AN INTRODUCTION TO URANIUM ORE PROCESSING

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INTRODUCTION

During the past few years many noteworthy technological advances have been made in the processing of uranium ores. Processes which previously were unknown in the field of hydrometallurgy have been developed and now are used in many of the domestic uranium mills. Additionally, these processes, particularly ion exchange and solvent extraction, are finding application in the recovery of other metals from their ores.

Rather than attempting to summarize the developments in uranium ore processing over the past several years, this paper is intended to introduce the reader to those processes most commonly used. The particular uranium recovery process employed in each of the uranium mills in the Western United States is shown in Table 1, along with the plant location and the approximate tonnage of ore treated daily.

By the latter part of 1958 when all 23 mills shown in the table are in operation, and if the contemplated process changes are completed in a few of the mills now operating, the breakdown by processes will be as follows:

Type of Process	Number of Mills Using Process	Percentage of Total Daily Millfeed
Solvent Extraction	10	38
Resin-in-pulp (Acid & Alkaline)	7	27
Carbonate Leaching	5	25
Column Ion Exchange	3	10

The total number of mills using the various processes is two greater than that shown in Table 1 because two plants are expected to utilize two separate processes. In any event, it is interesting to note the popularity of solvent extraction, a relative newcomer that was first operated on a continuous basis at the Shiprock mill in September 1956. The RIP (resin-in-pulp) process, basically one of ion exchange, and column ion exchange together will be used for recovering uranium from roughly the same total millfeed as solvent extraction. The carbonate leaching process has many advantages which cannot be overlooked and for certain ores this process most assuredly will continue to be favored over acid leaching.

Starting now with the ore as delivered to the mill its progress will be traced through the various steps of the processing operation.

ORE RECEIVING AND STORAGE

The customary procedure is to weigh the incoming ore trucks on platform scales and to direct the truck to the area or bin where the shipper's ore is to be accumulated. After dumping, the truck returns to the scales where the truck tare weight is recorded and the net wet weight of ore determined.

Either at the time of weighing or as soon as dumped, a 10 to 20-pound grab moisture sample is taken from each truck load. These moisture samples are placed in covered containers and at frequent intervals are delivered to the laboratory for moisture analysis, so that the dry weight of ore in each truckload can be determined.

As soon as sufficient tonnage has accumulated, the shipper's lot is fed to the crushing and sampling plant. Almost without exception, primary crushing is done by jaw crushers which reduce run of mine ore (12 inch maximum) to approximately 2 inches. In some plants sampling is begun on this coarse product; whereas, in other plants a further size reduction, generally to about ¾ inch, is accomplished prior to cutting the first sample. Sampling receives a great deal of attention because of its importance not only for ore settlement purposes, but also for determining the monthly average millfeed grade for concentrate payment purposes.

After crushing and sampling, the ore is either conveyed to the fine ore bins for processing, or it is trucked to the stockpile area.

GRINDING

Grinding is either dry or wet depending on subsequent processing. The uranium-vandium mills that salt roast the raw ore for vanadium recovery crush or dry grind to only 10 to 14 mesh.

Grinding at other operations is conventional wet grinding, in either rod or ball mills, in closed circuit with classifiers or cyclones. The fineness of grind required depends upon the type of ore and the leaching method employed. In the mills where sulfuric acid is used to leach or extract the uranium, it generally is necessary to grind only to grain size or approximately 28 mesh.

