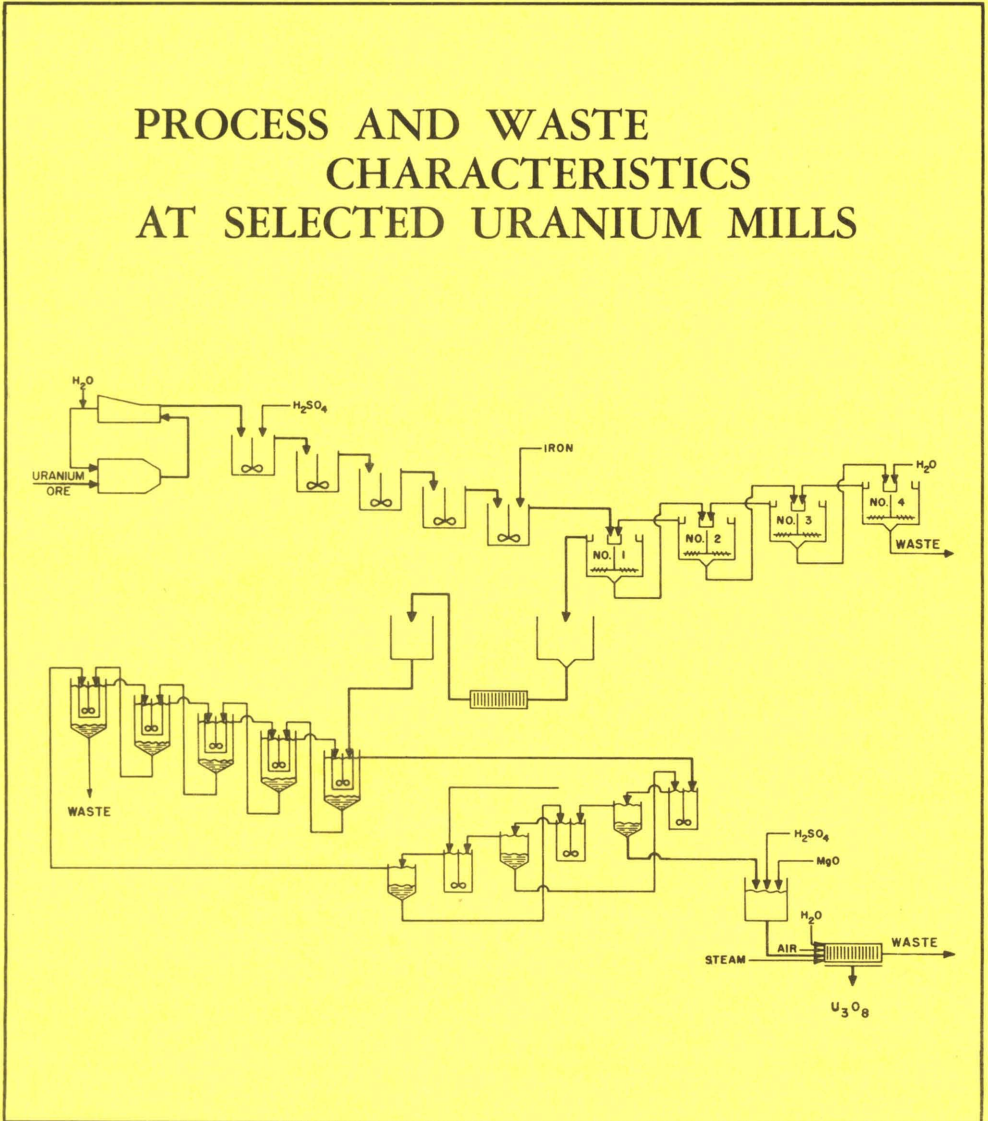


PROCESS AND WASTE CHARACTERISTICS AT SELECTED URANIUM MILLS



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PROCESS AND WASTE CHARACTERISTICS AT SELECTED URANIUM MILLS

Prepared by

Radiological Pollution Activities Unit
Field Operations Section
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U. S. Department of Health, Education, and Welfare
Public Health Service
Division of Water Supply and Pollution Control

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

1962

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FOREWORD

This report contains the findings of detailed studies of process and waste flows at five typical uranium mills. The studies were initiated in 1957 by the Public Health Service for the purpose of characterizing the liquid and solid wastes resulting from uranium milling processes.

Uranium mills extract the naturally radioactive uranium from its ores and produce a concentrated product that is subsequently refined elsewhere for use in nuclear weapons and reactors. The extraction and recovery processes employed are determined by the character of the ore and its uranium content. The five mills reported on here typify the processes normally encountered, i.e., acid or alkaline leaching of the ore, concentration and purification of the leach liquor by ion exchange or solvent extraction, and chemical precipitation of the dissolved uranium.

Although the radioactive waste materials, especially Radium-226, were of primary interest in these studies, useful information regarding the chemical characteristics of milling wastes was also obtained. The entire body of information thus developed forms an excellent basis upon which to characterize the waste products from the industry as a whole. This has resulted in an "Industrial Waste Guide for the Uranium Milling Industry", which is published as a separate SEC Technical Report.

The generous cooperation and assistance of many individuals and agencies have contributed greatly to the successful completion of these studies. The work was supported in part by funds made available through the Environmental and Sanitary Engineering Branch, Division of Reactor Development, U. S. Atomic Energy Commission.

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THE RESIN-IN-PULP URANIUM EXTRACTION PROCESS. MINES DEVELOPMENT COMPANY, EDGEMONT, SOUTH DAKOTA.

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Introduction and Background

During the summer of 1957, the Public Health Service carried out a field study of liquid wastes resulting from the extraction of uranium from its ore in a typical refinery using the resin-in-pulp extraction process. The study was performed in cooperation with the South Dakota State Department of Health, the Mines Development Company of Edgemont, South Dakota, and the United States Atomic Energy Commission. It was the first of a series of such surveys by the Public Health Service to develop detailed knowledge of the characteristics of wastes, particularly radioactive wastes arising from the extraction of uranium from its ores. Specific objectives of the studies include detailed analysis of the extraction process, characterization of the resulting liquid wastes, evaluation of their water pollution and public health significance, and development of adequate and suitable waste control measures. At the same time, parallel field studies of the fate of these wastes in the water environment were carried out. ¹

The uranium refinery at Edgemont, South Dakota, is located on the banks of the Cheyenne River about 35 river miles above Angustora Reservoir, a recreational lake (see Figure 1). This refinery of intermediate capacity for ore processing, is a typical example of the acid leach-resin-in-pulp process. At the time of the field survey it was processing slightly more than 500 tons per day of ore that assayed about 0.20 per cent U_3O_8 . The mill had been in operation about 1 year prior to this study. Virtually all liquid wastes were delivered to tailings ponds for storage and volume reduction by evaporation and seepage. There was a small direct liquid discharge to Cottonwood Creek, a tributary of the Cheyenne.

The Cheyenne River near Edgemont, South Dakota, is a relatively shallow stream with a sandy bottom. Flow is often turbid, and at the time of the field survey biological life was relatively sparse. River flows have been recorded from 1928 to 1933 and from 1947 to the present by the U. S. Geological Survey at a

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servable variation between sampling stations. The biological samples showed correspondingly low concentrations of gross radioactivity. Ground water samples had dissolved alpha and beta activity in the same range as was indicated by the Cheyenne River water samples.

In 1957, a sample of slimes tails before entering the slimes tailings pond yielded gross alpha and beta activities of 590,000 and 780,000 $\mu\mu\text{c}/\text{l}$, respectively. Virtually all of this activity was in suspended solids, and the dissolved activities were 980 and 930 $\mu\mu\text{c}/\text{l}$, respectively. A liquid sample from the slimes pond indicated similar dissolved activities, with only slight suspended radioactivity. Subsequent water samples (June 1957) indicated no significant radioactivity above background in the Cheyenne River or in Cottonwood Creek, although the small direct drainage from the sands pond to this creek contained 1,400 and 1,800 $\mu\mu\text{c}/\text{l}$, respectively, of dissolved gross alpha and beta radioactivity. No radium analyses were made prior to the mill survey of July 1957.

In terms of radioactive waste disposal, radium is the most hazardous radioelement involved in the extraction of uranium from its ores. Only the uranium is wanted, and all of its radioactive daughters, including radium, are disposed of as waste products. Of all of these decay products, radium has by far the lowest maximum permissible concentration in water.² Hence, the amount involved, as well as the course of its passage through the extraction process, is of considerable interest. Of special concern is the question of how much radium becomes dissolved in the processing of ore, and where this dissolved portion goes. One of the prime aims of this study, therefore, was to perform a radium balance through the mill, and in so doing to answer the foregoing questions.

The Mill Process ³

Briefly, ore received at the mill is crushed and ground, and leached with sulfuric acid to dissolve the uranium. The coarse sands are separated and discharged to waste, and the remaining slurry, or IX feed, containing the slimes or fine solids, proceeds to ion exchange resin banks. Here the uranium is extracted from the feed solution by resin beads, and is in turn stripped from the beads, precipitated, filtered and dried to form yellowcake, which is the final product of the process. This uranium concentrate is then shipped to other facilities for further refining and processing. The IX feed solution, having been stripped of its uranium, becomes the slimes tails, and is neutralized with lime and sent to the slimes pond. Figure 2 is a schematic flow diagram of the entire process.

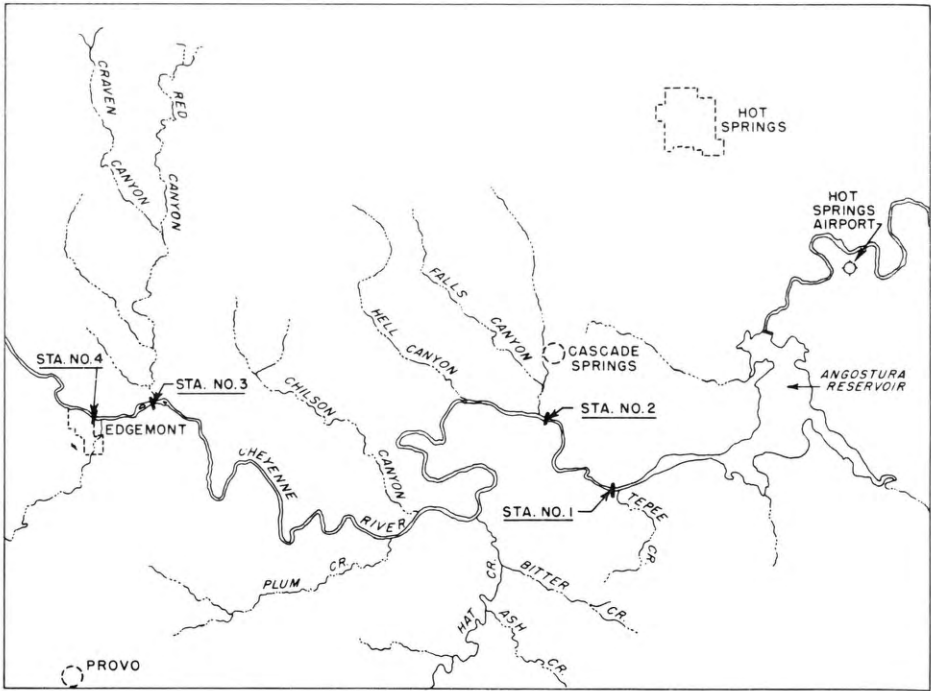


Figure 1. Radioactivity monitoring stations, Cheyenne River, 1956.

gaging station located just upstream from Cottonwood Creek. There are some 7,143 square miles of drainage area above this gage. From 1947 to 1955 the average annual flow in the river at Edgemont ranged from 20.5 to 144 cubic feet per second (cfs); the minimum monthly average flow for this 9 year period ranged as low as 0.02 cfs and as high as 1.6 cfs. The flow drops to zero every year for varying periods; in 1952 there were only 6 days of zero flow, while in 1950 there were 62 days. Over the 9-year period there were 296 days of zero flow; in other terms, the records indicate that on the average the river flow at Edgemont has been zero for 8.1 per cent of the days.

During February 1956, before the mill went into operation, a radioactivity background survey of the Cheyenne River below Edgemont was made by the South Dakota State Department of Health and the Public Health Service. At that time samples of river water, mud or sand, and aquatic life were collected at four locations and analyzed for gross alpha and beta radioactivity. The sampling stations are shown in Figure 1. Biological samples included plankton, algae, insects, and minnows. The water samples contained 10 to 40 micromicrocuries per liter ($\mu\mu\text{c}/\text{l}$) of dissolved alpha activity and 10 to 120 $\mu\mu\text{c}/\text{l}$ of dissolved beta activity. Suspended radioactivity was practically nil. River mud samples contained an average of 10 and 15 micromicrocuries per gram ($\mu\mu\text{c}/\text{g}$) of dry solids of alpha and beta activity respectively, with no ob-

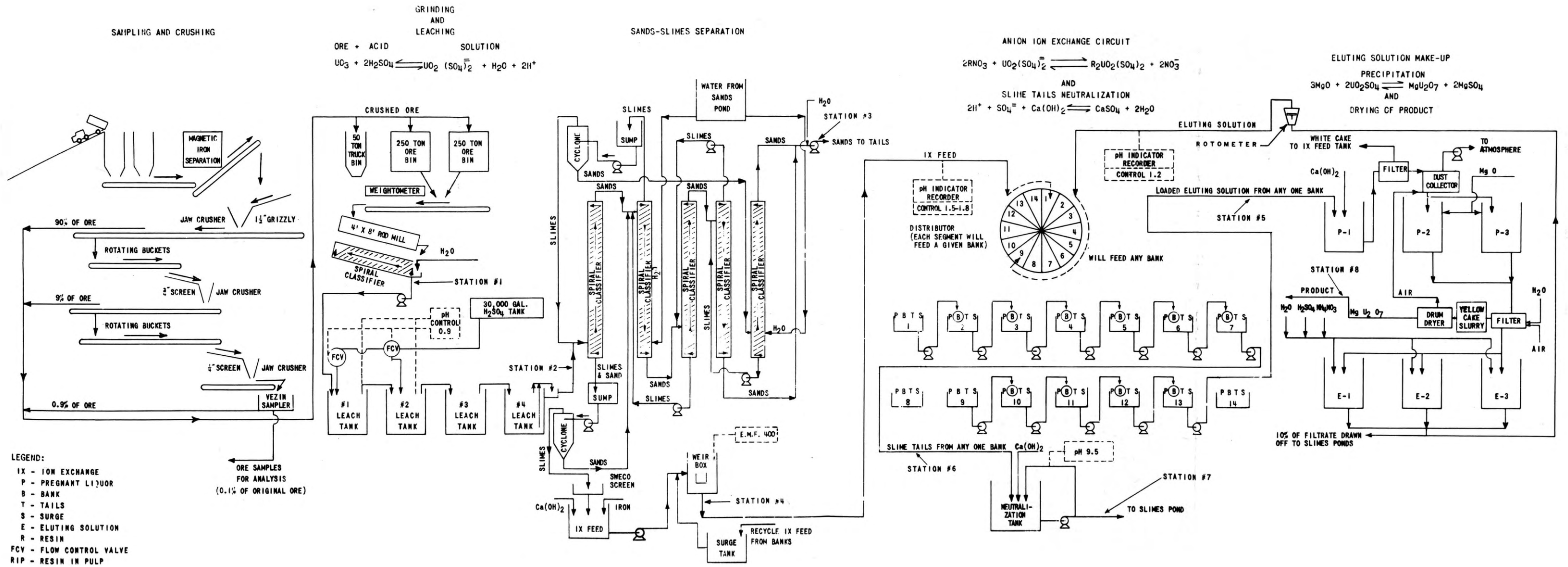


Figure 2. Flow diagram of resin-in-pulp process. Mines Development, Inc., Edgemont, South Dakota, July 1957.

SAMPLING

Trucks are used to dump the uranium ore into either of two ore bins from the ramp shown at the far left in Figure 2. The ore is fed to the sampling plant from these bins by a conveyor belt. A magnetic iron separator removes metal scraps, nuts, bolts, etc. In the sampling plant the ore passes over a 1-1/2 inch vibrating grizzly, then goes to a 1-1/2-inch jaw crusher, and falls on a conveyor belt. Ten per cent of the ore is removed from the belt by calibrated rotating buckets and 90 per cent goes directly to the mill. The 10 per cent passes over a 3/4-inch screen, goes to a 3/4-inch jaw crusher, and drops to a conveyor belt. Ten per cent of this (one per cent of the original ore) is removed by calibrated rotating buckets, and the remainder leaves for the mill. The retained material (1 per cent) goes to a 1/4-inch screen and a 1/4-inch jaw crusher, and falls to a conveyor belt from which a Vezin sampler removes 10 per cent. The remainder leaves for the mill. The sample amounts to 0.1 per cent of the original ore feed, or two pounds of ore per ton of ore fed. This representative sample is assayed for its U_3O_8 content. After leaving the sampling plant the crushed ore goes to either of two 250-ton ore bins or to a 50-ton truck bin from which specification material can be taken for blending.

GRINDING

The mill bins each have two bottom discharge hoppers. One means of blending control consists of regulation of the feed rates from these four chutes. Another method of blending involves scheduling of various shippers lots through the mill. Factors considered for primary blending purposes include the grade of ore, particle size of sand grains, slimes content, and oxidizing or reducing characteristics of the ore.

