Newly developed ion exchange methods can recover uranium from copper waste dump leaching solutions for less than \$8 per lb U_3O_8.

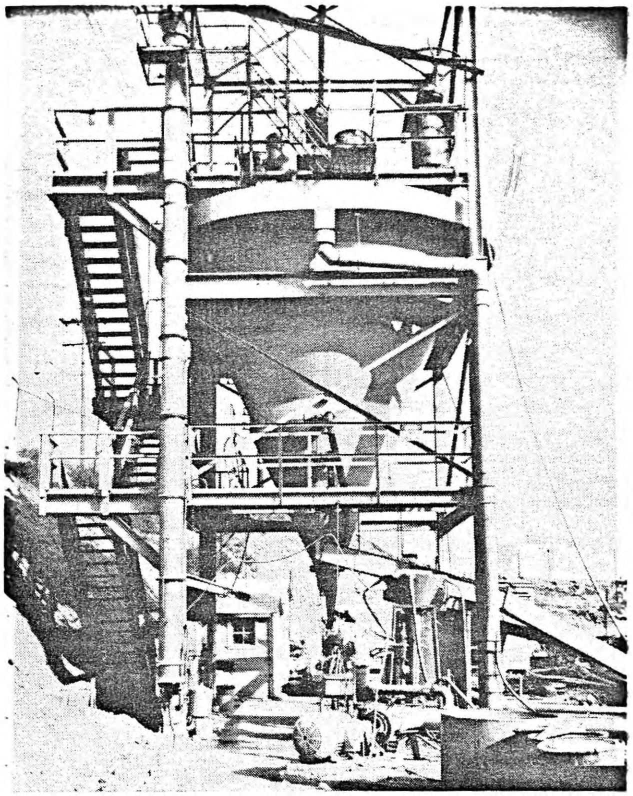

Fig. 1—*The cone contactors at Kennecott's Bingham Canyon mine handle about 28,000 gpm of copper leach solution. The multiple compartment countercurrent ion exchange column is at the left.*

Byproduct Uranium Recovered With New Ion Exchange Techniques

D. R. GEORGE, J. R. ROSS and J. D. PRATER

In the United States nearly 200,000 tons of copper per year are being produced by leaching waste rock and oxidized copper ore with dilute sulfuric acid-ferric sulfate solutions and precipitating the copper on scrap iron. The flow of solutions is in excess of 80 million gpd. A survey conducted by the U.S. Bureau of Mines in late 1965 at 14 mines in Arizona, Utah and Nevada, showed that with a few exceptions, the solutions contain from two to a maximum of 15 ppm U_3O_8, and there is strong evidence that these represent equilibrium concentration and not merely an accumulated in-process inventory resulting from recycling the solutions for many years. Consequently, it is believed that uranium could be recovered at a constant rate as long as mining and leaching operations continue. Preliminary surveys and estimates by the USBM indicate a production potential of possibly 1000 tons of U_3O_8 per year at a cost of less than \$8 per lb if the major process streams from most of the large copper mines in the western United States were to be treated.

Laboratory research by the USBM showed that the uranium could be efficiently recovered as a specification-grade uranium concentrate by a combination of ion exchange resin and solvent extraction of liquid ion exchange techniques. A joint pilot plant investigation by Kennecott Copper Corp. and the USBM was conducted on solutions from the Bingham Canyon mine to evaluate a new system of countercurrent ion exchange developed during the laboratory studies. In subsequent small-scale

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continuous tests, recovery of uranium from the pregnant eluate by solvent extraction and chemical precipitation techniques was investigated.

DESCRIPTION OF SOLUTIONS

Leaching of waste ore dumps at the Bingham Canyon mine has a current rate of solution flow of 28,000 gpm, and a design capacity of 6000 tons of copper per month by cementation on shredded tin cans in cone contactors. In addition to copper, the leach solutions contain significant amounts of the sulfate salts of iron, aluminum and magnesium, and are similar in composition to leach solutions at other copper leaching plants.

The U_3O_8 content of the heading solution is about 13 ppm, whereas the cementation plant effluent contains about 12 ppm. This decrease, also observed at other mines, may be the result of precipitation of uranium as uranous phosphate under the highly reducing conditions existing in the cementation circuit. The U_3O_8 concentration has remained nearly constant since this study was initiated in 1965, notwithstanding that during this time the solution flow has been raised from 10 million gal to 40 million gal per day. In addition, analytical records dating back to 1955 show a U_3O_8 concentration of about 12 ppm.