In carbonate leaching the solutions are very selective toward uranium but are not capable of penetrating grain

TABLE I - URANIUM ORE PROCESSING PLANTS

	Location	Company	Tons of Ore Per Day	Uranium Leaching Solution	Uranium Recovery Process Used
1.	Rifle, Colorado[1]*	Union Carbide Nuclear Company	1,000	Sulfuric Acid	Solvent Extraction (EHPA)
2.	Uravan, Colorado*	Union Carbide Nuclear Company	900	Sulfuric Acid	Ion Exchange Columns
3.	Grand Junction, Colorado*	Climax Uranium Company	450	Sulfuric Acid	Solvent Extraction (EHPA)
4.	Durango, Colorado*	Vanadium Corporation of America	430	Sulfuric Acid	Chemical Precipitation and Fusion
5.	Gunnison, Colorado	Gunnison Mining Company	200	Sulfuric Acid	Solvent Extraction (EHPA)
6.	Maybell, Colorado	Trace Elements Corporation	300	Sulfuric Acid	Resin-in-pulp (ion exchange)
7.	Monticello, Utah[2]	Government-owned	550	Sulfuric Acid Sodium Carbonate-Bicarbonate	Resin-in-pulp (ion exchange)[3] Caustic Precipitation
8.	Salt Lake City, Utah	Vitro Uranium Company	550	Sulfuric Acid	Solvent Extraction (DDPA)
9.	Moab, Utah	Uranium Reduction Company	1,500	Sulfuric Acid	Resin-in-pulp (ion exchange)
10.	Mexican Hat, Utah	Texas-Zinc Minerals Corporation	775	Sulfuric Acid	Solvent Extraction (Amine)
11.	Shiprock, New Mexico	Kerr-McGee Oil Industries, Inc.	300	Sulfuric Acid	Solvent Extraction (EHPA)
12.	Bluewater, New Mexico	Anaconda Company	3,000	Sulfuric Acid Sodium Carbonate-Bicarbonate	Resin-in-pulp (ion exchange)[3] Caustic Precipitation
13.	Edgemont, South Dakota	Mines Development, Inc.	350	Sulfuric Acid	Resin-in-pulp (ion exchange)
14.	Tuba City, Arizona	Rare Metals Corporation of America	300	Sulfuric Acid	Resin-in-pulp (ion exchange)
15.	Split Rock, Wyoming	Western Nuclear Corporation	400	Sulfuric Acid	Resin-in-pulp (ion exchange)
16.	Ford, Washington	Dawn Mining Company	400	Sulfuric Acid	Ion Exchange (columns)
17.	Fremont County, Wyoming	Lucky Mc Uranium Corporation	750	Sulfuric Acid	Ion Exchange (columns)
18.	Grants, New Mexico	Homestake-New Mexico Partners	750	Sodium Carbonate-Bicarbonate	Caustic Precipitation
	Subtotal		12,905		
	Mills Under Construction as of June 1, 1958				
1.	Riverton, Wyoming	Fremont Minerals, Inc.	500		
2.	Grants, New Mexico	Homestake-Sapin Partners	1,500		
3.	Grants, New Mexico	Kermac Nuclear Fuels Corporation	3,300		
4.	Grants, New Mexico	Phillips Petroleum Company	1,725		
5.	Lakeview, Oregon	Lakeview Mining Company	210		
	Subtotal		7,235		
	Grand Total		20,140		

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[1] Union Carbide Nuclear Company also buys ore at Slick Rock, Colorado and Greenriver, Utah where it is upgraded as feed for the Rifle, Colorado mill.

[2] Operated for the U. S. Atomic Energy Commission by National Lead Company, Inc.

[3] At both Monticello and Bluewater there is also a carbonate leach — filtration — caustic precipitation plant that treats a portion of the total tonnage.

* These mills salt roast to recover vanadium.

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boundaries as effectively as acid solutions. Therefore, when carbonate leaching is employed finer grinding is required to expose the uranium mineralization to the leaching solution. A nominal 65 mesh grind (70% minus 200 mesh) generally is sufficiently fine for carbonate circuits.

The wet grinding circuits in most mills produce pulps of from 40% to 60% solids which are ready for leaching. In a few cases, where grinding is more difficult and the classifiers or cyclones overflow at a more dilute pulp density, it is necessary to thicken ahead of leaching.