The grinding facility consists of a 4- by 8- foot rod mill in open circuit, with a 42-inch spiral classifier. The feed to this grinding section is very fine, not only because the sandstone ores are poorly cemented but also because crushing and repeated handling before the mill bins cause a large portion of the ore to be broken down into individual grains. The resulting feed is easily ground to minus-12-mesh. Water is added at the spiral classifier to make a slurry. Water for the mill is obtained from an artesian well at a natural temperature of 53°C.

LEACHING

The slurry from the grinding plant is pumped to a series of four wood-stave tanks, each measuring 14 feet in diameter and 14 feet high, where leaching is carried out. Each tank is equipped with a 48-inch rubber covered propellor mounted on a 4-1/2-inch diameter rubber covered shaft; these tanks are operated in series.

Most of the ore received at this mill is easily leached. Most of the uranium is in an oxidized state, and hydrocarbons or other reducing elements are not present. Excessive sliming is not a problem, because the ore is loosely cemented and contains very little clay, bentonite, etc.

Sulfuric acid is automatically metered to the first two leach tanks from a 30,000-gallon acid storage tank in quantity sufficient to maintain pH from 0.9 to 1.4, depending upon the type of ore being processed. Two continuously recording pH meters with calomel electrodes are used at the leach tanks and are coupled to controllers that automatically regulate the acid feed. Leaching is carried out at about 40°C, with no attempt to regulate heat in the system. The retention time in each leach tank is about 3 hours and the pH of the pulp overflow from the fourth tanks is usually under 1.5.

SAND-SLIME SEPARATION

The slurry, or pulp, from leaching, with the uranium in solution, undergoes sand-slime separation in five 30-inch by 17-1/2-foot spiral classifiers and two 10-inch cyclones. Three 2-inch vertical sand pumps and two 3-inch pumps are used in this section. Sands advance from the first to the fourth classifier, and from the second cyclone to the fifth classifier, are washed, and pumped to the sands tailings pond. To facilitate pumping, fresh water is added at the pump. Water recycled from the sands tailings pond is introduced at the second and fifth classifiers to wash the leached sands and to reduce pulp density for a sharper separation in the cyclone. To minimize losses of uranium-bearing solution, the spiral classifiers are set at a relatively steep slope, which results in a small pool surface and long drainage deck.

The overflow from the first cyclone contains 5 to 10 per cent solids that are minus-300-mesh in size. After screening to remove wood chips and other trash, this overflow goes to a 21- by 21-foot wooden tank for storage ahead of the ion exchange circuit. Powdered iron is usually added at this tank to adjust the solution EMF to 400, in order to keep vanadium in its tetravalent state and thus prevent poisoning of the resin during ion exchange. The ion exchange feed has a pulp density of about 1.05; entrained solids are minus-300-mesh, pH is 1.7 to 1.9, EMF is 400, and the concentration of U_3O_8 in solution is about 1.0 gram per liter (1,000 parts per million). This pulp, with a small amount of recycle IX feed from the banks, is pumped to a small elevated constant head tank, from which it is metered by means of a weir to the distributor for the resin tanks.

ION EXCHANGE

Basically, the uranium is absorbed from the IX feed solution on anion exchange beads. The beads are then stripped of their uranium by an acidifier nitrate solution, and the uranium is sub-

solution is thus drained to the bank pumps. Control of the solution level provides smooth continuous flow from bank to bank, and minimizes surging and overloading of any of the banks.

The beads must be hosed intermittently to keep them wet and promote drainage, once a bank has been drained of solution. The beads tend to swell and stick together when dry, but separate readily if kept wet. The bank taken off the adsorption cycle is washed to remove slimes adhering to the beads, in order not to contaminate the eluting solution. After elution, the beads are washed to remove excess nitrate. Wash water is kept to a minimum, and is recycled to the IX feed storage tank.

Eluting solution is made up in three wooden tanks. At any time, one tank is delivering fresh eluate to the RIP banks, one is receiving filtrate from yellowcake filtration, and the third, full of filtrate, is being adjusted with acid and nitrate. Fresh eluate entering the RIP section has about 56 grams per liter (g/l) of nitrate ion and is acidified with sulfuric acid to a pH of 1.2.

Considerable purification and concentration of uranium results in the RIP circuit. The anion resin beads extract in the neighborhood of 99.7 per cent of the uranium in solution, but only a small fraction of the dissolved iron, vanadium and aluminum. After elution, the pregnant eluate sent to precipitation assays 10 to 20 times the uranium assay of the IX feed solution, and contains 10 to 12 g/l of uranium, expressed as U_3O_8 . This uranium-rich solution is pumped to a pregnant eluate holding tank.

URANIUM EXTRACTION

The pregnant eluate is next filtered and clarified, before uranium precipitation, in order to obtain a clean concentrate uncontaminated by slimes solids carried into the pregnant eluate. Sufficient milk of lime is added to bring the pH up to 3.5 with subsequent precipitation of calcium sulfate, or whitecake, which is returned to the IX feed tank. The pregnant eluate is then clarified by a 38-frame plate and frame filter press. This preliminary filtration also controls filtrate buildup. Sulfates are controlled also by bleeding off about 10 per cent of the yellowcake filtrate to slimes tails.

The clarified pregnant eluate is next cycled through a yellowcake dust collector, which strips it of dust from the yellowcake dryers. It then proceeds to one of two 12- by 14-foot precipitation tanks, where magnesium oxide is added in dry form to produce a diuranate precipitate. Enough MgO is added to produce a solution pH of 6.8. The magnesium oxide is rather slow-acting but produce a large floc as compared to other precipitation agents. Precipitation required from 4 to 10 hours.

All of the chemical reactions involved are indicated on Figure 2, as well as in the process described by Dayton.³

sequently precipitated from the nitrate solution.

The resin-in-pulp (RIP) section consists of 14 rubber-lined steel tanks, or banks, each containing two stainless steel baskets which are 4-1/2 by 4-1/2 feet in cross section and 5 feet high and have 30-mesh openings. The baskets hold a 10-inch bed of 20-mesh resin beads. The bank is filled with pulp slurry, and the motor-driven baskets oscillate up and down in the tank at 6.3 cycles per minute, to ensure good contact of bead surfaces with the pulp.

The distribution of solutions in the RIP section is accomplished by an ingenious device that eliminates all need for expensive valving in this section. The central unit is a distributor wheel through which IX feed solution and eluate enter the banks. The wheel is divided into 14 compartments, each connected by pipe to one bank. A pH indicator and recorder continuously gives pH of the IX feed and eluting solution, and meters indicate and control the flows of these solutions. Full flexibility of operation is obtained with the system, a detailed description of which is given by Dayton.³

The banks are alternated between an adsorption (loading) cycle, during which bead surfaces are loaded with uranium from the pump, and an elution (stripping) cycle, during which the uranium is stripped from the beads by a stripping solution. In normal operation, 7 banks are on adsorption, 5 are on the elution cycle, one between these two cycles is being washed, and one bank is on standby.

The countercurrent principle is used during loading and stripping. The uranium-rich IX feed solution enters the bank containing the most completely loaded resin; fresh eluate is added to the bank where the beads have the least amount of absorbed uranium. Pregnant eluate is taken from the bank where the beads are most heavily loaded with uranium, and the stripped IX feed leaves from the bank containing the least loaded resin. The bank that is taken off the loading cycle is the next bank placed in the circuit at the end of the stripping cycle. Solution from the seventh bank on the adsorption cycle is sent to the slimes tails neutralization tank.

Control is obtained by quick fluorimetric uranium analysis of samples taken at the first and second banks from the discharge ends of the adsorption and elution cycles. For instance, the lead bank is taken off adsorption and another bank is added at the end of the adsorption cycle when the uranium concentration in the IX effluent to tails builds up to a predetermined level. Otherwise uranium would be lost to the tailings.

The banks are drained by means of bottom discharge ports fitted with a hollow vertical plunger. The solution level in the banks is controlled as desired via large funnels connected by means of flexible rubber hose to the hollow plunger. Excess

Table 1. SAMPLING STATIONS WITHIN THE MILL

Station number	Description
1	Raw ore slurry before entering leach tanks.
2	Leached ore slurry before sand-slime separation.
3 ^a	Sand slurry proceeding to sands tailings pond.
4	IX feed solution.
5	Loaded eluting solution from RIP circuit.
6	Slimes tails from IX banks, after absorption of uranium and before neutralization.
7	Neutralized slimes tails proceeding to slimes pond.
8	Yellowcake.

^a Additional dilution water is added to this process stream beyond the sampling point, to facilitate pumping.

Sampling inside and outside the uranium mill was performed by personnel of the Public Health Service and the South Dakota State Department of Health. Sampling within the mill commenced on July 25 and was completed on July 30, 1957. During four days of this period, samples at each station within the mill were collected hourly for eight hours and composited; in the middle of the survey the mill samples were collected hourly for an uninterrupted 24-hour cycle and were composited into 3-hour samples. This program resulted in four 8-hour composite and eight 3-hour composite samples at each of the eight sampling stations within the mill. A full set of samples was shipped to the Robert A. Taft Sanitary Engineering Center of the Public Health Service, in Cincinnati, Ohio, for gross radioassay and chemical analysis; identical samples were sent to the Occupational Health Field Station, Public Health Service, Salt Lake City, Utah, for radium analysis.

A primary purpose of the study was to make a complete balance of all radium entering and leaving the mill in both dissolved and undissolved form, and separate radium analyses were performed on the solid and liquid phases of the samples. For this purpose, the hourly samples collected during the 8-hour periods on July 25 and 26 were composited into a single sample for radium analysis for each mill station. The hourly samples collected over the 8-hour periods on July 27 and 30 were similarly composited. The hourly samples taken for the 24-hour period during July 28 and 29 were composited into a single sample for each station for radium analysis.

Samples of the direct drainage to Cottonwood Creek were collected on each of the latter three days of the survey. A single representative sample of dry sands was obtained from the sands pile, and a single representative sample of wet solids was taken from the slimes pond. Liquid samples were collected from the

The precipitated slurry is pumped to one of two frame filter presses for yellowcake filtration. A layer of filter paper and a layer of nylon filter fabric are used on the press frames. After filtration the cake is washed with water and given an air blow. Below the filter presses are removable drip pans, which are installed over a paddle re-pulper that extends the full length of the filter. The drip pan is removed and the filter opened; the precipitate is scraped off the frame and drops to the re-pulper, which keeps the cake fluid while it is delivered to an agitator. The concentrate that forms on the drum is scraped off and drops to a hopper, from which it is drummed for shipment.

The drum dryer operates under a slight vacuum, and the exhaust is pulled through a dust separator fitted with ceramic baffles. Clarified eluate is introduced at the top of the separator and percolates down, stripping the uranium concentrate from the dryer exhaust. The scrubbed air is vented to atmosphere.

The filtrate from the yellowcake presses goes to the eluting solution tanks, where it is adjusted with acid and nitrate to make fresh eluant. Ten per cent of the filtrate is delivered to the slimes tails to prevent sulfate buildup.

The slimes tails from the RIP banks are sent to a neutralization tank, where lime is added to bring the pH to about 9.5. After neutralization, these wastes are delivered to the slimes tailings pond, a large lagoon located near the Cheyenne River.

The Mill Survey

For purposes of analyzing the mill process and characterizing the resulting liquid wastes, eight sampling stations were set up within the mill (Table 1); the field survey was carried out from July 25 through July 30, 1957. Six other sample types were collected outside the mill. These included:

- a. Liquid from the slimes tailings pond.
- b. Wet solids from the slimes tailings pond.
- c. Liquid from the sands tailings pond.
- d. Dry sand from the sands tailings pile.
- e. Silt and wet solids from the slimes pond outlet to the Cheyenne River.
- f. Direct liquid drainage to Cottonwood Creek.

Sampling stations 1, 2, 4, 5, and 8 were main mill process streams, whereas 3, 6, and 7 represented liquid waste streams.

The general procedure for gross radioactivity determination is described elsewhere.⁴ Dissolved and undissolved solids were analyzed separately, and a self-absorption analysis was performed for a representative sample from each station. This procedure also is described elsewhere.¹

CHEMICAL

Chemical analysis of the various samples was performed by standard methods outlined in detail elsewhere.⁵ Nitrates were determined by the phenoldisulfonic acid method, and sulfates, calcium, and magnesium by the gravimetric methods outlined. Iron was determined by the phenanthroline method, manganese by the periodate method, and chlorides by the mercuric nitrate method. The results for manganese may have some error due to interferences caused by iron and chlorides, and in future work it is planned to determine manganese colorimetrically by the ammonium persulfate method to correct for these problems.

Analytical Results

During the survey period the average rate of ore processing was 517 tons per day. Table 2 shows the average slurry flow at each mill sampling station, as well as the specific gravity and suspended solids content. Slurry flows were based upon observations within the plant and on computations that accounted for specific gravity of the dry solids, dry solids flows estimated from ore processed, specific gravity of the liquid phase, and observed specific gravity of the slurry. The slurry flow at Station 3 is not the entire flow going to the sands pond, as considerably more dilution water was added just following the sample collection point at this location.

Table 3 presents radium concentrations, dissolved and undissolved, in the various mill process streams as well as at the several locations outside the mill. These are the average results for the survey period, and are given in stet of slurry, and in stet dry suspended solids. As can be seen, there is good agreement between the dissolved radium concentrations at Stations 2, 4, 5, and 6, and between Station 7 and the slimes pond liquid. Similarly, the concentrations of radium per gram of dry solids agree well at Stations 1 and 2, at Stations 4, 5, and 6, at Station 7 and slimes pond, and at Station 3 and sands pond (dry sands).

Gross alpha and beta radioactivity, dissolved and undissolved, for the mill stations is given in Table 4, in $\mu\mu\text{c}/\text{l}$. The dissolved gross alpha and beta radioactivity shows a large gain as the result of acid leaching, and, as expected, slimes neutralization results in a major reduction of the dissolved gross activities in the slimes liquid at Station 6. The results for Station 1 (Tables 3 and 4) indicate that the radium constitutes about 16 per cent of the gross alpha activity of the ore.

sands and slimes ponds on each of three days. One representative mud sample was collected at the slimes pond outfall to the Cheyenne River. Duplicate sets of these samples were shipped to the Public Health Service laboratories in Ohio and Utah for the analyses noted above.

A record of the tonnage of ore processed was obtained frequently during the survey from the weightometer preceding the rod mill. Weir discharge records for flow were kept regularly at the weir box preceding the RIP section, and the quantity of eluate flow was obtained from plant equipment. Water flows at the various points of addition were obtained from plant personnel, as were estimates of chemicals used in the process. These included ammonium nitrate, magnesium oxide, lime, iron, and sulfuric acid. Water from Cottonwood Creek was pumped to the sands pond during the survey period in order to provide sufficient water in the sand-slime separation and for diluting the sand slurry. Estimates of solids concentrations, pulp density, etc., at various points in the mill were obtained from the operating personnel.

Laboratory Procedures

RADIOACTIVITY

Radium was determined generally by coprecipitation with barium sulfate. Following pretreatment of the various types of samples to put the radium in solution, the procedure consisted essentially of evaporation with sulfuric acid, removal of polonium, coprecipitation of radium with barium sulfate, purification, and alpha counting of the precipitate. Rather extensive pretreatment of the undissolved solids of the mill samples was necessary to entirely dissolve them. Those samples that contained large quantities of undissolved solids were centrifuged for separate radium analysis of liquid and of solid phases. The solids were then washed with water to wash out the liquid not removed by centrifuging, and this wash water was added to the liquid portion to be analyzed for radium.

Most of the samples had high concentrations of suspended and settleable solids. The gross radioactivity analyses of the suspended and dissolved solids were performed independently on separate representative portions. This procedure eliminated the need for a large number of absolute quantitative transfers for the radioactivity determinations. A known volume of sample was filtered through a membrane filter and washed. The filter and filtered solids were removed and ashed at 600°C to constant weight. The filtrate was evaporated to dryness and ashed at 600°C to constant weight. Solids concentrations were based upon the total sample volume.

Table 4. GROSS RADIOACTIVITY.

Station	Gross Alpha, $\mu\mu\text{c}/\text{l}$		Gross Beta, $\mu\mu\text{c}/\text{l}$	
	Undissolved	Dissolved	Undissolved	Dissolved
1	3.66×10^6	1.71×10^3	4.79×10^6	1.02×10^3
2	2.86×10^6	473×10^3	3.96×10^6	613×10^3
3	1.08×10^6	3.08×10^3	0.992×10^6	2.05×10^3
4	0.880×10^6	388×10^3	0.962×10^6	555×10^3
5	0.010×10^6	$2,930 \times 10^3$	0.017×10^6	$5,740 \times 10^3$
6	0.810×10^6	94.5×10^3	0.866×10^6	47.5×10^3
7	0.725×10^6	1.08×10^3	0.610×10^6	1.28×10^3

also determined for the liquid portions of samples from other mill stations, and was essentially zero at liquid portions of samples from other mill stations, and was essentially zero at Stations 1, 2, and 3, but was 15, 8, 200, and 230 mg/l, respectively, at Stations 4, 5, and 6. Based on the flows in Table 2 (liquid portion), the ore processing rate of 517 tons per day, and a chemical estimate of the nitrate ion required for exchange with uranium, the nitrate ion use during the survey was calculated to be about 15 pounds per ton of ore processed. This is in good agreement with the mill records.

Table 5. QUALITY OF WASTE FLOWS AND PONDS CONTENTS.