PRELIMINARY ION EXCHANGE TESTS

Laboratory tests showed that the uranium can be recovered by absorption on strong base anion exchange resins but that the ferric iron present in the heading solutions at 200 to 400 times the concentration of uranium was also strongly absorbed. Greater selectivity and higher uranium loadings were obtained by loading the resin from the copper cementation launders' effluent, but uranium loadings were still low. With 12 ppm solution, equilibrium U_3O_8 loadings for Rohm and Haas Co.'s Amberlite IRA-425 and Dow Chemical Co.'s Dowex 21K are only 16 gr per liter or one lb per cu ft. This is less than 25% of the equilibrium loading to be expected when processing typical solutions produced by leaching uranium ores with dilute H_2SO_4.

Recovery of uranium by solvent extraction with tertiary alkyl amines was also examined, but later terminated when it was found that extraction efficiency and loadings were low at pH values above 1.5 and solvent losses were deemed excessive for solutions of such low uranium concentration.

A system composed of a series of ion exchange columns through which the solution is pumped downflow through compacted beds of resin could be used for recovering uranium from copper waste, but there are several serious operating limitations:

a. The solutions must be highly clarified because when low grade solutions are processed, loading cycles are so long that even minute amounts of suspended solids cause blockage of the resin beds.

b. Even with clear solutions, the pressure drop across a series of packed beds is high and pumping costs become significant at the high flow rates desired when treating low grade solutions.

c. Because less than one lb U_3O_8 per cu ft can be loaded on the resin, conventional column elution or regeneration techniques yield eluates of comparatively low U_3O_8 content and chemical costs for elution and subsequent uranium recovery are high.

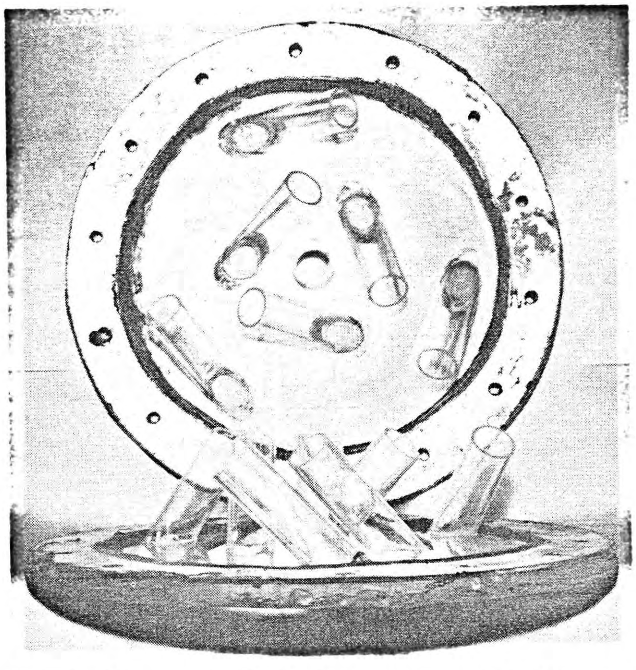


Fig. 2—*The one in. thick clear plastic orifice plates are drilled with six 1.5 in. diam. holes at a 45° angle and a vertical center hole. They are spaced at 120° intervals on circles with radii of three and six in. A 1.25 in. ID rigid plastic tube of 4.5 in. long is cemented in each hole so that the tops of the tubes flush with the upper surface of the plate.*

Laboratory investigations subsequently led to the development of the countercurrent ion exchange system which overcame many of the difficulties encountered when using standard methods.

DESIGN AND OPERATION OF EQUIPMENT

The *absorption* or *resin loading phase* of the pilot plant test used a multiple-compartment countercurrent ion exchange column.

The column was constructed of 14 gage, 304 stainless steel, has a 14 in. diam and is approximately 36 ft high. It is comprised of eight 4 ft flanged sections plus a short conical bottom section, and a 24 in. diam top section fitted with a peripheral overflow launder. Each of the sections has a sampling port at mid-point to permit withdrawal of solution and resin samples (Fig. 1). Feed solution is introduced into the cone at the base of the column at a rate which fully fluidizes the resin charge and the depleted solution overflows the launder at the top, but not in sufficient velocity to cause the resin to overflow.