LEACHING

The extraction of uranium from ore is accomplished either by sulfuric acid or sodium carbonate-bicarbonate leaching. Each ore presents its own leaching problems and the choice between acid and carbonate leaching is, of course, dependent upon extraction and costs. In the past the tendency has been toward acid leaching, except for ores which contain excessive amounts of acid consuming constituents such as limestone and dolomite. Recently, however, advances in the technique of carbonate leaching have made this process competitive with acid leaching for many types of ore.

In either case, the ease with which uranium is extracted depends upon the uranium mineralization. Neither acid nor carbonate leaching will solubilize tetravalent uranium, such as occurs in uraninite. Therefore, it is necessary to provide an oxidant to covert U(4) to U(6), the uranyl form. The secondary or oxidized uranium minerals are more readily soluble. Uranium occurs also in refractory minerals as euxenite and samarskite which would require rather vigorous chemical treatment to solubilize the uranium. In the Temple Mountain area of Utah and in the lignites, the uranium is associated with asphaltic material or other hydrocarbons which must be destroyed by controlled roasting to obtain reasonable uranium extraction.

In acid leaching mechanical agitation, as opposed to air agitation, has been adopted almost universally in the domestic uranium mills. It is customary to add enough acid to maintain a pH of from 1.0 to 1.5 and to provide an oxidant in the form of manganese dioxide or sodium chlorate. Leaching time varies from a few hours to as much 24 hours. In some instances the leaching temperature is maintained at 100° F. to 140° F. to increase the rate of dissolution. Acid consumption varies appreciably depending on the lime content of the individual ores. For the industry as a whole acid consumption ranges from 40 to 500 pounds per ton of ore.

Carbonate leaching requires considerably longer contact time than acid leaching, and 48 to 96-hour leaching is not uncommon. Both atmospheric and pressure leaching with either mechanical or air agitation have found application in domestic carbonate leaching plants. The reagent concentrations in carbonate leach solutions usually are in the range of 40 to 100 grams sodium carbonate (Na_2CO_3) and 10 to 20 grams sodium bicarbonate ($NaHCO_3$) per liter. Bicarbonate must be present to neutralize the hydroxyl ion formed in the dissolution process or to prevent precipitation of the uranium. An oxidant also is essential to carbonate leaching; and aeration, alone or in conjunction with permanganate or copper-ammonia, has proved most effective. Carbonate leaching is done at near boiling temperatures, or when under pressure at temperatures in the range of 220° F. to 275° F. Pressure leaching at elevated temperatures greatly reduces the required retention time of the ore in the leach solution. For example, in testwork performed at the Grand Junction pilot plant only 7 hours contact time was required in an autoclave at 70 psig and 250° F. to attain extractions equal to those attained by leaching for 70 hours in Pachucas at 0 psig and 180° F. (Beverly, 1957).

LIQUIDS - SOLIDS SEPARATION

Following acid leaching either a complete or partial liquid-solids separation is made depending upon the process used for recovering the solubilized uranium. For column ion exchange or for solvent extraction all solids should be separated from the pregnant acid liquor, and this is accomplished by either filtration or countercurrent decantation (CCD) or a combination of both.

For the resin-in-pulp (RIP) process, a sand-slime separation is effected by means of classifiers and cyclones, the slimes (minus 325 mesh) remaining with the pregnant liquor. For this reason the RIP process is favored when treating very slimey or clayey ores, the thickening or filtration of which would be extremely troublesome.

In the carbonate leaching plants now operating either two or three-stage filtration is utilized to obtain a clear pregnant liquor. However, the resin-in-pulp process also can be used on carbonate leach liquors and in this case a sand-slime separation can be made in the same manner as in the acid-RIP process. No uranium mill is using the carbonate-RIP process at this time but within a few months the acid-RIP plant at Monticello is expected to be converted to carbonate-RIP in order to treat more efficiently the high lime ores tributary to that mill.

URANIUM RECOVERY — CARBONATE LEACH — FILTRATION PROCESS

Pregnant liquor from the filtration circuit is first clarified and then goes to precipitation where an excess of caustic soda (NaOH) is added to destroy the bicarbonate and to precipitate the uranium as a sodium diuranate ($Na_2U_2O_7$). This uranium precipitate is filtered, washed, dried and packaged in 55-gallon drums for shipment to the AEC at Grand Junction where it is weighed, sampled, analyzed, and paid for on the basis of contained U_3O_8.