Sampling station	Material dissolved in liquid sample, mg/l						
	Sulfate	Chloride	Calcium	Magnesium	Iron	Manganese	Nitrate nitrogen
Slimes to Tails (Station 7)	2,330	205	730	75	0.14	~0	500
Liquid from Slimes Pond	2,190	200	820	80	~0	1.3	460
Sands to Tails (Station 3)	2,180	240	570	120	Trace	7.0	~0
Liquid from Sands Pond	1,970	275	440	150	~0	~0	~0
Drainage to Cottonwood Creek	1,090	170	360	65	~0	~0	Trace

As has been indicated, one of the primary purposes of this survey was to make a radium balance throughout the process, if possible. Table 6, based upon the data in Tables 2 and 3, presents the radium balance for the mill, and indicates the various paths by which specific quantities leave the mill. The acid leaching process dissolves a certain amount of radium as well as the uranium. Some of the suspended radium remains tied up with the sands (about 170 micromicrograms of radium per gram of dry

Table 2. PROCESS STREAM CHARACTERISTICS

Mill Sampling Station	Slurry flow gal/min	Specific Gravity of slurry	Dry suspended solids by weight, per cent
1	91	1.52	60
2	91	1.53	59
3	91	1.45	64
4	146	1.05	7.2
5	12	1.13	~ 0.07
6	142	1.05	7.2
7	151	1.05	8.2

Table 5 indicates the results of the chemical analyses of samples of waste flows and pond contents. These results are given in milligrams per liter (mg/l) of the liquid portion of the samples, and represent only dissolved chemicals. Nitrates are expressed as nitrate nitrogen, rather than nitrate ion. It should be noted that the sands pond was also receiving water pumped from Cottonwood Creek during the survey.

The general agreement between Station 7 and the slimes pond and Station 3 and the sands pond is evident. Nitrate nitrogen was

Table 3. RADIUM CONCENTRATIONS

Station	Radium in $\mu\mu\text{g/l}$		Radium in dry suspended solids, $\mu\mu\text{g/g}$
	Dissolved	Undissolved	
1	98	605,000	650
2	2,150	640,000	710
3	114	163,000	170
4	2,450	273,000	3,640
5	2,290	2,050	~ 2,800
6	2,450	288,000	3,760
7	350	250,000	2,930
8	--	--	150
Liquid from Slimes Pond	270	--	--
Liquid from Sands Pond	8	--	--
Drainage to Cottonwood Creek	17	--	--
Dry Sands	--	--	150
Solids from Slimes Pond	--	--	2,470
Slimes Pond Outlet Ditch	--	--	58

solved gross alpha activity of 1,080 $\mu\mu\text{c}/\text{l.}$, about 30 to 35 per cent is due to dissolved radium.

In similar fashion rough balances of the gross alpha and beta radioactivity can and have been made. They need not be reproduced here, as radium is the specific radioelement of major interest, and its balance has been shown. Of interest, however, is the fact that the undissolved radium varies between 15 and 38 per cent of the undissolved gross alpha activity at Stations 1 through 7, while dissolved radium constitutes from 0.1 to 35 per cent of the dissolved gross alpha activity. Details of these figures can be obtained by a simple computation with the data of Tables 3 and 4.

Although dissolved radium is not concentrated in the ion exchange section, dissolved gross radioactivity is. Table 4 indicates that the dissolved gross alpha and beta radioactivity was concentrated by a factor of 8 to 10 in the RIP section, or between Stations 4 and 5. This is in good agreement with the estimated concentration of uranium by a factor of 10, as quoted by mill personnel and by Dayton.³

Summary and Conclusions

About 17 per cent of the gross alpha activity of the ore processed at the uranium refinery under study was due to the presence of radium. At the ore processing rate of 517 tons per day, the liquid and solid wastes from ore processing contained about 0.6 milligrams of radium per ton of ore processed, or a total of approximately 300 milligrams per day. The bulk of this radium 99.8 per cent, remained in undissolved form throughout the process, and was effectively retained in the sands and slimes tailings ponds.

About 0.2 per cent of the radium that entered the mill with the ore either left the refinery in the final uranium concentrate or was delivered in dissolved form to the slimes or sands pond. Specifically, it has been estimated that some 310 $\mu\text{g}/\text{day}$ of dissolved radium went to the slimes pond, about 60 $\mu\text{g}/\text{day}$ went to the sands pond, and about 150 $\mu\text{g}/\text{day}$ of radium left the mill in the dried yellowcake.

The radium content of the dried sands was about 150 micro-micrograms per gram ($\mu\mu\text{g}/\text{g}$) of sands, while the radium content of dried slimes solids was 2,500 or more $\mu\mu\text{g}/\text{g}$. Sands accumulation was in the neighborhood of 440 tons per day, while slimes accumulated at a rate of about 80 tons per day. Effective retention and confinement of these solids and of the tailings pond liquids resulted in practically no radium leaving the plant site during the survey, except for that contained in the uranium concentrate that was drummed and shipped. The very small amount of direct drainage to Cottonwood Creek was from the sands pond and contained little radium or nitrate nitrogen.

sands) and is discharged with them to tails at Station 3. A portion of the dissolved radium (150 microgram per day) present at Station 4 goes with the loaded stripping solution at Station 5, although the data of Table 3 indicate that dissolved radium is not extracted or concentrated by the ion exchange section. As will be seen, virtually all of this carried over radium becomes a part of the yellowcake that is shipped out of the mill. The neutralization of the slimes tails with lime results in precipitation of a substantial fraction (about 85 per cent) of the radium dissolved in the liquid at Station 6, as shown by both Tables 3 and 6.

Table 6. RADIUM BALANCE

Station	Radium, mg/day		
	Undissolved	Dissolved	Total
1	301	0.049	301
2	316	1.06	317
3	81	0.057	81
4	217	1.95	219
5	0.1	0.150	0.25
6	223	1.90	225
7	225	0.316	225

As a check on the data in Table 6, the radium content of the ore can be estimated within reasonable limits of error. If radioactive equilibrium of radium with uranium is assumed on the basis of 517 tons per day of ore that assays 0.20 per cent U_3O_8 , it has been calculated that 270 milligrams per day of radium enter the mill with the ore. This is in satisfactory agreement with the totals of Table 6.

Further computations indicate that virtually all of the radium present at Station 5 ($150 \mu\text{g/day}$) becomes a part of the final uranium concentrate. If 96 per cent over-all recovery of uranium is assumed and notice is taken that the yellowcake is approximately 75 per cent uranium as U_3O_8 , calculations indicate that roughly 1.2 tons of yellowcake are produced per day. If the radium concentration of $150 \mu\text{g/g}$ of dry solids in Table 3 is used about 160 micrograms per day ($\mu\text{g/day}$) of radium leave the mill with the yellowcake. This is quite close to the figure of $150 \mu\text{g/day}$ for Station 5 (Table 6).

From Table 6 it is evident that about 300 milligrams per day of radium enter the mill. About 80 milligrams per day leave with the sands at Station 3, and 220 milligrams continue through the process to the slimes pond. Some 60 micrograms per day of dissolved radium are discharged to the sands pond and about 300 micrograms per day of dissolved radium go to the slimes pond. The data in Tables 3 and 4 for Station 7 indicate that of the dis-

in long term contamination of the watercourse, and they could significantly contaminate equipment at downstream domestic or industrial water treatment plants.

Liquid wastes from the slimes ponds at this and similar mills should be released to surface waters only in accordance with existing regulations and on the basis of detailed information as to local downstream water uses. This liquid, free of suspended solids, contains considerably more than allowable concentrations of radium and of nitrate nitrogen. At the uranium refinery studied, such control is especially important in view of the zero flows and extended low flow periods that occur in the Cheyenne River. As has been noted, these flows are such that little or no dilution of the effluent would occur for extended periods of time. Any susceptible ground water supplies located near the slimes tailings ponds of such refineries should be tested periodically for nitrate nitrogen and radioactivity content, as infiltration of the slimes pond liquid into the ground water may occur at the pond.

As regards measurement of radioactivity in the effluent from the slimes tailings pond at Edgemont, South Dakota, it appears reasonable to suppose from these studies that the dissolved radium content will generally be in the neighborhood of 30 per cent of the dissolved gross alpha activity. It seems feasible, for routine measurement purposes, therefore, to analyze these samples for dissolved gross alpha activity and apply the factor of 0.30 to compute dissolved radium. An occasional analysis for radium itself will then serve as a check, and refine the percentage figure to be used. In this way, adequate control can be provided and the costs and labor of sample analysis for routine control can be minimized. This percentage figure might also prove adequate within reasonable limits of error for application at other mills using the same process, but this cannot be known until further studies are carried out.

Increases or decreases in the rate of ore processing at the Edgemont, South Dakota, refinery, or changes in the U_{308} content of the ore, should be proportionately reflected in many of the waste quantities. This applies particularly in the case of radium. Thus, if no important process change is assumed, a capacity increase to, say, 750 tons of ore per day, at 0.20 per cent U_{308} should result in about 440 milligrams per day (mg/day) of radium entering the slimes tailings pond. Any basic change in the type of ore received would, of course, affect these figures, especially the latter.

It is not intended here to generalize very much beyond the local situation studied. Each uranium refinery waste disposal problem is individual, and must be interpreted in terms of specific local water uses such as domestic water supply, irrigation of croplands, recreation, etc., as well as in terms of the specific

The data in Table 3 indicate that some of the radium becomes dissolved during the acid leach process (see data for Stations 1 and 2). Radium was not concentrated, however, by the RIP section the concentration of dissolved radium in the loaded stripping solution (Station 5) was essentially no different from that in the IX feed (Station 4) or the slimes to tails (Station 6). The opposite occurred in regard to gross alpha and beta radioactivity: the gross alpha activity in the IX feed was $3.88 \times 10^5 \mu\mu\text{c}/\text{l}$, in the loaded stripping solution it was $29.3 \times 10^5 \mu\mu\text{c}/\text{l}$, or greater by a factor of 7.5; and in the slimes to tails it was reduced to $0.95 \times 10^5 \mu\mu\text{c}/\text{l}$, or a factor of 4.1 as against the IX feed. The gross beta activity behaved similarly; the loaded stripping solution had a concentration 10.3 times that of the IX feed, while the slimes to tails showed only 8.6 per cent of the dissolved beta activity of the IX feed. Hence, the data indicate that although uranium was concentrated as usual by the RIP section, radium was not concentrated here.

Slimes neutralization before discharge to the tailings pond reduced the dissolved radium concentration from 2,450 to 350 $\mu\mu\text{g}/\text{l}$, or by about 85 per cent. Liquid from the slimes pond showed a comparable concentration of dissolved radium about 270 $\mu\mu\text{g}/\text{l}$. The data for Station 7 indicate about one-third of the dissolved gross alpha activity in the slimes pond liquid was due to radium.

The nitrate nitrogen concentration in slimes pond liquid was 460 mg/l. While this is probably of no public health significance in this case, such concentrations could be of considerable importance at other locations where public water supplies are involved. These quantities of nitrogen could also provide sufficient nutrient material to result in undesirable blooms of algae and other biota in streams and reservoirs. Shortly after the field survey was completed the use of sodium nitrate in place of ammonium nitrate was instituted at the refinery, but it is doubtful that this would appreciably alter results presented here.

WASTE DISPOSAL PRACTICE

As has been noted, there has been quite careful control of wastes at the Mines Development Company refinery at Edgemont, South Dakota. Sand and slime solids have been effectively confined at the plant site, and liquid waste releases have been at a minimum.

Waste disposal from this mill and from mills employing a similar process should continue to be carefully supervised, and should in any instance be based upon available knowledge of downstream water uses and of the fate of the wastes in the water environment. The sand and slimes solids should generally be effectively retained and confined, as they contain considerable radium and other radioelements. Their release to a stream would result

THE ACID LEACH-SOLVENT EXTRACTION URANIUM REFINING PROCESS.

I. GUNNISON MINING COMPANY, GUNNISON, COLORADO.

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Introduction

This is a report of an in-plant survey of the Gunnison Mining Company, a uranium refinery utilizing the acid leach solvent extraction process; Part II describes a study performed at the Climax Uranium Company mill at Grand Junction, Colorado, which has a similar process. This study was performed by the Public Health Service during August 1958 with the cooperation of the Colorado Department of Public Health, the Gunnison Mining Company, and the U. S. Atomic Energy Commission.

The Gunnison Mining Company refinery is located at Gunnison, Colorado, on the Gunnison River, about 130 miles upstream from Grand Junction, Colorado, and the confluence of the Gunnison and Colorado Rivers. At the time of the survey there were no direct discharges to the Gunnison River. Figure 1 outlines the flow diagram for this refinery and the process is described in detail in the following sections.

The Gunnison uranium refinery began operation about 8 months prior to this survey. At the time of survey, it was processing an average of 330 dry tons per day of ore that assayed from 0.21 to 0.49 per cent U_{308} , and was producing uranium concentrate at a rate of about 1,500 pounds per day. All wastes from the mill were retained in a tailings pond, with no direct discharge to the Gunnison River.

The Mill Process

ORE RECEIVING, SAMPLING, AND CRUSHING

Loaded ore-trucks are emptied into a 50-ton ore hopper, from which ore is fed on a 30-inch conveyor belt to the sampling plant. A magnet removes tramp iron from the ore as it discharges from this conveyor onto a vibrating grizzly. Ore less

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waste characteristics and mill process. Available dependable dilution in the receiving waters is also a critical factor in control of these wastes. No two problems are likely to be precisely the same, and in the dual interest of radiological safety and economy, such waste disposal problems should each be carefully analyzed as individual cases insofar as necessary. It is hoped that the information presented herein will provide some insight into the waste disposal problems at acid leach resin-in-pulp mills generally, but the data should not be applied to other mills without considerable caution.

Acknowledgment

The generous cooperation and assistance of the following organizations and individuals is hereby gratefully acknowledged: Harold Webb, Plant Superintendent, and personnel of the Miles Development Company; the U. S. Atomic Energy Commission; D. E. Rushing and W. J. Garcia, Public Health Service, Salt Lake City, Utah; M. Nelson and R. Spicer, South Dakota State Department of Health; J. K. Neel, Public Health Service, Kansas City, Missouri; A. F. Bartsch, N. D. Wastler, S. D. Shearer, J. T. Jones, R. C. Kroner, H. L. Faig, and R. J. Lishka, Public Health Service, Cincinnati, Ohio

than 3 inches in size drops through the grizzly onto a 24-inch conveyor, while larger pieces are crushed in a jaw crusher, and then rejoin the ore flow. The 24-inch conveyor feeds a vibrating screen through which ore less than 3/4-inch in size drops onto another 24-inch conveyor belt; larger pieces are crushed in a gyratory crusher and then fall onto the belt. As the ore leaves the end of this conveyor, a 10 per cent sample is taken by a chain and bucket sampler, while the remainder of the ore is conveyed to one of two 250-ton fine-ore bins.

The sample is screened, the larger pieces are crushed in a jaw crusher, and a 10 per cent sample is taken by a second chain and bucket sampler; the balance of the original sample is conveyed to the fine-ore bins.

The remaining sample is again screened and crushed, and enters a vezin sampler from which a 5, 10, 15, or 20 per cent sample may be taken as required. The balance of the original sample proceeds to the fine-ore bins. The final sample collected amounts to about 0.1 per cent of the original ore fed to the process, or two pounds per ton. This representative sample is assayed for its U_3O_8 content.

An additional 50-ton fine-ore bin is available for temporary storage of special ores or excess fine ore. This is not ordinarily used, however, and only a small stockpile is usually maintained. Blending is not practiced; the ore is processed immediately upon receipt at the plant.

GRINDING

The fine-ore bins feed a conveyor belt that transports the ore to the rod mill. Feed tonnage is determined by a weightometer connected to the belt. The ore goes to a 6- x 12-foot rod mill in series with a 48-inch spiral classifier. As the ore enters the rod mill, it is slurried by the addition of water and a small amount of sodium carbonate solution (for corrosion prevention.)

Slurry from the classifier discharges into a sump where sodium chlorate is added to oxidize ferrous iron to the ferric state and to maintain an EMF of over 400 in the leach tanks. The slurry is pumped to the operating floor, passes through a small cyclone that returns plus-35-mesh particles to the rod mill feed, and enters the leach tanks.

LEACHING

There are four acid leach tanks, each 16 feet in diameter and 16 feet deep, which are arranged for series flow. Steam is added to the first tank to maintain a temperature of 85°F., and concentrated sulphuric acid is added to the first two tanks to maintain a pH of 0.8 in the leach liquor leaving the last tank. Average leaching time is about 17 hours. Constant agitation is provided by a propellor-type mechanism in each tank.

to repulp the sand-slime slurry, as previously described. There is recovery of some solvent that has been carried over, which rises to the surface of the liquor in the raffinate tank.

SOLVENT STRIPPING AND YELLOWCAKE PRODUCTION

The pregnant organic liquor from the solvent extraction process goes to a bank of three mixing and settling tanks, where the uranium is stripped from it with a counter-current flow of a 10 per cent sodium carbonate solution. The barren organic is returned to a holding tank for recycling through the solvent extraction system.