The novel feature of the column is the presence of orifice plates between each of the flanged sections, constructed of one in. thick clear plastic drilled with seven 1.5 in. diam holes and located as shown in Fig. 2. The six inclined tubes impart a swirling action to the resin just above the orifice plate and eliminate dead resin areas. Efficiency is increased because the effect of using several columns, rather than a single long, one-stage column, is imparted by the use of the orifice plates. There is

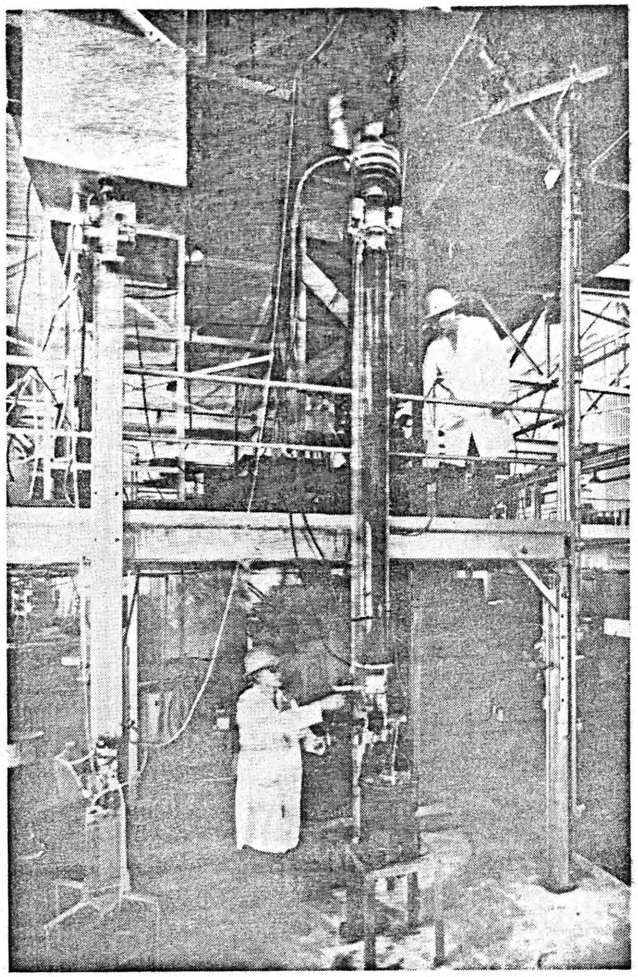


Fig. 3—*Uranium is eluted in the 10 ft long, 4 in. ID continuous countercurrent elution column at a solution flow rate of 0.5 to 1.5 gpm.*

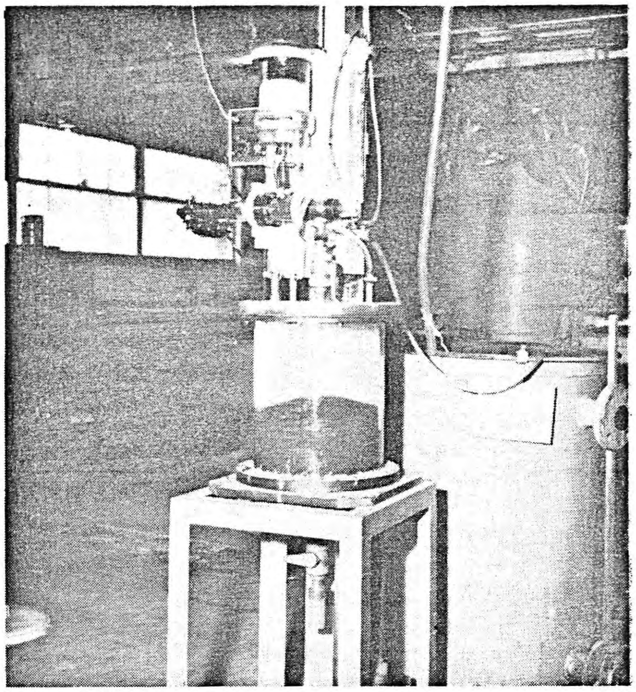


Fig. 4—*The resin withdrawal system works continuously during elution with a screw feeder discharging the resin into a receiver of about one cu ft capacity.*

no mixing of the resin between sections while solution is flowing up the column.

The column operates with a continuous flow of solution except for a brief interruption at regular intervals, during which the solution inlet valve is closed for 15 to 30 sec. A volume of loaded resin containing an amount of uranium equivalent to that absorbed during the contact period is rapidly withdrawn from the bottom compartment by opening the resin outlet valve. At the same time equivalent volumes of resin move rapidly down the column through the orifice holes, and from each compartment into the next below. The resin outlet valve is then closed, the solution flow resumed and a charge of fresh resin, equivalent in volume to the amount withdrawn, is dumped into the top section. This relatively simple operation lends itself to completely automatic operation which could be easily and inexpensively installed.