Barren filtrate is generated by contacting the solution with the CO_2 in flue gases which restores the carbonate-bicarbonate concentrations. The regenerated solution then is ready for recycle to the grinding and leaching circuits.

Average reagent consumption for the carbonate leach-filtration process is the equivalent of about 30 pounds of NaOH per ton of ore.

As mentioned previously this process is the only one feasible for high lime ores, and because of the non-corrosiveness of the solutions, special materials of construction are not required. However, other factors, such as vanadium, which extracts and coprecipitates with the uranium; gypsum and sulfides, which consume carbonate; and the filtration rate must be considered in any evaluation of this process.

URANIUM RECOVERY — COLUMN ION EXCHANGE

In this process the clear pregnant acid solution from the liquid-solids separation is passed through a series of ion exchange columns, where the uranium is selectively absorbed as an anionic complex by strong-base polystyrene quaternary amine resin beads ranging in size from minus 16 to plus 50 mesh. When the resin in a column becomes loaded, the flow is advanced to the next column and the uranium is eluted with an acid solution of sodium or ammonium salts of chlorides or nitrates. The uranium is precipitated from the pregnant eluting solution by neutralization with ammonia or magnesia. The uranium precipitate is filtered, washed, dried and packaged for shipment. In most instances, the barren eluant is made up and recycled so as to minimize reagent consumption.

Ion exchange columns generally are about 12 feet high and 7 feet in diameter and contain about 5 feet of resin (200 cubic feet) resting on a sized gravel bed about 18 inches deep. The columns are installed in sets of three or four, and for large flows two or more sets are employed in parallel.

In 1953 the first commercial plants to use column ion exchange began operation in South Africa. The mill at Shiprock, New Mexico which started operating in 1954 was the first to use column ion exchange in this country. The Shiprock mill later was converted to solvent extraction, but as indicated by Table 1, there are three mills in the United States presently using the column ion exchange process.

URANIUM RECOVERY — RESIN-IN-PULP (RIP)

As mentioned previously, this is essentially an ion exchange process that has been found to be particularly well suited for treating slimey or clayey ores that are difficult to settle or filter. The uranium anion exchange is accomplished in open rectangular tanks referred to as banks in which stainless steel wire-screen baskets holding resin beads are moved up and down through the flowing pregnant slime pulp. This slime pulp is controlled at a density of about 1.06 (6% to 8% solids) and a pH of about 1.5. The resin is the same type as described above except that the beads are much coarser (plus 20 mesh) so as to be retained within the 28 mesh screen baskets. After a bank of baskets has been on adsorption, in contact with the pregnant liquor, for a predetermined length of time, the flow is advanced to the next bank and the uranium is eluted from the loaded resin by filling the bank with either an acidified chloride or nitrate solution. Uranium precipitation from the pregnant eluate is by neutralization, the same as in column ion exchange. Following elution, the bank of baskets is put back in the circuit so that it is the last loading bank that the pulp enters before being discharged as tailing.

The design of RIP plants has been standardized to the extent that each plant has 144 banks, and each bank contains from 2 to 10 baskets that range in size from 4' x 4' x 4' to 6' x 6' x 6'. Each basket contains from 10 inches to 17 inches of resin so that the resin volume per basket ranges from about 15 to 50 cubic feet depending on the basket size. Resin loadings vary from 2½ to 4 pounds U_3O_8 per cubic foot. The resin has a life of from 2 to 4 years depending on the chemical and physical characteristics, frequency of regeneration to remove "poisons", the physical abuse, and the precautions taken to prevent mechanical losses.