The pregnant sodium carbonate solution is passed through a filter press for removal of iron as ferrous carbonate. Sludge from the press is returned as a slurry to the rod mill, while the filtrate proceeds to one of two precipitation tanks, each of which is 12 feet in diameter. Concentrated sulphuric acid is added to neutralize the sodium carbonate, and the solution is heated with steam to about 165° F. to drive off any excess carbon dioxide that may be present. Magnesium oxide is then added to bring the pH to about 7. During this process the mixture is constantly stirred by a mechanism within the tank. Uranium is precipitated as a sodium salt. When precipitation is complete, the tank contents are filtered and the yellowcake recovered by use of a filter press. Filtrate from the press is returned to the slimes thickeners, and the yellowcake goes to a drying furnace. The dried produce is drummed, weighed, and shipped to an Atomic Energy Commission facility. Yellowcake is produced only during the day shift.

The Mill Survey

For purposes of analyzing the mill process and characterizing the resulting liquid waste, ten sampling stations were selected. Samples were collected on an hourly basis from August 7 to August 11, 1958 and were composited at each sampling point over the periods shown:

Cycle 1 (24 hours): 4 PM, August 7 to 4 PM, August 8.

Cycle 2 (36 hours): 4 PM, August 8 to 4 AM, August 10.

Cycle 3 (36 hours): 4 AM, August 10 to 4 PM, August 11.

The sampling stations selected are described in Table 1.

All samples were collected inside the mill building, with the exception of those at Stations 6 and 8, which were collected at the points of discharge to the tailings pond.

During the survey plant flows were obtained at various stations and locations from the operating records of the mill and directly by the survey party. Mill records provided frequent data as to the flow of barren organic pregnant acid liquor and Na_2CO_3 stripping solution. Installed flowmeters gave data as to the acid flow to the

SAND-SLIME SEPARATION

Slurry leaving the leach tanks is diluted with the overflow from the number 3 thickener (see Figure 1), and the combined flow enters a 30-inch classifier. This is the first of four classifiers provided for sand-slime separation, the remaining three being 24-inch size. The sands proceed through the four classifiers and are discharged to a slurry tank. In this advance of the sands, they are washed with thickener overflow; number 2 classifier receives the overflow from number 2 thickener, and number 3 classifier, the overflow from number 1 thickener. Fresh water is used in the number 4 classifier.

The overflow from each classifier carries the slimes into the thickeners. Figure 1 shows the manner in which this is done, each classifier discharging its overflow into the thickener that is adjacent to it.

The slimes proceed through each of the four thickeners, are washed counter-currently during their travel, and the spent slimes are discharged to the slurry tank from the number 1 thickener. The washed sands and slimes are combined in the slurry tank, repulped with raffinate from the solvent extraction process, and discharged to tails. Equipment is available for feeding lime to the slurry tank, but this is not done.

ACID LIQUOR STORAGE

Pregnant acid liquor from the number four thickener proceeds to a 22-foot diameter by 10-foot deep storage tank. An EMF adjusting tank and two filter presses are provided following this storage tank. These units are incorporated into the plant for the purposes of (a) reducing ferric iron to ferrous iron, in order to eliminate interference in the solvent extraction process, and (b) removing the small amount of slimes remaining in the pregnant acid liquor, so as to eliminate difficulties in the solvent extraction process. Usual practice at the time of the survey, however, was to bypass most of the acid liquor around these units into a second storage tank. This practice at times caused emulsification of the solvent due to the presence of slimes in the acid liquor entering the solvent extraction process.

SOLVENT EXTRACTION

Pregnant acid liquor from the storage tank is pumped to a constant head tank above the operating floor, from which it flows into the first of two solvent extraction tanks. Uranium is extracted from the acid liquor by the organic solvent by alternate cycles of agitation and quiescence. There are five such mixing-settling cycles in these tanks. Flow of the organic solvent is counter-current to that of the acid liquor. The raffinate, or barren acid liquor, is discharged into a holding tank from which a portion is pumped directly to the tailings pond, while the remainder is used

dissolved radium. All other analyses were performed at the Cincinnati laboratory.

Yellowcake production amounted to 1,258 pounds, 1,250 pounds, and 3,245 pounds during sampling cycles 1, 2, and 3 respectively. As noted earlier, yellowcake production was carried on only during the day shift and cycles 1 and 2 each included a single day shift, whereas cycle 3 included two day shifts.

Analytical Results

Figure 2 is a schematic flow diagram that indicates the liquid, solids, and slurry flows at the various process location. At each station the slurry flow is given first, with solids and liquid flows next in order. These figures were obtained on the basis of observed specific gravities, tonnages of ore, and other laboratory and field data; computations treat the flow as being composed on two separate streams, liquid and solids. Flows are given to the nearest gallons per minute (gpm). These figures and all succeeding results represent combined computations for cycles 2 and 3 of the survey period, as the samples for cycle 1 were not analyzed.

Late in cycle 2 and extending well into cycle 3 of the survey a batch of custom ore was processed. This ore assayed 0.49 per cent or more U_{308} , compared to the more usual ore assaying about 0.22 per cent U_{308} . Because of this, and as a result of the time lags at several points in the process (for instance, the acid leach process took about 17 hours), it was necessary to combine the data for cycles 2 and 3 in order to make balancing computations.

Table 2 presents certain process stream characteristics for the stations sampled. Slurry flows in gallons per minute, specific gravity of slurry, specific gravity of dry solids, and the per cent dry suspended solids by weight are shown for each sampling station. Table 3 indicates the solids balance for the process during cycles 2 and 3. Approximately 330 tons per day of ore were processed during the survey, as indicated at Station 10. Acid leaching dissolved about 6 per cent of this total tonnage; i.e., 19.8 tons per day left the leach tanks in the dissolved state. The pregnant acid liquor (Station 5) contained about the same amount of dissolved solids.

Table 3 shows that the total plant output (Stations 8, 9, and 6) was about 332 tons per day ($318.5 + 0.7 + 12.6$), which is in excellent agreement with the 330 tons per day of ore processed. The total solids into the slurry tank (Stations 3 + 4 + the raffinate solids going to the slurry tank) total 318 tons per day, which agrees with the output to tails (Station 8) of 318.5 tons per day. The dissolved solids into the slurry tank (Stations 3 + 4 + the raffinate solids to the slurry tank) total 10.0 tons per day, which is in agreement with the dissolved solids output at Station 8. The

first leaching tank and the flow of wash water to the number 4 classifier. Flows at Stations 6 (raffinate to tails) and 8 (sand-slime slurry to tails) were measured hourly in terms of the amount of time required to fill a 55-gallon drum. Hourly readings from the weightometer, together with plant records of the per cent moisture in the belt feed, yielded accurate data regarding tonnage of ore processed. The daily yellow-cake production was obtained from plant records.

Table 1. GUNNISON MILL SAMPLING STATIONS

Station Number	Description
1	Classifier effluent
2	Acid leach tank effluent
3	Sands entering slurry tank
4	Slimes entering slurry tank
5	Pregnant acid liquor to solvent extraction
6	Raffinate to tails
7	Pregnant organic to stripping circuit
8	Sand-slime slurry to tails
9	Yellowcake
10	Acid leach tank feed

Plant equipment and records included hourly observations of pulp density and per cent solids by weight at Stations 1, 2, 3, 4, 8, and 10. Notes were made of any process interruptions during the survey.

Daily composite samples were collected and assayed by plant personnel for the U_3O_8 content of the mill heads (from the rod mill), the tails (from the slurry tank), the leach tank effluent, the pregnant acid liquor, and the raffinate, and these data were made available for this survey. Records of chemical consumption (acid, sodium carbonate, etc.) for the month preceding the survey were also made available, and chemical use figures for the survey period were obtained.

Sampling was performed by personnel of the Colorado Department of Public Health and the Public Health Service. The yellowcake samples were collected by mill personnel, a small vial of about 30 grams being composited from the day's production. All other samples were collected hourly during each cycle indicated.

All samples collected during the survey were shipped to the U. S. Public Health Service, Robert A. Taft Sanitary Engineering Center, at Cincinnati, Ohio. Portions of selected samples were then sent to a private laboratory for analysis of dissolved and un-

total dissolved solids output (Stations 6 plus 8) of 22.6 tons per day is in good agreement with the dissolved solids after acid leach and in the pregnant acid liquor.

Table 2. PROCESS STREAM CHARACTERISTICS ^a

Station	Slurry Flow, gals/min	Specific Gravity of slurry	Dry Susp. Solids by Weight, %	Specific Gravity of dry solids
1	-	1.52	55.4	2.61
2	97	1.36	39.6	2.52
3	50	1.33	38.7	2.64
4	63	1.30	38.1	2.49
5	175	1.01	~ 0.005	-
6	122	1.01	~ 0.004	-
7	29.5	(2)	2 ^b	2 ^b
8	166	1.19	26.0	2.37
9	3 ^c	3 ^c	3 ^c	n.d.
10	99	1.35	41.2	2.61

^a Average of cycles 2 and 3.

^b Liquid (negligible suspended solids).

^c Solid sample.

Table 4 indicates the concentrations of radium 226 in dissolved and undissolved form at the several stations. Undissolved radium is that portion retained on a millipore filter, while dissolved radium represents that contained in the filtrate. The data are representative of cycles 2 and 3, and are given as micromi-

Table 3. SOLIDS BALANCE ^a

Station	Tons per Day		
	Suspended	Dissolved	Total
10	328.0	1.6	329.6
2	309.5	19.8	329.3
3	120.8	3.3	124.1
4	187.5	1.2	188.7
5	~ 0	19.9	19.9
6	~ 0	12.6	12.6
8	308.5	10.0	318.5
9	0.7	0.0	0.7
Raffinate to slurry tank	~ 0	5.5	5.5

^a During cycles 2 and 3.

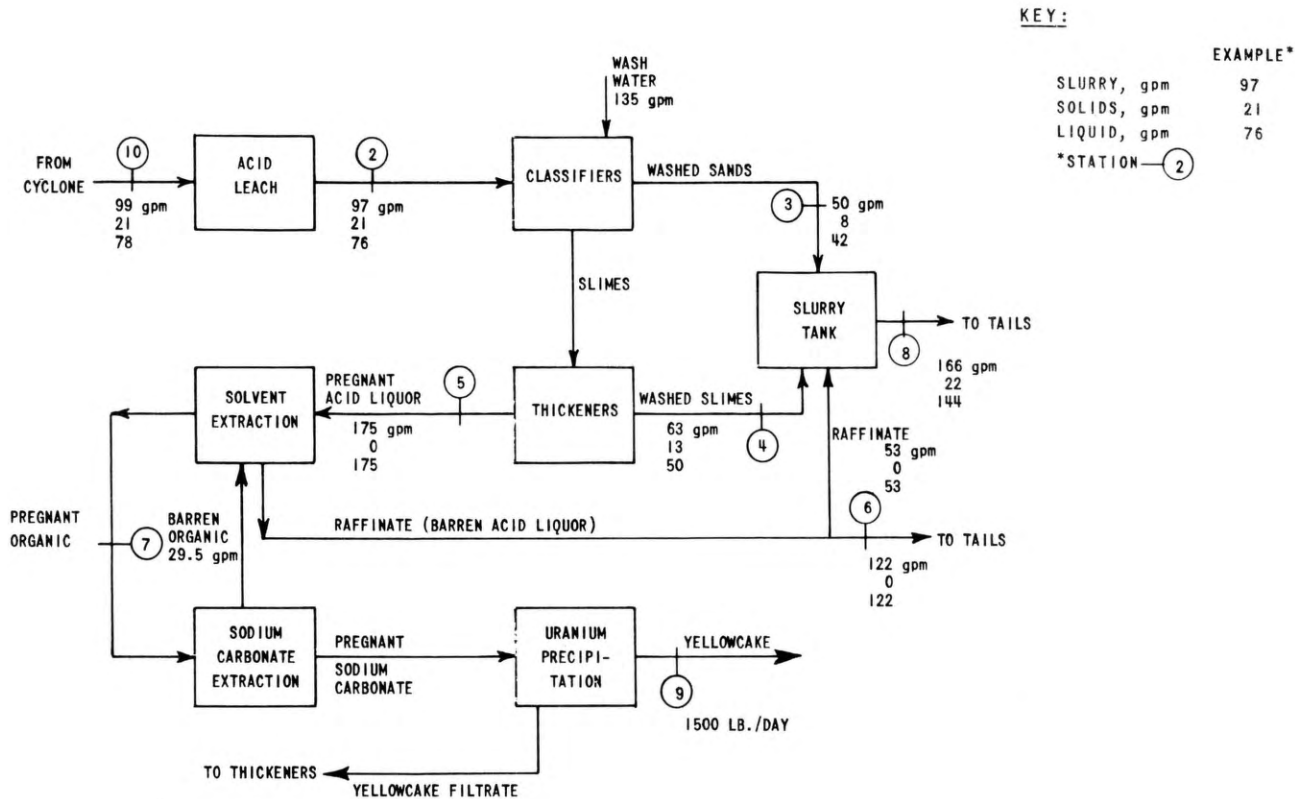


Figure 2. Schematic flow diagram, Gunnison Mining Co., uranium mill, August 1958.

Table 6. CHEMICAL QUALITY OF MILL EFFLUENTS

Determination	Concentration, mg/l	
	Station 6	Station 8
	Raffinate	Sands-slimes slurry
Total acidity as CaCO ₃	10,000	5,400
Mineral acidity as CaCO ₃	9,000	3,500
Hardness as CaCO ₃	1,850	1,550
Sulfate	12,600	10,000
Chloride	180	275
Iron	48	82
Manganese	17	7
Copper	0.2	0.2
Selenium	0	0
Sodium	1,400	800
Fluoride	12	13
Beryllium	2.4	2.1
Vanadium	0.06	0.03
Arsenic	11	17

pended solids). Although the suspended solids in mg/l of the pregnant and barren acid liquors were low, with correspondingly slight alpha activity on a per liter basis, the suspended solids that were present contained relatively high alpha activity on a per gram basis.

Table 4 clearly shows that little radium-226 was dissolved by the acid leach (see Stations 10 and 2, dissolved radium), and radium stayed mainly in the undissolved state through the entire mill process. The uranium concentrate (Station 9) contained only 35 micromicrograms of radium-226 per gram, dry weight. While the pregnant and barren acid liquors (Stations 5 and 6) contained relatively high-radium suspended solids, in small quantities, the dissolved radium content of these liquors was also relatively high. This indicates that very little radium was extracted from the pregnant acid liquor, and this is also borne out by the low radium content of the yellowcake.

The radium-226 and gross alpha balances that follow clarify these conclusions.

Samples of the barren acid liquor, or raffinate, (Station 6) and of the sands-slimes slurry going to the tailings pond (Station 8) were analyzed for various chemical constituents of interest. The results are shown in Table 6. Only the liquid portions of the samples were analyzed, and the results, in mg/l, represent only dissolved chemicals. The pH of the raffinate was 1.3., and that at Station 8 was 2.1.

Table 4. RADIUM CONCENTRATIONS

Station	Radium 226 in total sample, $\mu\mu\text{g}/\text{l}$		Radium 226 in dry undissolved solids, $\mu\mu\text{g}/\text{g}$
	Undissolved	Dissolved	
10	271,000	125	490
2	345,000	270	640
3	94,500	180	235
4	338,000	110	680
5	50	490	905
6	130	480	3,500
7	70	3	130
8	156,000	155	505
9	a	a	35

^a Solid sample

ograms of radium-226 per liter of slurry, as well as per gram of dry suspended solids.

Portions of the samples were also assayed for gross alpha and beta radioactivity; these results are given in Table 5.

The dissolved alpha activities show clearly the effects of the various steps in the process. A sharp increase in activity resulted from the acid leach (to 250,000 $\mu\mu\text{c}/\text{l}$ at Station 2), and the bulk of this activity was contained in the pregnant acid liquor from the thickeners (Station 5). Most of it was removed by solvent extraction (see Station 6, barren acid liquor), and appeared finally in the yellowcake as uranium (Station 9, 306,000 $\mu\mu\text{c}/\text{g}$ of dry sus-

Table 5. GROSS RADIOACTIVITY CONCENTRATIONS.

Station	Activity in total sample $\mu\mu\text{c}/\text{l}$				Activity in undissolved solids, $\mu\mu\text{c}/\text{g}$	
	Undissolved		Dissolved		Alpha	Beta
	Alpha	Beta	Alpha	Beta		
10	2,560,000	3,000,000	5,900	15,300	4,630	5,440
2	1,980,000	2,740,000	250,000	830,000	3,680	5,090
3	304,000	494,000	17,400	50,600	760	1,230
4	1,810,000	1,840,000	8,400	33,200	3,640	3,700
5	1,400	1,550	272,000	475,000	25,800	28,000
6	780	680	5,900	11,500	20,800	18,000
7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
8	973,000	1,052,000	14,000	38,300	3,140	3,400
9	a	a	a	a	306,000	445,000

^a Solid sample

The values in Table 8 were computed directly from the radium concentrations of Table 4 and the slurry flows of Table 2; a value of 1,500 lbs per day of concentrate for Station 9 was used.

An initial test of the results was made on the basis of the uranium assays, yellowcake production, and the assumption of radioactive equilibrium between uranium and radium in the raw ore. The yellowcake production rate during the survey was 1,500 lbs/day, containing about 1.0 per cent moisture and 82 per cent U_3O_8 . If radium-226 were in equilibrium with this much uranium there would be 156 mg/day of radium-226 involved in the process. The uranium assays of raw ore ("heads") and tailings indicated an over-all efficiency of about 90 per cent for uranium recovery; hence it is estimated that about 173 mg/day of radium-226 entered the mill with the 330 tons per day of ore. This is in good agreement with the data of Table 8.