Resin was transferred to the Salt Lake City Metallurgy Research Center once a day for *elution* or *regeneration*. The resin was continuously eluted in the countercurrent elution column (Fig. 3) which was constructed from a 10 ft length of four in. ID glass pipe. A provision for heating the column was made by means of a water jacket constructed from an eight ft. length of six in. ID glass pipe. Elution of uranium is accomplished by continuously feeding loaded resin into the top of the column and under controlled conditions, continuously withdrawing eluted resin through a discharge opening at the bottom so that the working volume of resin is maintained at about 0.85 cu ft. The eluting solution is simultaneously introduced through an annular distributor at the base of the column. A portion of the pregnant eluate overflowing the launder at the top is continuously recycled to the resin feed tank and the slurry of resin and solution overflow into the column.

During elution, resin is continuously withdrawn by gravity through the drop hole in the base of the column into a 1.5 in. ID variable speed screw feeder which in turn discharges the resin to a receiver of about one cu ft capacity. The receiver (Fig. 4) is hydraulically closed with the column, an arrangement which permits withdrawing resin but not solution from the base of the column.

The use of a hydraulically closed receiver is desirable for laboratory and pilot plant studies because it permits ready shutdown of the system. On a plant scale, however, the receiver would be replaced by a simple jackleg to discharge resin continuously through a submerged leg into an open tank or to a resin collection pipe from which it would be hydraulically conveyed to the loading column continually.

OPERATING CONDITIONS AND TEST RESULTS

The pilot plant test was conducted for a six week period on a three shift per day, five day per week basis. The resins used were strong base anion exchange resins and the inventory consisted of 22 cu ft of Amberlite IRA-425 and three cu ft Dowex 21K. Both resins were of the coarse bead variety,

TABLE 1: Summary of operating results

Solution flow, gal per sq ft per min	Feed assay, U_3O_8, ppm	Tails assay, U_3O_8, ppm	Resin inventory, cu ft	Resin withdrawal, cu ft per 4 hr	Resin loading, U_3O_8, lb per cu ft	Recovery: U_3O_8, %	Recovery: U_3O_8, grams per hr per cu ft resin
10	12	1.8	20	0.32	0.63	85	1.16
15	10.5	2.2	15	0.45	0.56	79	1.89
20	7.5	2.5	10.6	0.40	0.49	67	2.14

minus 16—plus 20-mesh, used in resin-in-pulp type uranium milling circuits.

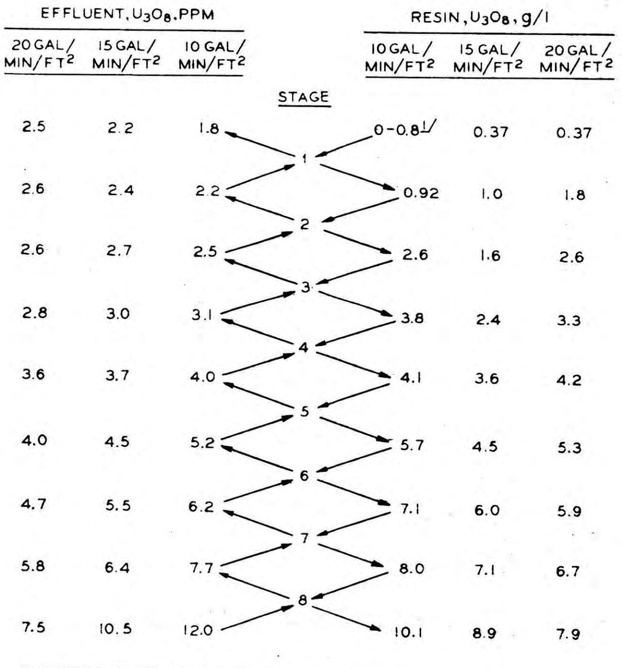
Feed solution for the test was the effluent from the old copper cementation launders at Kennecott's Bingham Canyon plant. The pH was 3.4 to 3.5, the temperature 90°F and the density about 1.09. For the first three weeks of the test solution containing 12 ppm U_3O_8 was available, but during the last three weeks most of the feed to the launder cementation plant was diverted to the new cone precipitation plant and variable amounts of water from Bingham Creek inadvertently introduced into the cementation launder system. At times the U_3O_8 content of the solution was as low as five ppm, and eventually the grade of the solution became so irregular that it was decided to terminate the test.

