation of the data showed that the lowest extractions were obtained from ores in which a major portion of the uranium is present as carnotite and other uranium-vanadium minerals. A test was therefore made to determine the solubility of synthetic carnotite in sodium and ammonium carbonate solutions. In these tests, approximately 10 grams of freshly precipitated synthetic carnotite were added to a liter of standard sodium carbonate and ammonium carbonate solution and leached in the autoclave for four hours under standard conditions. Analyses of the resulting solutions showed that the synthetic carnotite was completely dissolved by the sodium carbonate solution but that less than 30 per cent of the carnotite was dissolved by the ammonium carbonate solution.

These data showed that the low extractions obtained from carnotite type ores was due to the poor solubility of carnotite in ammonium carbonate solutions. Previous test work on Sample 48-7, which is a carnotite type ore, had shown, however, that the extraction of uranium could be increased by increasing the concentration of reagents in the leaching solution. A series of tests were therefore made to investigate the effects of leaching solution composition and per cent solids during leaching on the extraction of uranium from a carnotite ore (Lukachukai Ore, Sample 17-10). The tests were run under standard conditions of temperature, pressure, and time as described earlier. Preliminary results from these tests are presented in Table III and confirm the limited solubility of carnotite in ammonium carbonate solutions. However, as shown, higher extractions can be obtained by maintaining the leaching solution composition and reducing the per cent solids during leaching.

Table IIIEffect of Solution Composition and Per Cent
Solids on Uranium Extraction

<u>Solution Composition</u> <u>Grams/Liter</u>		<u>% Solids</u>	<u>% U₃O₈ Extraction</u>
<u>(NH₄)₂CO₃</u>	<u>NH₄HCO₃</u>		
100.0	20.0	50	33.5
100.0	20.0	25	65.1
33.3	6.67	25	12.0

Tests are currently underway to determine the reason for poor solubilization of carnotite. It is thought that conversion of carnotite ($K_2O \cdot 2 UO_3 \cdot VO_4 \cdot nH_2O$) to the more insoluble ammonium uranyl vanadate may be responsible. In addition, the data presented in Table II indicate that the presence of vanadium decreases the solubility of uranium in ammonium carbonate solutions.

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