A separate computation, based on the assumption of 0.22 per cent U_3O_8 in the raw ore (because of the time lag between raw ore and concentrate in the mill), the tonnage processed, and radioactive equilibrium between uranium and radium, indicates about 180 milligrams of radium-226 enter the mill daily.

The radium balance is in generally good agreement throughout the process with the exception of some discrepancy between the undissolved radium results for Stations 2 and 10, before and after the acid leach. Due to the presence part of the time of the smaller batch of higher grade ore, and to the large time delay during the acid leach process step, the result for Station 2 may not be fully representative for the survey period and may be somewhat high. Other than this, the undissolved radium data indicate 146 mg/day entering from the cyclone, 142 mg/day at Stations 3 and 4 combined (separate washed sands and slimes slurries) and 142 mg/day at Station 8 (the combined slurries). Total mill input and output therefore agree adequately so far as undissolved radium is concerned.

The dissolved radium data also indicate good balances. The 467 $\mu\text{g/day}$ in the pregnant acid liquor, together with the outputs of 49 and 38 $\mu\text{g/day}$ in the washed sands and slimes, respectively, yield 554 $\mu\text{g/day}$. This is accounted for adequately by the 319 $\mu\text{g/day}$ in the raffinate to tails (Station 6), the 25 $\mu\text{g/day}$ in the yellowcake, and the 141 $\mu\text{g/day}$ at Station 8 a total of 485 $\mu\text{g/day}$. The dissolved radium entering and leaving the slurry tank totals 226 $\mu\text{g/day}$ (Stations 3, 4, and the portion of raffinate to the slurry tank) as against 141 $\mu\text{g/day}$ at Station 8. It appears possible here that some of the radium initially dissolved in the raffinate precipitated on mixing with the washed sands and slimes slurry in the slurry tank.

It is also of interest to note that the dissolved radium leaving the acid leach tanks (142 $\mu\text{g/day}$) does not account for the 554 $\mu\text{g/day}$ at Stations 3, 4, and 5. This, together with the observed con-

ACID LEACH - SOLVENT EXTRACTION PROCESS

Table 7. CHEMICAL CONSUMPTION

Chemical	Amount used per ton of ore processed, lbs.
H ₂ SO ₄	70.2
MgO	0.86
Kerosene	0.225 ^a
DEHPA	0.0054
TBP	0.0054
Separan	0.354
Na ₂ CO ₃	15.6
NaClO ₃	2.89
Decanol	0.016

^a Gallons.

Chemicals used in the mill process are indicated in Table 7, together with average consumptions per ton of ore processed. These data are averages for the month preceding the survey, and were supplied by company officials.

During the mill survey, about 36,000 lbs H₂SO₄, about 900 lbs of NaClO₃, and an average of about 5,000 lbs of Na₂CO₃ were used per day. MgO and Separan were used at rates of about 310 and 97 lbs per day, respectively.

One of the primary purposes of this survey was to determine the amounts of radium-226 in the process at various locations, and the amounts in suspended and dissolved form in the effluents. To that end, a radium balance for the process has been carried out (Table 8).

Table 8. RADIUM BALANCE

Station	Radium - 226, mg/day		
	Undissolved	Dissolved	Total
10	146	0.068	146
2	180	0.142	180
3	26	0.049	26
4	116	0.038	116
5	0.048	0.467	0.52
6	0.087	0.319	0.41
7	0.012	~0	0.01
8	142	0.141	142
9	0.025	-	0.025
Raffinate to slurry tank	0.038	0.139	0.18

were in agreement. Figure 3 presents the arithmetic-probability analysis of the minimum daily and minimum monthly average flows for the continuous years of record. This curve shows that half the time the minimum daily flow has been equal to or greater than 135 cfs, while the minimum monthly average flow has been equal to or greater than 150 cfs; the minimum daily flows ranged from 96 to 200 cfs, with an average of 136 cfs, and the minimum monthly flows ranged from 111 to 252 cfs, with an average of 160 cfs. During the survey period, August 7 through August 11, 1958, the flow ranged from 790 to 825 cfs, with an average of 803 cfs. A hydrograph of daily flows for this station for the period October 1, 1957, through September 30, 1958, is shown in Figure 4. The discharge records from which this hydrograph was plotted show that the average flow for the water year was 838 cfs, while the average flow for the six-month period October 1957 through March 1958 was 355 cfs. This is a typical hydrograph of rivers in the western United States, in which the spring snow-melts produce high runoffs during the three spring months and the flows for the remainder of the year remain relatively steady.

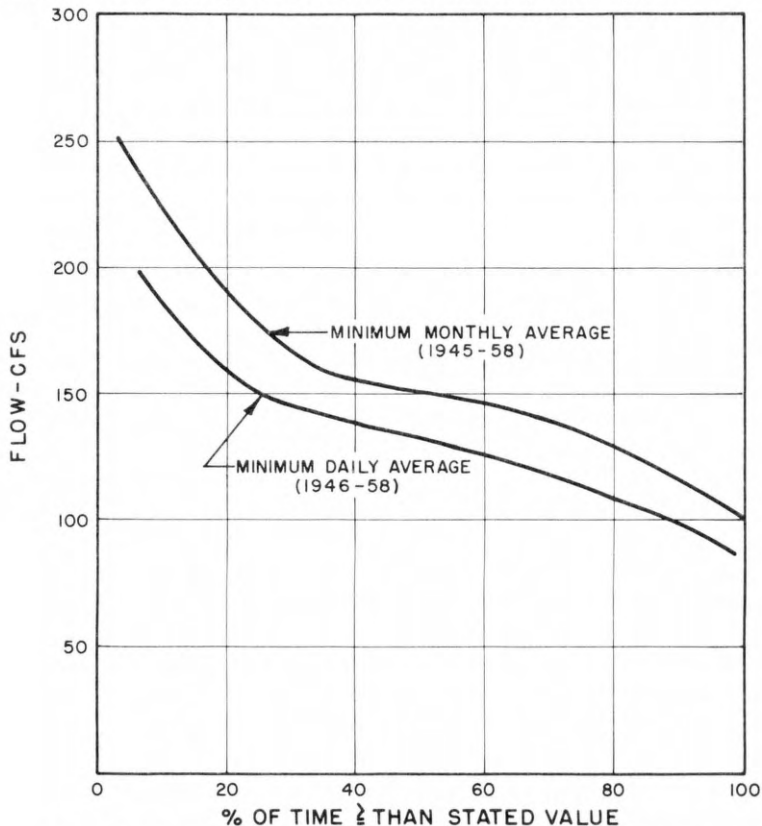


Figure 3. Occurrence of minimum daily and monthly average flows, Gunnison River near Gunnison, Colorado.

It must be pointed out that the probability methods utilized are statistical ones and are subject to variations such as length

Table 9. GROSS ALPHA BALANCE

Station	Gross alpha Radioactivity, mc/day		
	Undissolved	Dissolved	Total
10	1,380	3.2	1,380
2	1,040	130	1,170
3	85	4.7	90
4	620	2.9	620
5	1.4	260	260
6	0.5	3.9	4
7	n.d.	n.d.	n.d.
8	880	13	890
9	210	a	210
Raffinate to slurry tank	1	1.7	2

^a Solid sample.

centrations (Table 4) at the process points, indicates that, insofar as radium is concerned, dissolution is not complete at Station 2, but continues as far as Station 5, the pregnant acid liquor.

Table 9 indicates a similar balance for gross alpha radioactivity at the various mill locations. This balance is based upon the flows of Table 2 and the concentrations from Table 5. The agreement for the various stations is good; for instance, the total mill output (Stations 6, 8, and 9) of 1,104 millicuries per day (mc/day) agree with the input at Stations 2 and 10. Dissolved alpha activity values also agree well enough throughout the process, and the course of uranium is quite evident from the data on dissolved alpha, chronologically, at Stations 10, 2, 5, 6, and 9.

AVAILABLE DILUTION

During the period of the survey at this refinery there were no effluent discharges to the Gunnison River. In anticipation, however, of effluent discharges that may become necessary in the future, hydrologic studies have been made of the discharge records for the Gunnison River near Gunnison in order to estimate the available dilution expected. Records were obtained from the gaging station operated by the U. S. Geological Survey almost adjacent to the mill property.

Discharge records for this station are available from October 1911 through September 1958; continuous daily discharge measurements are available for the period October 1, 1945, through September 30, 1958. Only these continuous records were analyzed. In order to obtain reasonable estimates of flow frequencies expected, arithmetic-probability and Gumbel type ⁸ curve fitting techniques were employed. In general, the two types of analyses

of record, stream regulation, amount of upstream irrigation, etc. For this particular gage the years of continuous record include only a 14-year period. Since September 1937, the flow at this station has been partly regulated by Taylor Park Reservoir about 37 miles upstream. There are also about 22,000 acres of irrigated land above the station.

So far as can be ascertained, no public water supplies are taken from the Gunnison River below Gunnison, Colorado. The extent of other uses of the stream is not known in detail, but extensive downstream diversion for irrigation purposes occurs, with the possibility that individual ranch families use the river water in its raw state for domestic purposes.

WASTE DISPOSAL

During the mill survey a large unused tailings pond area was available, and all wastes from the mill process were retained indefinitely in this pond area.

About 12 per cent of the gross alpha activity of the ore that was being processed at the uranium refinery under study was due to the presence of radium. The liquid and solid wastes from ore processed at the rate of 330 tons per day contained about 0.6 milligrams of radium per ton of ore processed, or a total of approximately 150 mg/day. Some 99.6 per cent of this radium remained in undissolved form throughout the process and was effectively retained in the tailings ponds.

About 0.4 per cent of the radium that entered the mill with the ore either left the refinery in the final uranium concentrate or was delivered in dissolved form to the pond. Specifically, an estimated 480 micrograms of dissolved radium per day went to the tailings pond, and about 25 micrograms of radium per day left the mill in the dried yellowcake.

These studies indicate that two waste constituents in particular are present in potentially hazardous quantities: radium-226 and arsenic (see Tables 6 and 8).

As indicated earlier, the effluents from the Gunnison Mining Company uranium mill contained per day about 500 micrograms of dissolved radium-226. The records of flow of the Gunnison River near the refinery indicate that if all of this dissolved radium were released routinely to the river, the dissolved radium content of the river water would show an increase from essentially zero at high or flood flows to about $1.2\ \mu\mu\text{g}/\text{l}$ at average or usual flows, and to about $2.0\ \mu\mu\text{g}/\text{l}$ at low flows, which are relatively rare.

Thus, by itself, the quantity of dissolved radium regularly produced as waste from this refinery, while detectable in the river, would not constitute a major hazard in terms of existing standards.⁹ In practice, of course, it is not usually released to the

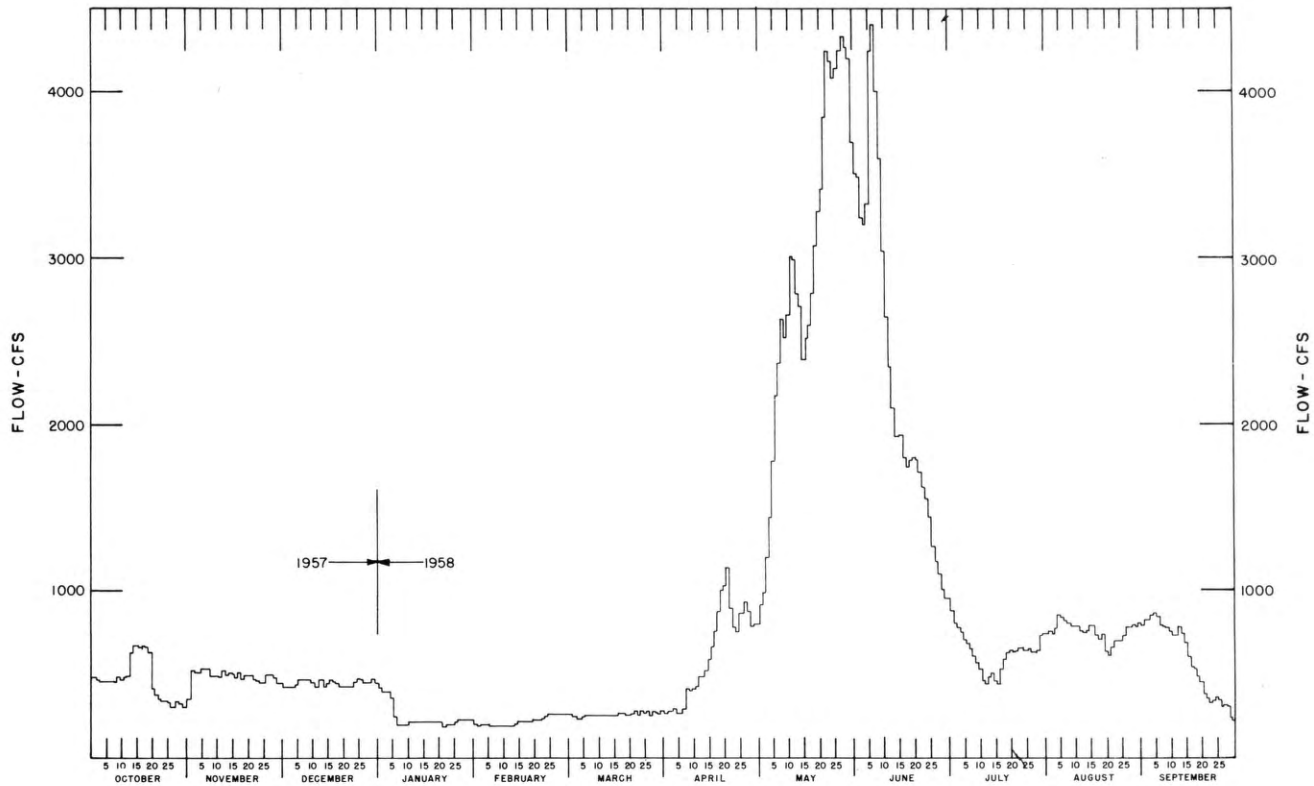


Figure 4. Daily flows for Gunnison River near Gunnison, Colorado.
Water year 1958.

THE ACID LEACH-SOLVENT EXTRACTION URANIUM REFINING PROCESS II. CLIMAX URANIUM COMPANY, GRAND JUNCTION, COLORADO

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Introduction

An in-plant survey of the Climax Uranium Company uranium refinery at Grand Junction, Colorado, was performed by the Public Health Service during August 1958 with the cooperation of the Colorado Department of Public Health, the Climax Uranium Company, and the U. S. Atomic Energy Commission.

The Climax Refinery is located on the Colorado River, about 30 miles upstream from the Utah-Colorado State Line. It provides an example of the acid-leach solvent extraction process for uranium recover. Vanadium is also recovered at this plant. Figures 1 and 2 present the process flow diagram for this refinery and the waste pond arrangement respectively, which are discussed in detail in the following sections.

Mill Process

ORE RECEIVING, SAMPLING AND CRUSHING

Ore delivered to the plant by truck is weighed and unloaded into truck bins. Each load is run separately through a jaw crusher, which reduces it to a maximum size of two inches. A sample, varying in size from two pounds per ton on large lots (20 tons or more) to about four pounds per ton on small lots (8 to 10 tons), is taken automatically during crushing. High grade ore is hand sampled or specially sampled, according to the size of the lot. Crushed and sampled ore goes either to the stockpile or to fine-ore storage bins. From these bins it proceeds to the rod mill where it is ground to less than 14-mesh size (2 to 4 per cent retained on 14-mesh screen). During this process water is added to the ore so that the finely ground material leaves as a slurry for the next phase.

*Respectively, Sanitary Engineer, Radiological Pollution Activities Unit; Sanitary Engineering Director, Colorado River Basin Water Quality Contro. Project, Public Health Service, Denver, Colorado; Captain, U. S. Army, Fort McPherson, Atlanta, Georgia; Health Physicist; and Senior Assistant Sanitary Engineer, Radiological Pollution Activities Unit.

river directly, although the extent of possible seepage from the tailings pond is not known.

The undissolved radium-226 wasted daily from the mill to the tailings pond constitutes a much more significant source of potential environmental contamination. As has been shown elsewhere, ¹⁰ the initially undissolved spent ore solids can result in a relatively high degree of water pollution if discharged to a river and permitted to accumulate on the stream bed. It is also true here (see Table 4), as at other mills, that the lighter suspended solids that are carried by the effluents contain relatively high radium concentrations. As a result of these considerations, it is quite important that tailings or spent ore solids should be retained at the plant site effectively and regularly, and should not be released to the Gunnison River in any regular or significant quantity.

The problem of arsenic is somewhat different. From the data of Table 6 and Figure 2 (liquid flow rates) it can be shown that the two main effluent streams, Stations 6 and 8, carry about 20,000 grams of dissolved arsenic per day to the tailings pond. No estimate of the arsenic content of undissolved tailings solids has been made.

If this quantity of arsenic were released routinely and the available dilution in the Gunnison River, was considered the arsenic content of the river would, for a considerable portion of the year, equal or slightly exceed the allowable concentration based upon the Public Health Service Drinking Water Standard. ¹¹ For instance, the minimum monthly average flow, which would be exceeded only 50 per cent of the years, is 150 cfs (see Figure 3). At this flow, the arsenic concentration would be about 0.057 mg/l or slightly more than the allowable 0.05 mg/l.