Feed solution for the test was pumped from a sump in the launder system to a 700 gal settling tank to remove trash and occasional heavy concentrations of cement copper, and overflowed into a second 700 gal storage tank from which it was pumped to the column through a flow meter. Effluent from the column overflowed at the top to a resin catch tank and then joined the effluent from the cementation plant. Composites of the feed solution were assayed every shift, the effluent every two hr and whenever resin was withdrawn from the column the U_3O_8 loading was determined by stripping a measured volume of resin. Near the end of the test period samples of solution and resin were withdrawn from the center of each column section and assayed. Control assays for uranium were performed at the site by a rapid colorimetric procedure and duplicate samples were frequently checked at the laboratory.

The absorption column was operated for three weeks at a flow of 10 gpm, for one week at 15 gpm and for a final two weeks at 20 gpm. These flows are essentially equivalent to flows expressed as gpm per sq ft as the column area was 1.02 sq ft. The total volume of solution processed was 473,000 gal containing 38.05 lb of U_3O_8, with a weighted average assay of 9.7 ppm U_3O_8. Resin withdrawals were made at four hr intervals. Table 1 summarizes the results and Fig. 5 shows the absorption profile for operations at the three flow rates tried.

Elution was studied primarily at a solution-to-resin ratio of about 3:1 and a resin feed rate of 100 ml per min. Under these conditions, resin retention was 235 min and solution retention time 31 min at a constant column temperature of 55° to 60°C. The principal variable studied was the eluting solution strength. During the first two weeks a 1*M* H_2SO_4 solution was used. After elution the resin still contained 1.5 gr per liter U_3O_8 (0.1 lb per cu ft) which adversely affected its capacity to extract uranium when recycled to the loading column. By decreasing the resin flow to 70 ml per min and the solution flow to 210 ml per min, the residual U_3O_8 loading was reduced to 0.8 gr per liter. As this was still too high, the eluting solution strength was changed to 1.5 *M* H_2SO_4 for the balance of the test. Under these conditions the resin was eluted to an average residual U_3O_8 loading of 0.37 gr per liter when flows of 100 ml of resin and 300 ml of solution per min were maintained. Longer retention time of the resin or higher aqueous to resin flows probably would reduce the residual U_3O_8 loading to an even more desirable level. Higher acid concentrations would also be expected to improve elution efficiency.

Approximately 1200 gal of pregnant eluate were produced during the test and, depending on the resin loading, the U_3O_8 concentration ranged from about 2.5 to nearly 4 gr per liter. The weighted average assay was, in gr per liter, 3.02 U_3O_8, 0.68 Fe, 0.18 Si and 100 H_2SO_4 with copper and aluminum present in concentrations of 0.5 to 1.5. The copper and aluminum were present principally as the re-



1/ MIXTURE OF NEW AND REGENERATED RESIN

Fig. 5—*Uranium profiles from 14 in., eight compartment countercurrent ion exchange column pilot plant tests.*

sult of incomplete washing of the resin prior to elution and to the presence of entrained cement copper which dissolved in the warm H_2SO_4 solution.

DISCUSSION OF ADSORPTION AND ELUTION

A metallurgical balance for the entire test period showed that 38.05 lb of U_3O_8 were fed to the absorption column and that 30.3 lb were present in the pregnant eluate. This represents a recovery of 79.6%. The calculated uranium recovery based on feed and tailing assays was 80.5%.

As shown in Table I, uranium recoveries and resin loadings decreased with increasing feed rates. The uranium recovery at 10 gpm per sq ft was 10 to 15% lower than was predicted from small-scale countercurrent loading tests made with all new resin. This difference is primarily attributable to incomplete elution of uranium from the recycled resin. Substantially complete recovery of uranium from this poorly amenable solution cannot be expected unless the recycled resin is essentially free of uranium.

It should be noted that H_2SO_4, chosen because it permits recovery of uranium without introducing foreign anions into the copper leaching and cementation circuits, is not the most effective eluant for uranium. Chloride, and particularly nitrate solutions, would be preferable, but by employing a sulfate elution system solvent extraction of the pregnant eluates with alkyl amines can be used to effect final recovery of uranium as a very high grade product.