URANIUM RECOVERY — SOLVENT EXTRACTION (SX)

In this process clear pregnant acid liquor is contacted in a continuous countercurrent manner with an immiscible organic liquid containing an extractant that is capable of complexing the uranium. The uranium is transferred to and concentrated in the organic liquid which by volume is only about one-fifth that of the acid liquor. Uranium is re-extracted or stripped from the organic with an aqueous solution and the stripped organic is recycled to the extraction circuit. The strip solution is by volume only a fraction of the organic volume and, therefore, the uranium is further concentrated during the stripping operation. Depending on the solvent used and the aqueous to organic ratios employed, the strip solution contains 30 to 100 times the uranium content of the acid leach liquor. Uranium is precipitated from the strip solution which yields a product containing from 75% to 85% U_3O_8.

The organic extractants generally are used as 0.1 to 0.3 molar solutions in kerosene and these extractants are of three types, namely, acidic, neutral and basic. The two acidic solvents that have found application are the di(2-ethylhexyl) phosphoric acid (EHPA) and the mono(dodecyl) phosphoric acid (DDPA). EHPA is used by Kerr-McGee Oil Industries, Inc., Shiprock, New Mexico; Climax Uranium Company, Grand Junction, Colorado; Gunnison Mining Company, Gunnison, Colorado; and the new Union Carbide Nuclear Company mill at Rifle, Colorado. DDPA is used only in the Vitro Uranium Company mill in Salt Lake City.

The best known of the available neutral solvents is tributyl phosphate (TBP) that has been used for several years for extracting uranium from nitrate solutions in the AEC's feed materials plants. TBP will not extract from sulfuric acid leach liquors so has no application in ore processing as an extractant; however, it has found use in the EHPA process as an additive to the solvent to prevent formation of a third phase during the stripping operation.

The basic solvents are the amines such as the Rohm and Haas Amine 9D-178 which is used in the Texas-Zinc Minerals Corporation mill at Mexican Hat, Utah.

The most commonly used solvent extraction equipment is a mixer-settler. As the name implies, a mixer is a tank in which the organic and aqueous phases are intimitely mixed by agitation prior to flowing to a larger tank (settler) where the phases separate or disengage. Often the mixer is set within the settler and such units are referred to as " internal mixer-settlers". Generally four to six mixer-settler units or stages of contact, are used in extraction and from two to four smaller units are used in stripping. Mixer-settlers are installed in a stepdown arrangement so that one phase flows by gravity while the other phase is pumped or air-lifted in the opposite direction.

To illustrate the solvent extraction process a flowsheet for recovery of uranium by the EHPA process is shown in Figure 1. Although EHPA is quite selective toward uranium, there are other ions that also will be extracted if proper precautions are not taken. For instance, ferric iron is extracted and therefore must be kept below 0.5 grams per liter. To minimize ferric iron extraction provisions generally are made to reduce the pregnant solution prior to extraction. Vanadium also is extracted by EHPA but can be minimized by maintaining a pH of about 1.0. At a pH of 2.5 and above, vanadium extraction by EHPA is so favorable that two mills have installed EHPA extraction circuits specifically for vanadium recovery.

As indicated by Figure 1, EHPA is stripped with a sodium carbonate solution at about a 10:1 solvent-to-stripping solution ratio. To facilitate phase disengagement, it is customary to provide heat to operate the stripping units at 95° F. to 105° F. In the precipitation of the uranium, sulfuric acid is first added to destroy the carbonate and then the uranium is precipitated with ammonia or magnesia.

The DDPA and amine solvent extraction processes are somewhat different from the EHPA process in so far as stripping and product recovery are concerned. Basically, however, all solvent extraction processes are similar and a detailed explanation of each process is beyond the scope of this paper.

Solvent extraction processes have grown rapidly in popularity because of the simplicity, ease of operation, low capital and operating costs, flexibility, wide choice of extractants, and the possibility of recovering by-products such as vanadium, molybedenum, and thorium. Another advantage often cited is that of producing high purity uranium salts at the mills, and much study and publicity have been given this possibility in recent months. (Long, 1958).