From the standpoint of chemical pollution the mill effluents clearly should continue to be retained indefinitely, as has been the practice in the past. This retention, however, raises the question of the potential accumulation of arsenic at the rate of 20,000 g/day in the soil near and surrounding the tailings pond. The possibility that the accumulating quantities of arsenic may leach to the river in increasing amounts, or to nearby well supplies (such as that used by the Gunnison Mining Company) should not be ignored. For a time, a minimal amount of monitoring of the river and any nearby wells for arsenic appears to be desirable.

Acknowledgment

The generous cooperation and assistance of the following are gratefully acknowledged: personnel of the Gunnison Mining Company; the U. S. Atomic Energy Commission; Stan May, Colorado Department of Public Health; Bill Fixen, Public Health Service Region VIII, Denver; and E. A. Pash, G. Harlow, Carl Shadix and Carl Hirth, Public Health Service, Cincinnati, Ohio.

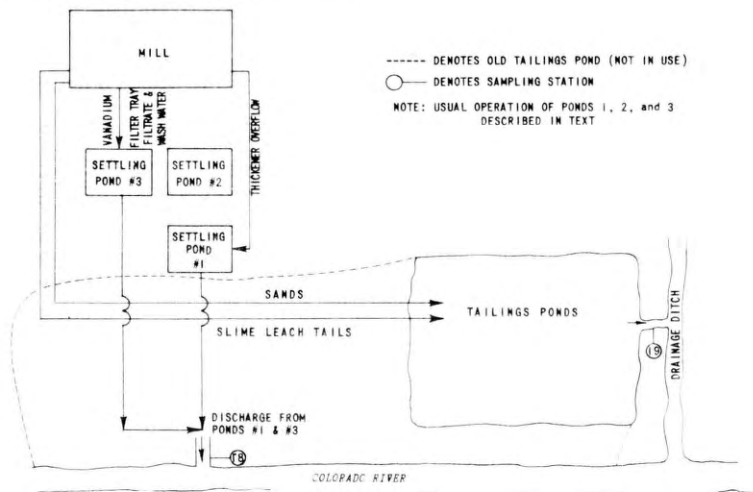


Figure 2. Mill area and pond arrangement of Climax Uranium Co., Grand Junction, Colorado, August 15-18, 1958.

CONDITIONING AND CLASSIFICATION

Slurry from the rod mill is pumped to acid-conditioning tanks, of which there are six arranged in series. A strong H_2SO_4 solution (2-1/2 to 7 per cent acid) is added in the first tank; most of this solution is recirculated from storage tanks following the sand leach. A more dilute solution of HCl and H_2SO_4 is also added, this being recirculated from the roaster gas scrubbing unit. The pH in the first three conditioning tanks is about 1.0 to 1.5, rising in the last three conditioning tanks in the range of 1.5 to 4.0. Some raffinate from the solvent extraction process is also returned to the No. 1 conditioning tank along with the acid liquor from the sand leach.

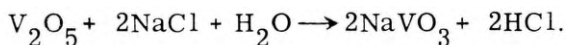
The purpose of this conditioning is to destroy the lime in the ore, and change CaCO_3 to insoluble CaSO_4 .¹³ This prevents formation of the water-insoluble calcium vanadate during the roasting process; instead, the water-soluble sodium vanadate is formed. Acid conditioning takes about 1-1/2 hours.

Upon leaving the acid conditioning tanks, the slurry is subjected to a second conditioning with ammonia to neutralize the remaining acid and to raise the pH to about 6.5. The principal purposes of this neutralization are (a) to avoid corrosion, and (b) to precipitate any uranium and vanadium dissolved during acid conditioning or entering in the recirculated acid solutions. Precipitation will occur in the pH range of 5.3 to 7.5.

Upon completion of conditioning the slurry is partially dewatered in a cyclone separator before proceeding to a hydraulic sizer. Liquor from the cyclone goes to the thickeners. In the sizer, sands and slimes are separated hydraulically. An attempt is made to maintain the slimes coming out of this unit in such a

material is fed to a gas-fired rotary dryer, which reduces the moisture content to about 13 per cent. The dried material passes through a 50-ton storage bin and thence to a gas-fired 10-hearth roaster, operating at 1400° F. to 1600° F.

The roasting process converts insoluble vanadium compounds in the ore to water-soluble sodium vanadates. This reaction can be written



The hydrochloric acid gas is recovered for use in the acid conditioners, by passing the roaster gas through the scrubbing units. The uranium compounds remain insoluble in water. Calcines are split into two "streams" on leaving the roaster. One "stream" is carried on a vibrating conveyor to a Baker cooler in which cooling takes place by heat transfer into cooling water circulated around the outside of the mechanism. In this process there is no contact between calcines and water. The second "stream" is carried on a vibrating conveyor to a quench tank where it is quenched with filtrate and wash water from an Oliver filter that follows the thickeners.

Cooled calcines from the Baker cooler are reground in a ball mill; quenched calcines go to a spiral classifier. Sands from this classifier join the cooled calcines entering the ball mill. The classifier overflow is thickened in two 32-foot thickeners. Thickener overflow is processed for vanadium, underflow for uranium.

VANADIUM EXTRACTION

The thickener overflow feeds five vanadium precipitation tanks of 7,100-gallon capacity each. Precipitation is carried out as a batch process; the typical operation in any tank is as follows:

The tank is filled with thickener overflow, agitation begun, and the contents brought almost to the boiling point by injection of steam. Concentrated H_2SO_4 is then added in an amount sufficient to lower the pH to below 4.0. The tank contents are agitated until complete precipitation of vanadium as sodium polyvanadate (redcake) is effected. The time required for this may vary from 1/2 to 3 hours, depending upon the "grade" and characteristics of the liquor. The tank contents are then run onto a filter tray and the liquor is drained to Pond No. 3. The redcake is washed with water to leach sulfates from the cake. The amount of water used is roughly equal to the volume of the tank, e. c., about 7,500 gallons. Wash water is also drained to Pond No. 3. Washed redcake is fused at 650°C in a fusion furnace, and emerges as V_2O_5 product, which is then cooled and drummed for shipment.

URANIUM EXTRACTION

Underflow from the thickener is filtered on an Oliver filter and the filtrate, together with water used to wash the filter cake,

manner that 85 per cent of the solids are less than 200-mesh in size. All larger particles are removed as sands.

SAND LEACH

Sands from the sizer go to a spiral classifier for dewatering. Overflow from the classifier goes to the thickeners, while the underflow is discharged to one of ten acid leach tanks where the uranium and some vanadium are leached from the sands. As the sands leave the classifier, concentrated H_2SO_4 is added at a rate of about 105 pounds H_2SO_4 per ton of dry solids. The acid leach process is conducted as a batch operation; a tank is filled with the sands-acid slurry and then handled as a unit[†]

The leach tanks are constructed with false bottoms so that the sands will be retained, while the liquor content of the tanks can be drained off as underflow. When a tank is filled, the underflow is recycled through the sands for about 2 hours. At the start of the recycling operation, $NaClO_3$ is added to the liquor in an amount equal to 3-1/2 pounds per ton of dry sands in the tank. At the same time the liquor is heated to 90 degrees Fahrenheit by a heat exchanger, using steam as the source of heat. At the end of 2 hours, recycling is stopped, and the tank contents are allowed to "cure" for about 8 hours. At the end of the curing period the acid liquor is drained into a storage tank. Fresh water is then flushed through the sands and run into the same storage tank until the pH is in the range of 1.8 to 2.3. The water flow into the leach tank is then stopped and the liquor remaining in the tank is diverted into a second small (4,500 gal.) storage tank to be used for roaster gas scrubbing. The spent sands are then removed from the leach tank by repulping with water and discharged to the tailings pond.

Acid liquor from the first storage tank, which contains uranium and vanadium leached from the sands, is returned to the No.1 acid conditioning tank as described in the previous section.

THICKENING AND ROASTING

The components comprising the thickener feed are slimes from the classifier receiving sands from the sizing operation, and filtrate from the disc filters following the thickeners. As this combined flow enters the thickening tanks, Separan (200 pounds per day) is added to improve sedimentation. Overflow from the thickeners is discharged to Settling Pond No. 1, while the underflow, about 30 per cent solids, is filtered on disc filters. The filtrate is returned to the thickener feed as mentioned above.

The filter cake drops into a screw conveyor and proceeds to a mixer where $NaCl$ is added at the rate of 15 per cent by weight of dry solids. This material with about 40 per cent water is still too wet to serve as dryer feed, so it is mixed in a pug mill with the previously dried filter cake- $NaCl$ mixture in an amount sufficient to reduce the moisture content to about 25 per cent. This

quently, the effluent samples collected from these ponds did not reflect the discharge which would have occurred if the ponds were being operated in their normal manner.

Since the survey in 1958, an additional tailings pond has been constructed. The large tailings pond, shown discharging to the drainage ditch on Figure 2, now discharges to the new pond. No direct discharge to the river is anticipated from this new pond. In addition, the settling pond arrangement has been changed so that the only discharge to the river is from the vanadium extraction circuit. All other discharges now enter the tailings ponds.

Mill Survey

During the survey period, August 15 through August 18, 1958, nineteen sampling stations were established for the purpose of obtaining representative samples from the mill process for analysis. Table 2 describes the stations sampled; Figure 1 gives the locations. Sampling Stations 1, 2, 3, 4, 8, 9, 10, 13, 14, 16, and 17 were main mill process streams, whereas Stations 5, 6, 7, 11, 12, 15, 18, and 19 were representative of waste streams.

Sampling was performed by personnel of the Public Health Service and the Colorado Department of Public Health. Two sepa-

Table 1. CLIMAX MILL SAMPLING STATIONS

Station	Description
1	Classifier discharge to conditioning tanks
2	Conditioning tank effluent to hydraulic classifier
3	Thickener feed (65-foot tanks)
4	Sands to acid leach
5	Spent sands to tails
6	Influent to Pond No. 1
7	Effluent from Pond No. 1
8	Roaster feed
9	Roaster calcines
10	Thickener feed - vanadium circuit
11	Influent to Pond No. 3
12	Effluent from Pond No. 3
13	Vanadium product
14	Filter cake to solvent-extraction circuit
15	Slime leach tails
16	Filtrate to solvent extraction tanks
17	Uranium product
18	Combined effluent from Ponds Nos. 1 and 3
19	Sand-slimes tailings pond discharge

is returned to a storage tank from which it is used for quenching roaster calcines. Washed filter cake is repulped with water and goes to three acid conditioning tanks, in series. Here concentrated H_2SO_4 is added at about 230 pounds per ton of dry solids. The uranium in the cake, together with vanadium that was not water soluble, is dissolved in the acid during the contact time (about one hour) in these tanks.

Upon leaving the last of these tanks the slurry goes through three additional cycles of conditioning, filtration and repulping to extract the maximum amount of uranium. Cake from the last filter is repulped with water and pumped as "slime leach tails" to the tailings pond. Filtrate from the last filter is returned to the process.

The pregnant acid liquor filtrate from the first and second filters is settled for removal of slimes. The liquor then goes to one of three 7500-gallon storage tanks and then to the solvent extraction tanks. Here, uranium is stripped from the acid liquor with an organic solvent. The raffinate is returned to the No. 1 conditioning tank, while the pregnant organic goes to a storage tank, then into a circuit where the uranium is stripped from the solvent with a 10 per cent Na_2CO_3 solution. Barren organic is returned to the solvent extraction circuit, while the loaded Na_2CO_3 proceeds to one of two precipitation tanks, operated as a parallel batch process. When one of these tanks is filled, about 800 pounds of concentrated H_2SO_4 is added to neutralize the Na_2CO_3 , and the contents are brought to a boil with steam to drive off excess carbon dioxide. Ammonia is added to precipitate the uranium as an ammonium di-uranate. When precipitation is complete, the tank contents go to a filter press. Filtrate is returned to the No. 4 conditioning tank. Filter cake is fed to a gas-fired dryer operating at a temperature of $900^\circ F.$ where drying takes place, and the feed is converted to U_3O_8 (yellowcake), which is then drummed and shipped to an Atomic Energy Commission facility.

OPERATION OF SETTLING PONDS NOS. 1, 2, and 3

As shown in Figure 2, in addition to a large tailings pond, three smaller settling ponds, each approximately 150 feet square, are provided for settling thickener overflow and vanadium tank filtrate and wash water prior to their discharge to the river. Ordinarily thickener overflow enters Pond No. 1. This pond discharges to Pond No. 2, and thence to Pond No. 3, where the waste vanadium liquors enter. The only discharge from this series of ponds is from Pond No. 3 to the river.

During Cycle I of the mill survey, Pond No. 2 was being cleaned out. During Cycle II, Pond No. 2 was still out of operation and cleaning operations were underway in Pond No. 3. Because of this situation, the contents of Pond No. 1 were discharged directly to the river, as were those of Pond No. 3. Conse-

Table 2. SOLIDS IN PROCESS STREAM

Station	Tons per day		
	Suspended	Dissolved	Total
1	537	3.0	540
2	448	72	560
3	120	71	191
4	394	1.0	395
5	390	1.6	392
6	1.7	56	57
7	0.3	50	50
8	123	a	123
9	123	a	123
10	97	74	171
11	0.04	6.2	6.2
12	0.04	6.3	6.3
13	7.9	a	7.9
14	97	12	109
15	88	0.9	89
16	0.1	20	20
17	2.0	a	2.0
18	0.2	49	49
19	0	0.2	0.2

^a. Solid Sample

From Figures 1 and 3 comparisons between stations can be made of the flows entering and leaving various sections of the mill. For the over-all plant balance, the input to Station 1 can be compared with the total output of the spent sands, Station 5; the influent to Pond No. 1, Station 6; the influent to Pond No. 3, Station 11; the vanadium product, Station 13; the slime leach tails, Station 15, and the yellowcake product, Station 17. The effluent from the ammonia conditioners, Station 2, should be accounted for at the feed to the acid leach tanks, Station 4; Pond No. 1, Station 6; and the roaster feed, Station 8. The roaster calcines at Station 9 should divide between the filter cake at Station 14, and Stations 11 and 13. The roaster feed at Station 8 should compare with the calcines at Station 9. Lastly, the filter cake at Station 14 should be measurable in the filtrate to the solvent extraction tanks, Station 16, and in the slime leach tails, Station 15. These comparisons can also be used for estimating the quantities of water added between sampling stations.

Table 4 shows the gross alpha and beta radioactivity concentrations. The figures are an average for the two sampling cycles,

rate sampling cycles were selected during which samples were collected continuously. The sampling periods were:

Cycle I - 3:00 PM, August 15 - 11:00 PM, August 16, 1958
(32 hours)

Cycle II - 3:00 PM, August 17 - 3:00 PM, August 18, 1958
(24 hours)

Compositing of samples during these periods varied with the type and duration of operation. Adequate sampling was difficult at several locations due to the batch type operations described previously. Also, flow at several other stations was not continuous over the entire length of the sampling cycles. Detailed records were maintained for each sampling station in order that data derived from laboratory analyses could be adequately interpreted.

All samples collected during the survey were shipped to the U. S. Public Health Service Robert A. Taft Sanitary Engineering Center at Cincinnati, Ohio. Portions of all samples were sent to a private laboratory for determinations of dissolved and undissolved radium; all other determinations were performed at the Cincinnati laboratory.

Analyses and Results

To adequately determine the operating characteristics of the individual units of the mill process, a flow balance was calculated for the mill. This was accomplished by combining the laboratory analyses with the flow measurements taken on the effluent streams. To estimate the quantities of liquid, suspended solids, and dissolved solids at the various stages of the process during each cycle a solids balance throughout the plant was assumed. Because of this assumption the solids for each cycle necessarily balanced. The input to the plant on the basis of a balance was calculated as 540 and 583 tons of ore per day for Cycles I and II, respectively. Results from the two cycles as presented in this section of the report have been combined and adjusted to represent the mill processing 540 tons of ore per day; the solids flow at each station is presented in Table 2.

Figure 3 illustrates the average flow for the two cycles in terms of gallons per minute of liquid and solids at the stations sampled during the process. The flow at Stations 4, 5, 7, 11, 12, 13, 15, 16, and 17 were measured during the survey while the flows at the remaining stations were calculated from the solids balance.

Table 3 presents process stream characteristics, both measured and calculated. These and all other process stream characteristics are reported on the basis of uninterrupted operation at all stations and steady flow conditions for batch operations such as the sand leach and the vanadium precipitation operations.