Although incomplete elution was partially responsible for the decreased recovery as compared with laboratory tests, the sharp drops in recovery as the feed solution flows were increased beyond 10 gpm were principally the result of the decrease in the feed solution assay. If the feed assay had remained constant at 12 ppm U_3O_8, and assuming a tailing of 2.5 ppm U_3O_8, the drop in recovery between 10 gpm and 20 gpm probably would have been only 6%.

Part of the drop in resin loading as the flow rates were increased is attributable to the decrease in feed assay and also to a decrease in resin retention time. At an aqueous flow of 10 gpm, the resin inventory was 20 cu ft and the resin withdrawal rate 0.32 cu ft per four hr, resulting in a resin retention time of about 250 hr. At an aqueous flow of 20 gpm the resin inventory was 10.6 cu ft and the resin withdrawal 0.40 cu ft per four hr.

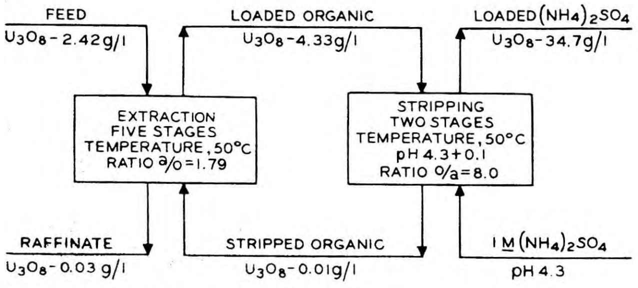


Fig. 6—*Solvent extraction of uranium with 5% Adogen 364 and stripping with 1M* $(NH_4)_2SO_4$ *plus* NH_3 *yielded about four lb* U_3O_8 *in 13 gal of pregnant strip solution.*

This is equivalent to a resin retention time of only 106 hr and represents a 60% reduction.

The importance of recovery should not be overemphasized, however, because the tailing solutions are recycled to the waste dumps and unrecovered uranium is not lost. Similarly, the resin loading should not be given too much emphasis because with sulfuric acid elution and subsequent solvent extraction, reagents for elution and recovery of uranium will be more or less independent of the resin loading. The most important consideration is the quantity of U_3O_8 that can be absorbed per unit of time per unit of resin. The test data show that, in spite of a 37.5% decrease in the uranium content of the feed, nearly twice as much uranium was recovered per hr per unit of resin at 20 gpm as at 10 gpm. At the same feed assay, recovery per unit of resin per hr would be more than three times as great at 20 gpm as at 10 gpm.

RECOVERY OF URANIUM FROM PREGNANT ELUATES

Because of the low U_3O_8 content and high H_2SO_4 concentration, neutralization of the eluate to precipitate and recover uranium would be expensive. Therefore, tests were made to investigate final recovery of uranium from the pregnant eluates by solvent extraction. This technique, sometimes referred to as the "Eluex Process," is used by the uranium milling industry. Laboratory studies showed that four to five stages of extraction would be required when using a 5% (by volume) solution of a tertiary alkyl amine plus 2% isodecanol dissolved in kerosine.

Stripping was studied using NaCl, Na_2CO_3, $(NH_4)_2CO_3$ and $(NH_4)_2SO_4$ solutions. The preferred stripping reagent is an approximately 1*M* solution of $(NH_4)_2SO_4$. Only two stages of stripping were required when operating at 50°C and when the pH of the stripping circuit was maintained at 4.3 ± 0.1 by continuous addition of ammonia. On this basis a small continuous solvent extraction circuit was operated for four to five days during which approximately 180 gal pregnant eluate containing 2.42 gr U_3O_8 per liter were processed to recover about four lb of U_3O_8 in 13 gal of pregnant strip solution containing 34.7 gr U_3O_8 per liter (Fig. 6).

Finally, uranium was recovered in a small continuous precipitation circuit by neutralization with NH_3. The product after calcination at 675°C for two hr assayed 98.4% U_3O_8 and met all specifications established for sale either to the AEC or to the nuclear power industry. Chemical consumption for extraction stripping and precipitation was 0.62 lb NH_3, 1.5 lb H_2SO_4 and 0.004 gal solvent per lb of U_3O_8. The use of H_2SO_4 for elution of the resin was approximately 15 lb per lb of U_3O_8 but most of this can be credited against the acid required for copper leaching, as the acid taken up by the resin is subsequently displaced during the uranium loading cycle and reports in the barren solution that is recycled to the leaching dumps. This amounts to approximately 1.2 lb H_2SO_4 per 1000 gal.