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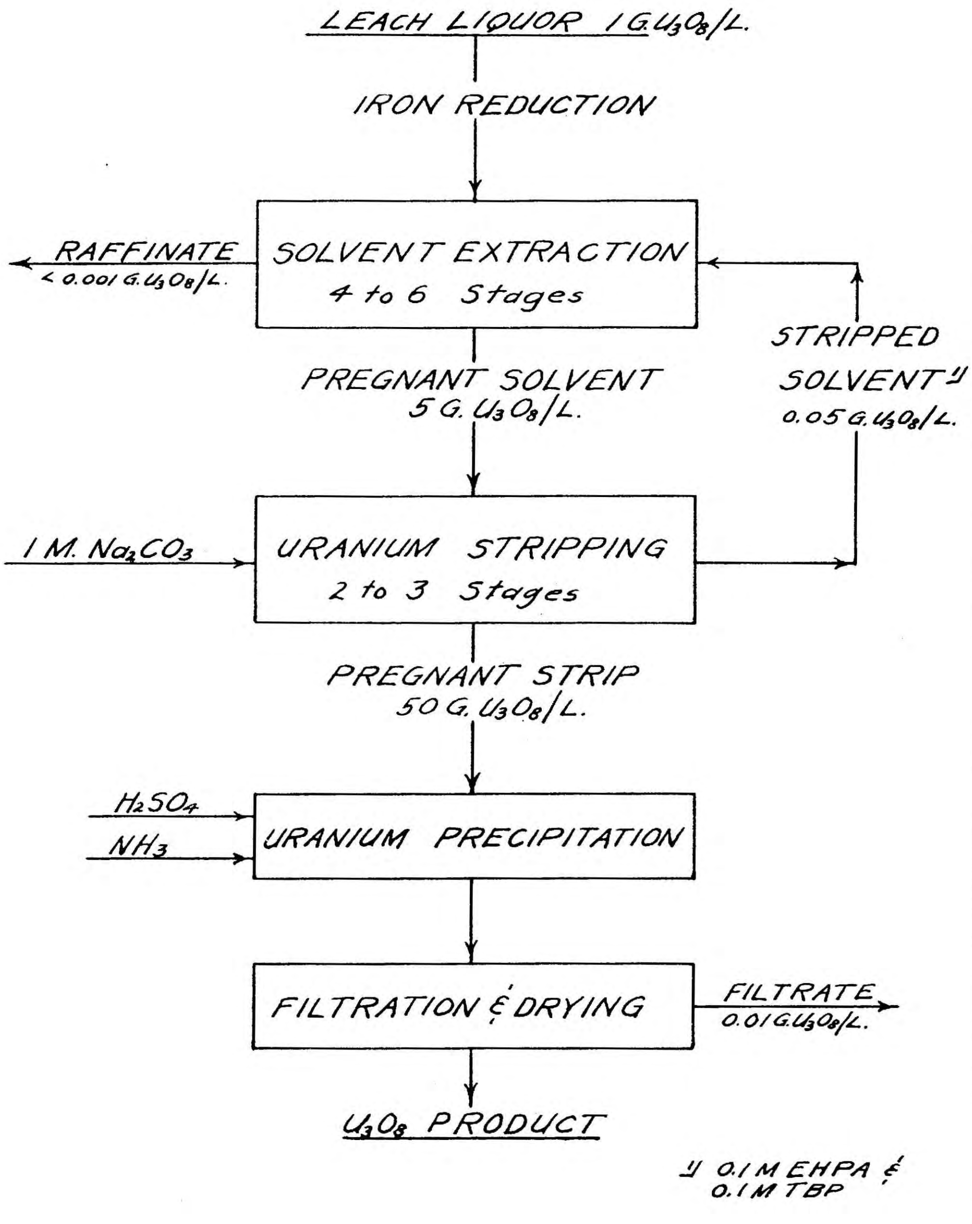

FIGURE 1 - FLOWSHEET FOR RECOVERY OF U_3O_8 BY EHPA