Table 3. PROCESS STREAM CHARACTERISTICS^a

Station	Slurry flow, gpm	Specific gravity of slurry	Dry suspended solids by weight, %	Specific gravity of dry solids
1	97	1.56	59.2	2.47
2	282	1.23	23.9	2.63
3	562	1.02	35.1	2.63
4	58	1.70 ^b	67.3 ^b	2.56
5	82	1.49	53.9	2.63
6	469	1.01	d	-
7	408	1.01	d	-
8	c	-	~ 87	2.13
9	c	-	~ 100	2.30
10	133	1.14	11.0	2.21
11	90	1.01	d	-
12 ^b	145	1.01	d	-
13	c	-	~ 100	2.73
14	35	1.33	35.0	2.60
15	41	1.22	29.5	2.66
16	50	1.08	d	-
17	c	-	~ 100	5.81
18 ^b	545	1.01	d	-
19	8	1.00	d	-

^a Average for two cycles

^b One cycle only

^c Solid sample

^d Liquid (negligible suspended solids)

cines at Station 8, 1,626 mc/day, can be equated to the 1,499 (16 + 5 + 1,478) mc/day calculated for Station II, the influent to Pond No. 3; Station 13, the vanadium product; and Station 14, the filter cake going to the uranium extraction process. In turn the activity at Station 14, 1478 mc/day, agrees well with the 1472 (1066 + 406) mc/day encountered at Station 15, the slime leach tails; and Station 16, the filtrate to the solvent extraction tanks. For the over-all plant balance, 1778 mc/day enter the plant as compared with 1990 (273 + 31 + 16 + 5 + 1066 + 599) mc/day that leave at Stations 5, 6, 11, 13, 15, and 17. It should be noted here that the concentrations of alpha and beta activity present in Table 4 are laboratory determinations and as such could be different from the actual activity that might be measured at the plant, if this had been possible. Material that was not in radioactive equilibrium during the process would tend to return to equilibrium in

Table 5. ALPHA ACTIVITY IN PROCESS STREAMS

Station	Undissolved	Dissolved	Total
1	1,778	< 1	1,778
22	1,790	4	1,794
3	1,653	6	1,659
4	423	< 1	423
5	272	1	273
6	30	1	31
7	7	9	16
8	1,778	a	1,778
9	1,626	a	1,626
10	1,257	4	1,261
11	10	6	16
12	2	4	6
13	5	a	5
14	1,477	1	1,478
15	1,066	< 1	1,066
16	4	402	406
17	599	a	599
18	1	13	14
19	< 1	< 1	< 1

a. Solid sample.

The radium concentrations in Table 6 have been combined with the flows in Table 3 (by cycle) to estimate the quantity of radium-226 in the process stream (Table 7 and Figure 4). Determination of this radium distribution was one of the main objectives of the mill survey. In balancing the radium input against output at the locations indicated previously, we see that the 256 mc/day at Station 2, the conditioner tank effluent, compare favorably with the 270 (59 + 4 + 207) mc/day at Station 4, the sand to the acid leach; Station 6, the influent to Pond No. 1; and Station 8, the roaster feed. The 219 mc/day of radium in the roaster calcines, Station 9, are accounted for in the 184 (2.1 + 182) mc/day at Station 13, the vanadium product, and Station 14, the filter cake from the Oliver filter. The 182 mc/day at Station 14 are in agreement with the 176 mc/day at Station 15, the slime leach tails. The over-all plant balance equates 331 mc/day at Station 1 to 232 (50 + 4 + 2 + 176) mc/day, leaving the plant at Stations 5, 6, 13, and 15, respectively. An examination of the results from Stations 1 and 2 in Tables 6 and 7, and consideration of the manner in which Station 2 balances when compared with other stations

Table 4. GROSS RADIOACTIVITY CONCENTRATIONS

Station	Gross radioactivity of total sample (slurry), $\mu\mu\text{c}/\text{l}$				Gross radioactivity of dry undissolved solids, $\mu\mu\text{c}/\text{g}$	
	Undissolved		Dissolved		Alpha	Beta
	Alpha	Beta	Alpha	Beta		
1	3,350,000	4,150,000	329	905	3,640	4,530
2	1,180,000	1,640,000	3,030	7,320	4,050	5,670
3	538,000	753,000	1,880	2,760	15,300	21,600
4	1,500,000	1,500,000	418 ^a	1,500 ^a	1,180	1,330
5	631,000	923,000	1,970	5,770	770	1,150
6	11,900	20,700	260	700	22,600	35,000
7	3,270	3,880	4,130	5,460	27,700	33,200
8	b	b	b	b	16,000	16,300
9	b	b	b	b	14,700	13,100
10	1,780,000	1,660,000	5,380	14,700	14,300	13,400
11	19,800	29,900	10,700	48,200	291,000	451,000
12 ^a	2,560	1,320	5,100	26,800	42,100	21,800
13	b	b	b	b	690	808
14	7,900,000	7,960,000	3,250	8,600	16,800	16,800
15	4,800,000	3,520,000	725	1,090	13,300	9,750
16	15,300	8,320	1,520,000	2,970,000	33,000	18,000
17	b	b	b	b	329,000	436,000
18 ^a	452	1,080	4,300	10,150	70,500	168,000
19	295	336	320	330	3,190	3,730

^a Single cycle.

^b Solid sample.

the sample before being assayed for radioactivity.

Radium-226 analyses were performed by a private laboratory after sample preparation at the Taft Center. Solids were separated from the liquid by means of a membrane filter and then ground to less than 100 mesh. The solids and liquid portions were then analyzed; results were reported in terms of $\mu\mu\text{g}/\text{l}$ of liquid sample and $\mu\mu\text{g}/\text{g}$ of solid sample. These results were then converted to the units presented in Table 6. As in the case of the alpha activity, the sand-slime separation apparently tends to concentrate the undissolved radium in the slimes. The effect of Pond No. 1 is also evident from Table 6. Here, the undissolved radium is settled, going from 1370 to 142 $\mu\mu\text{g}/\text{l}$ of slurry, while the dissolved activity increases from 125 to 475 $\mu\mu\text{g}/\text{l}$ of slurry. This is not as evident in Pond No. 3 where river water is returned from the Baker cooler.

NH_3 - 548,000 lb. per month

NaClO_3 - 3.5 lb. per ton of sands

WASTE DISPOSAL

Results of the survey indicated that Radium-226 was entering the river at Stations 18 and 19 at rates of approximately 0.16 and 0.005 mg/day, respectively. Of this quantity 0.11 mg was suspended radium and the remainder, dissolved. These quantities may have since decreased, due to tailings ponds rearrangement previously mentioned. A survey of the Colorado River in the vicinity of Grand Junction was conducted during August 1960 for the Colorado River Basin Water Quality Control Project. ¹⁴ At that time samples of river water and sediment were collected about 0.3 miles above the Climax Mill (Station G-1 at the lower end of a diversion channel at the mill (Station G-M), and below this diversion channel, about one-fourth mile above the mouth of the Gunnison River (Station G-2). The results of this survey are presented in Table 9. Each of the two consecutive cycles was of

Table 7. RADIUM - 226 IN PROCESS STREAM

Station	Radium - 226 mg/day		
	Undissolved	Dissolved	Total
1	331	0.10	331
2	255	0.92	256
3	230	1.07	231
4	59	0.02	59
5	50	0.06	50
6	3.5	0.33	3.8
7	0.32	1.05	1.4
8	207	a	207
9	219	a	219
10	220	3.5	224
11	0.06	0.02	0.08
12	0.01	< 0.01	0.01
13	2.1	a	2.1
14	181	0.50	182
15	176	0.01	176
16	0.16	0.33	0.49
17	0.05	a	0.05
18	0.11	1.45	1.6
19	0.01	< 0.01	< 0.01

^a Solid sample.

Table 6. RADIUM - 226 CONCENTRATIONS.

Station	Concentration in slurry, $\mu\mu\text{g}/\text{l}$		Concentration in dry undissolved solids, $\mu\mu\text{g}/\text{g}$
	Undissolved	Dissolved	
1	625,000	187	680
2	168,000	660	575
3	75,800	345	2,100
4	194,000 ^a	72 ^a	165
5	112,000	138	140
6	1,370	125	2,450
7	142	475	1,200
8	b	b	1,850
9	b	b	1,950
10	305,000	4,950	2,550
11	127	56	1,950
12 ^a	7.3	5.8	120
13	b	b	300
14	963,000	2,710	2,050
15	789,000	65	2,200
16	600	1,250	1,300
17	b	b	26
18 ^a	35	490	550
19	645	74	690

^a Single cycle.

^b Solid sample

tend to indicate that the laboratory analysis for the undissolved radium was higher than would normally be expected at Station 1. On the basis of these comparisons, the radium-226 passing Station 1 should more probably be about 240 mc/day in order to produce more over-all agreement throughout the process.

Chemical analyses were performed on several of the effluent samples collected during the survey; Table 8 presents these results. No reason is apparent for the large variations between the analyses from Cycles I and II at Station 19.

Chemical utilization was reported as follows:

- H_2SO_4
- 105 lb. per ton of sand, for sand leach
 - 250 lb. per ton of slime, uranium extraction
 - 400 lb. per tank, vanadium precipitation
 - 800 lb. per tank, uranium precipitation

Table 8. CHEMICAL ANALYSES OF EFFLUENT SAMPLES

Determination	Concentration mg/l station - Cycle			
	12-I	15-I	19-I	19-II
Total acidity, as CaCO ₃	500	250	310	150
Mineral acidity as CaCO ₃	250	20	10	0
Sulfate	2,400	1,300	7,600	1,300
Hardness, as CaCO ₃	2,500	2,100	3,600	1,300
Chloride	1,340	140	2,280	415
Sodium	1,800	135	1,350	420
Fluoride	12	13	13	6
Vanadium	.03	.03	.08	.007
Arsenic	0	0.2	3	0
pH	2.7	3.2	3.8	6.9

would be from seepage, pond overflow if this should occur and spills due to washout of pond walls. The latter is not very likely although not without precedent in the industry.

The increase in the alpha activity activity and radium and uranium concentrations at Station G-M is clearly detectable. In terms of the maximum permissible concentrations (MPC) of radio-nuclides in water outside of a controlled area, as specified by NBS Handbook 69 ¹⁵ the uranium concentration is well below the allowable 20 mg/l while the radium-226 is definitely above the allowable 3.3 $\mu\mu\text{c/l}$; however, due to the limited access to the diversion channel before reaching the main body of the river where the radium concentration is below the MPC, this cannot be considered of important public health significance.

Table 9. ANALYSES OF RADIOACTIVITY IN MUD AND WATER SAMPLES OF THE COLORADO RIVER - SURVEY RESULTS, AUGUST 1960 ^a

Station	Mud Sample ^b			Water Sample ^c			
	Alpha activity, $\mu\mu\text{c/g}$	Beta activity $\mu\mu\text{c/g}$	Ra-226 $\mu\mu\text{c/g}$	Alpha activity $\mu\mu\text{c/l}$	Beta activity, $\mu\mu\text{c/l}$	Ra-226 $\mu\mu\text{c/l}$	Uranium, $\mu\text{g/l}$
G-1 Cycle I	14.8	39.6	3.2			0.3	12
Cycle II	26.4	58.9	3.4	4.4	12.1	1.6	14
G-M Cycle I	386	478	13			3.9	44
Cycle II	659	615	19	10.7	-	4.8	35
G-2 Cycle I	249	509	3.7			1.1	22
Cycle II	343	546	4.8	7.0	31.6	1.5	21

^a Results are shown for two cycles.

^b Single sample collected each cycle.

^c Daily sample composited over each cycle.

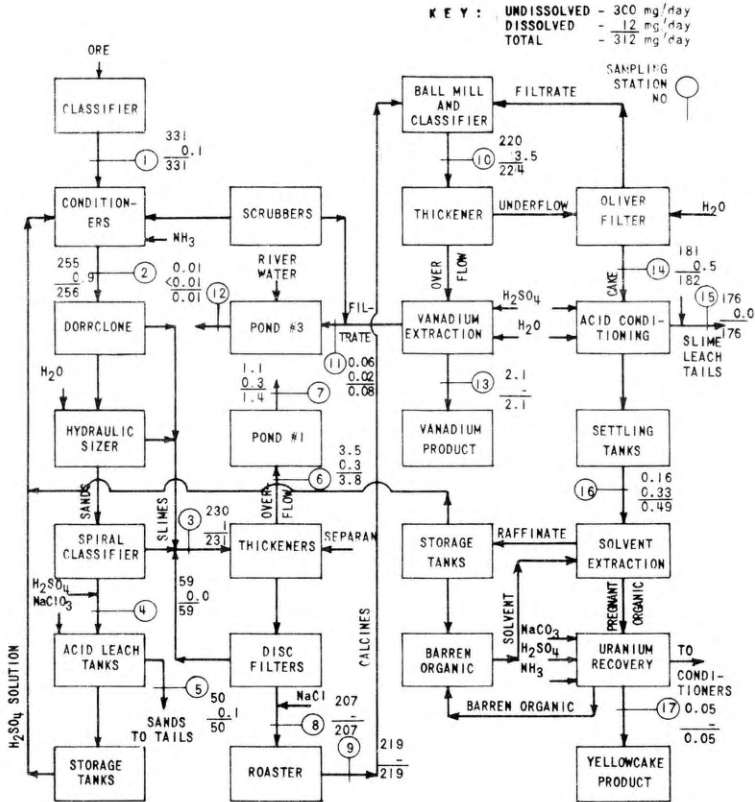


Figure 4. Schematic flow diagram for radium-226, Climax Uranium Company mill, August 1958.

approximately a week's duration.

Table 9 indicates the effect of discharges from the mill. In the case of the mud samples in all instances, the results of the second cycle are somewhat greater than the first due to the accumulation of sediment during the low flow period during the survey. As the water rises during the periods of high flow, with correspondingly high velocities, the sediment is scoured from the river bed and ultimately reaches Lake Mead, where it remains.

The increase in alpha and beta activity and Radium-226 and uranium concentrations in the river water due to the mill discharge is also illustrated in Table 9. When considered with the average flows of 31 and 103 cfs at Station G-M during the two survey cycles, this amounts to a contribution from the mill to the river of 0.27 and 0.81 mg/day of radium-226 and 2,420 and 5,320 mg/day of uranium. The figures for radium are higher than determined during the 1958 survey, possibly due in part to seepage from the lagoons. At such time as all of the mill effluent is retained, the gross activity and the uranium and radium contribution to the stream should decrease to the point where the only possibilities of radioactive wastes entering the river from the mill

THE CARBONATE LEACH URANIUM EXTRACTION PROCESS

I. HOMESTAKE-NEW MEXICO PARTNERS COMPANY, GRANTS, NEW MEXICO

J. B. Cohen*
H. R. Pahren
M. W. Lammering

Introduction

This report presents the results of an inplant survey of a uranium refinery that utilizes the carbonate leach extraction process for the separation of uranium from its ore. The study was performed by the Public Health Service during September 1959 with the cooperation of the New Mexico Department of Public Health, the Homestake-New Mexico Partners Company, and the U. S. Atomic Energy Commission.

The Homestake-New Mexico mill is located about 10 miles northeast of Grants, New Mexico. Operation began during 1958. The mill is rated at 750 tons per day; although between September 22 and September 28, 1959, the dates of the survey, about 900 tons of ore per day were processed. The ore assayed from 0.173 to 0.195 per cent U_3O_8 and yielded about 4,000 pounds per day of yellowcake. Wastes from the mill were discharged to a tailings pond, and the liquid portion not lost by seepage and evaporation was recycled for use as process water. There was no surface water in the vicinity likely to receive any of these wastes.

Figure 1 is a flow diagram of the process, which is described in detail in the following sections.

Process Description

ORE PREPARATION

Ore is brought from the nearby uranium mines by truck and stored outdoors until used. The ore is transferred by means of a bulldozer to a feed hopper, from which the ore is conveyed to a jaw crusher. Here the lumps are crushed to less than 3/4 inch.

A 10 per cent sample of the crushed ore is obtained by moving buckets as they pass through the stream of ore falling from a conveyor into a hopper. A second 10 per cent sample is obtained from the original 10 per cent, cut in a similar manner, to give a one per cent portion of the original ore. The stream representing one per cent of the ore is further crushed and then impinges on a ro-

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Acknowledgment

The generous cooperation and assistance of the following are gratefully acknowledged: Ralph Musgrave, Chief Metallurgist; and other personnel of the Climax Uranium Company; the U. S. Atomic Energy Commission; S. May, Colorado Department of Public Health; and G. Harlow and E. A. Pash, U. S. Public Health Service.

not react with many ore components other than the uranium minerals, and it is necessary to grind the ore to this size to provide the necessary amount of surface area for efficient leaching. The necessary particle size is determined by the type of ore processed. Limestone ores in which the uranium is finely dispersed throughout the matrix must be ground finer than sandstone type ores in which the uranium material is part of the bond between the sand grains.

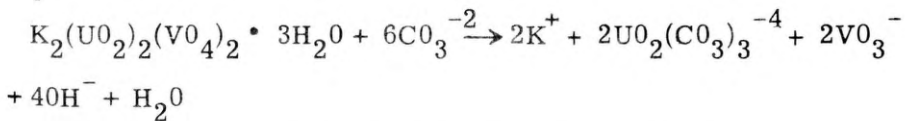
Mill solution is added to the ball mill with the ore. A spiral classifier separates any oversize particles and returns them to the ball mill. The specific gravity of the slurry from the classifier is automatically controlled at 1.20 by means of an automatic valve. The flow of additional mill solution added to the classifier is either increased or decreased, depending on the amount necessary to maintain the desired specific gravity in the classifier overflow. This effluent is pumped to a small cyclone separator where the coarse solids are separated from the slime.

The cyclone overflow is sent to a 75-foot thickener where the solids are further concentrated. About 20 pounds per day of Separan are added here to aid in solids separation. Overflow from the thickener is recycled to the mill solution storage tank. The thickener underflow is combined with the underflow from the two cyclones in an agitated tank. Combined effluent from the agitated tank flows to a sump, from which it is pumped to the leaching section.

LEACHING

Leaching of the uranium from the solid particles is accomplished with a sodium carbonate-bicarbonate liquor in six Pachuca tanks, 19 feet in diameter and 48 feet high, operating in series. There is a 7-hour retention time in each tank or 42 hours total retention in the leaching circuit. The Pachuca tanks are operated at 179°F. and at atmospheric pressure.

The insoluble quadrivalent uranium must be converted to the soluble hexavalent form. Soluble uranyl tricarbonate then forms in the carbonate solution, under the leaching conditions. The solubilization of the hexavalent form, such as the uranium mineral carnotite in order to produce the uranyl tricarbonate ion may be represented as follows: 16, 17



The Pachuca tanks are aerated to provide for the oxidation of reduced uranium compounds. Copper sulfate and ammonia are normally added to the ore slurry to catalyze the oxidation reaction. During the period of the survey however, a test run was made with cyanide instead of the copper sulfate and ammonia. Crude cyanide that contained about 50 per cent NaCN equivalent was

FILTRATION OF TAILINGS

The solids that are separated from the pregnant solution by the first stage filters are washed by a portion of the recarbonated barren solution. The remaining recarbonated solution is used to repulp the first-stage filter cake. This repulped slurry is then filtered by the second stage filters. The water used to wash the filter cake from the second stage filters is return water decanted from the tailings pond. Filtrate from the second stage filters is returned to the primary thickener. About 50 pounds per day of a flocculating agent, guar gum solution, is added to the filter feed to aid in filtration.

The filter cake from the second stage filters is repulped so that it may be pumped to the tailings pond. Part of the repulping water consists of fresh water from the plant well. The balance of the water is return water from the tailings pond.

Normally the water returned from the tailings pond passes through an ion exchange system to recover any dissolved uranium, and a flotation unit to remove any hydrocarbons before the water is used. During the period of the survey, however, the ion exchange system was not in operation and the return tailings water by-passed this step. The flotation unit, however, remained in operation. A gas flame was used to burn off any hydrocarbons in the froth from the flotation unit, before the froth flowed to the floor sump and the primary thickener.

TAILINGS POND

The tailings pond contained approximately 40 acres within the dikes, of which about 10 acres were occupied by clear water and about 10 acres by moist tailings. The remaining area was dry. At one end, an area is partially separated from the remainder of the pond. Water overflows from the main portion of the pond into this area, and from here is returned to the mill process.

The Mill Survey

For the purpose of analyzing the individual components that make up the entire extraction process, samples were obtained during two sampling cycles of 72 hours each. The sampling periods were as follows:

Cycle 1 - 7 AM, Sept. 22, 1959, to 7 AM, Sept. 25, 1959.

Cycle 2 - 7 AM, Sept. 25, 1959, to 7 AM, Sept. 28, 1959.

Table 1 gives a list of the sampling stations, together with a brief description of each..

A sample of the ore being fed to each ball mill was collected by plant personnel every hour and composited over a 24-hour

added to the ore at the rate of 0.8 pounds per ton of ore as it was conveyed to the ball mills. The cyanide reacts with the iron balls in the ball mills to form the complex ferricyanide ion, a strong oxidizing agent for uranium.

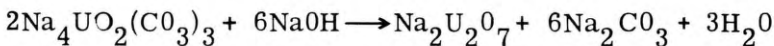
PREGNANT LIQUOR PREPARATION

The slurry from the final leaching tank flows to the first-stage rotary filters, where the solids are separated from the liquid containing the uranium or the pregnant solution. There are three filters in each stage of filtration. The filter cake is washed with recarbonated barren solution and this wash water becomes a part of the filtrate.

The pregnant solution is then pumped to an aerated flotation tank where any hydrocarbons in the solution are removed. If these hydrocarbons are not removed they interfere with the next step by preventing the complete precipitation of uranium with the caustic. A small amount of organic chemical is continuously added to promote frothing and to aid in removing chemical is continuously added to promote frothing and to aid in removing the hydrocarbons. The froth overflows to the floor sump, from which it goes to the primary thickener. The flotation tank underflow is sent to a second 75-foot settling tank for further clarification. Overflow from this settling tank flows to the pregnant liquor storage tank while the underflow is pumped to the primary thickener.

PRECIPITATION AND PREPARATION OF YELLOWCAKE

Pregnant solution is pumped to the first of three 20-foot diameter precipitation tanks operating in series. A 50 per cent sodium hydroxide solution is added at a rate of about 5,000 pounds per day to precipitate the sodium diuranate yellowcake. The reaction is as follows:



The precipitated yellowcake is concentrated in a 12-foot diameter thickener. Underflow from the thickener passes through a Burwell filter press that removes the solids. After the yellowcake is removed from the filter, it is dried in a gas fired drier, ground in a hammermill, and drummed for shipment to the U. S. Atomic Energy Commission.

Overflow from the yellowcake thickener and the filtrate from the Burwell presses are combined. This barren solution is padded through a Sperry filter press to remove any remaining yellowcake particles before it is pumped to the recarbonation tower where the boiler plant flue gas is passed countercurrent to the barren solution. Carbon dioxide in the flue gas neutralizes the excess caustic alkalinity thus forming additional carbonate and bicarbonate. The recarbonated barren solution is then reintroduced into the process at the first stage filters, following the leach process.

Analyses and Results

The results presented here are a combination of field data, laboratory analyses and flow balances; together they present an over-all picture of the units composing the carbonate-leach process. With physical data from the field and laboratory, a flow balance for the mill was obtained. This was done through the use of a solids balance and a total weight balance between the various mill process units. These results enabled the preparation of Figure 2, a schematic flow diagram giving the estimated slurry flow, separated in terms of solids and liquid, at each of the sampling points. Table 2 presents the physical characteristics of the process stream at the various stations. The data, including all balances, were measured or computed separately for each cycle and then averaged because of their close agreement. As previously mentioned, the 42-hour time lag between Stations 5 and 6 (the leaching process) tends to make a mill balance difficult, but averaging the two 72-hour cycles minimized this problem.

In Table 2 the data in columns (3) through (6) are laboratory determinations, while the slurry flows in column (2) were calcu-

Table 2. PROCESS STREAM CHARACTERISTICS ^a

Station (1)	Slurry flow, gpm (2)	Specific gravity of slurry (3)	Dry suspended solids by weight, % (4)	Specific gravity of dry solids (5)	pH (6)
1	b	-	94.1	-	-
2	508	1.09	c	-	10.1
34	580	1.23	25.4	2.64	10.1
5	183	1.48	54.6	2.59	10.1
6	178	1.54	52.8	2.66	10.0
7	285	1.32	39.1	2.72	9.6
8	117	1.10	c	-	10.1
9	80	1.10	c	-	10.1
10	b	-	99.4	-	-
11	d	1.10	c	-	12.0
12	73	1.07	c	-	10.2
13	70	1.00	c	-	-
14	150	1.01	c	-	9.8
16	82	1.08	c	-	10.3
17	81	1.10	c	-	12.0

^a Average of cycles 1 and 2

^b Solid sample.

^c Liquid (negligible suspended solids).

^d Flows not calculated.

Table 1. SAMPLING STATIONS

Station number	Description
1	Raw ore feed to ball mill
2	Mill solution
34	Combined overflow from classifiers
5	Slurry to leach tanks
6	Leach tank effluent
7	Waste to tailings pond
8	Pregnant filtrate from first stage filters
9	Pregnant solution to precipitation tanks
10	Yellowcake product
11	Barren solution from Burwell Press
12	Filtrate from second stage filters
13	Raw well water
14	Return water from tailings pond
16	Recarbonated barren solution
17	Combined barren solution to Sperry Press

period. The samples from the two ball mills were combined, pulverized, blended and resampled. Portions of the daily composite samples were weighted according to tonnage of ore fed to process and combined for each cycle (Station 1).

Equal portions were composited from each drum of yellowcake packaged during each three-day sampling period to give the yellowcake sample representative of Station 10.

Every 2 hours, samples were collected at both classifier overflows (Stations 3 and 4); combined slurries were pumped to the leach tanks (Station 5), and from the final leach tank (Station 6). These samples were composited for each cycle.

During Cycle 1 samples were collected from the drinking water fountain every two hours and composited (the plant raw water sample, Station 13). For the second cycle, one grab sample of water was obtained to determine if there was any difference in the two methods of collection, such as possible contamination of the composite sample by plant dust.

All other plant samples were collected by means of automatic samplers, and daily samples were composited for each 3-day period of the cycle.

The samples from this survey were sent to the Public Health Service's Robert A. Taft Sanitary Engineering Center, at Cincinnati, Ohio, where all physical, chemical, and radiological determinations, except radium analyses, were conducted. Duplicate portions of the liquid and solid samples were sent to a private laboratory for determination of dissolved and undissolved radium.

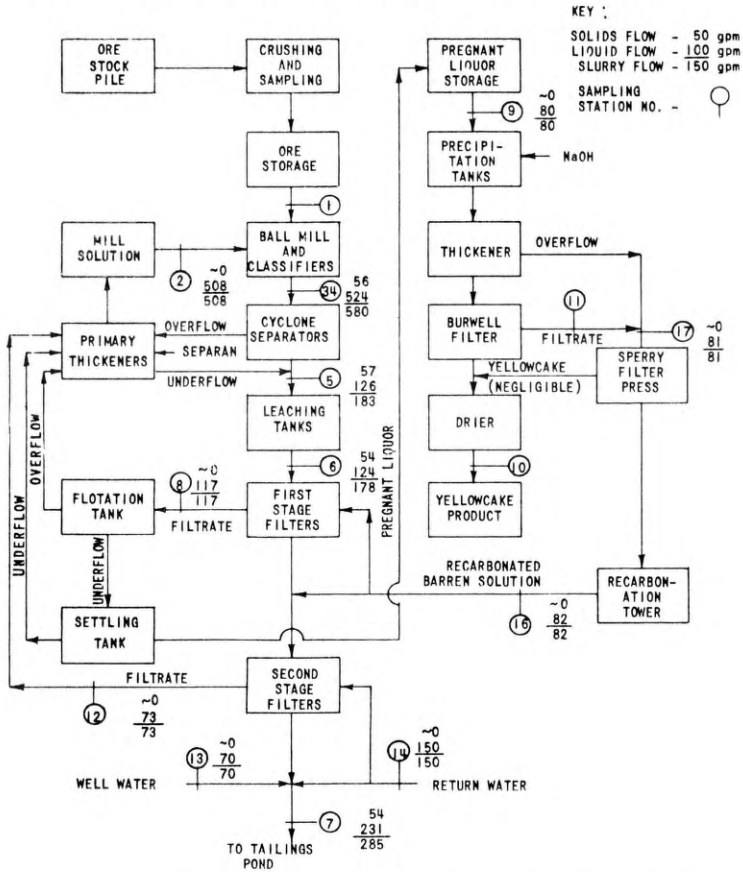


Figure 2. Schematic flow diagram of Homestake-New Mexico Partners mill, September 1959.

leaching at Station 5, the mill solution at Station 2 and the pregnant liquor storage at Station 9 respectively.

Results for the stations mentioned above show that the solids flows of Table 3 are fairly good. At the ball mill and classifier, 1184 (881 + 303) tons of solids per day enter as raw ore (Station 1) and mill solution (Station 2) compared to the 1183 tons per day leaving these units. In the yellowcake precipitation stage of the process, 57 tons per day of solids enter in the pregnant liquor (Station 9) compared to the 49 (2 + 47) tons per day leaving as yellowcake (Station 10) and recarbonated barren solution (Station 16). In terms of the over-all mill balance 894 (881 + 12 + 0.5) tons per day enter the plant as raw ore (Station 1), return water (Station 14) and well water (Station 13) compared to the 897 (895 + 2) leaving the plant via the tailings pond (Station 7) and as yellowcake product (Station 10). A balance at the thickeners shows 1304 (1183 + 85 + 36) tons per day entering from the classifiers (Station 34) and the primary and secondary filters (Stations 8 and 12). This is in good agreement with the 1326 (966 + 57 + 303) tons comprising

lated. Although the fresh water flow, used for repulping the final tails, at Station 13 was calculated as 70 gpm, additional fresh water entered the process at other points, including water for chemical feed preparation, water used for plant housekeeping, and makeup water needed because of evaporation and other losses.

Table 3 presents the average solids flow (average of cycles 1 and 2). Because of the selectivity of the leaching process for the uranium compounds and the low concentration of uranium in the ore, there was little detectable change through the mill as regards tonnages of undissolved ore solids.

Table 3. SOLIDS IN PROCESS STREAMS

Station	Tons per day		
	Suspended	Dissolved	Total
1	881	-	881
2	0.8	302	303
34	884	299	1183
5	883	83	966
6	868	111	979
7	883	12	895
8	0.6	84	85
9	0.2	57	57
10	2.0	-	2.0
12	0.9	35	36
13	~0	0.5	0.5
14	~0	12	12
16	0.2	47	47
17	0.1	55	55

Figure 2 shows that there are locations throughout the mill where quantities entering and leaving sections of the process can be directly balanced. The mill solution, Station 2, and the ore from storage, Station 1, entering the ball mill and classifier should be quantitatively accounted for at the exit from the classifiers, Station 34. Quantities present in the pregnant liquor at Station 9 should be measurable in the yellowcake product at Station 10 and in the recarbonated barren solution at Station 16. For the over-all plant balance, the ore entering at Station 1, the fresh water at Station 13, and makeup water at Station 14 should approximate the yellowcake produced at Station 10 and the slurry flow to the tailings pond at Station 7. A balance at the primary thickeners would equate the input from the classifiers at Station 34 and the primary and secondary filtrates at Stations 8 and 12 to the output to

Table 5. ALPHA ACTIVITY IN PROCESS STREAMS

Station	Gross Alpha Radioactivity, mc/day		
	Undissolved	Dissolved	Total
1	2,630	-	2,630
2	7	1,090	1,097
34	2,060	1,440	3,500
5	2,310	450	2,760
6	2,140	550	2,690
7	1,730	11	1,741
8	3	600	603
9	2	273	280
10	300	-	300
12	7	17	24
13	-	~ 0	0
14	-	9	9
16	2	12	14
17	12	2	14

dissolved alpha activity increased as the undissolved activity entered solution. A comparison of these two stations shows 2760 mc/day entering the leaching stage and 2690 mc/day leaving at Station 6. Table 5 also shows that 280 mc/day entered the uranium extraction stage of the process while 314 (300 + 14) mc/day were accounted for in the yellowcake product and the barren solution. A total of 4127 (3500 + 603 + 24) mc/day entered the thickening stages from the classifier (Station 34), and the filters (Stations 8 and 12), which is in excellent agreement with the 4137 (2760 + 1097 + 280) mc/day leaving for the leaching process (Station 5) as mill solution (Station 2) and as the pregnant liquor (Station 9).

The over-all plant balance required further study since the 2639 (2630 + 9) mc/day entering with the raw ore and the return water was in relatively poor agreement with the 2041 (1741 + 300) mc/day in the slurry to the tailings pond (Station 7) and in the yellowcake product (Station 10). A close investigation of the procedures used in collecting and analyzing the samples revealed that the discrepancy could have been due to the manner in which the samples are collected at Station 7. At this station a portion of the flow is collected in a large drum. To obtain a sample for analysis the contents are mixed and the tank is completely drained from below. A sample bottle is passed through the stream every few seconds until the drum is emptied. Because the heavier particles would tend to settle first at a higher flow, the sample would contain a disproportionately greater quantity of large solids than the

the slurry to leach tanks (Station 5), the pregnant liquor (Station 9) and the mill solution (Station 2) in that order.

The gross radioactivity concentrations determined in the laboratory are listed in Table 4. These data demonstrate how the leaching process affects the activity of the sample. Between Stations 5 and 6 (the leaching process) the undissolved activity decreases while the dissolved activity increases. The effect of particle size is also shown in this table. At those stations where the large solids had already been filtered and only the fine particles remained, the activity was several times greater than that of the unfiltered solids when considered in terms of $\mu\mu\text{c/g}$ of dry undissolved solids.

Table 4. GROSS RADIOACTIVITY CONCENTRATIONS

Station	Total Sample (Slurry) Radioactivity, $\mu\mu\text{c/l}$				Radioactivity in dry undissolved solids, $\mu\mu\text{c/g}$	
	Undissolved		Dissolved			
	Alpha	Beta	Alpha	Beta	Alpha	Beta
1	-	-	a	a	3,300	3,300
2	2,580	5,100	393,000	1,110,000	9,910	19,400
34	662,000	676,100	456,000	1,190,000	2,630	2,660
5	2,300,000	2,810,000	386,000	1,080,000	2,870	3,520
6	2,200,000	2,660,000	564,000	1,760,000	2,700	3,290
7	1,100,000	1,080,000	5,720	17,500	2,150	2,100
8	4,830	9,940	902,000	2,120,000	7,780	15,700
9	3,880	7,890	637,000	1,790,000	10,500	21,400
10	-	-	a	a	164,000	374,000
11	b	b	12,800	28,400	-	-
12	16,500	26,500	41,400	122,000	8,800	14,200
13	b	-	2.6	41	-	-
14	b	-	11,600	41,800	-	-
16	4,420	8,430	27,700	98,400	10,200	19,300
17	26,200	66,100	5,430	23,400	112,000	281,000

a Solid Sample.

b Liquid Sample.

Gross alpha quantities are presented in Table 5. The flows computed in Table 2 have been combined with the assay of Table 4 to trace the alpha activity through the various mill processes. The figures for the alpha balance are a function of flow and as such would be expected to vary with production.

The balance at the ball mill was good with 3727 (2630 + 1097) mc/day entering as raw ore (Station 1) and mill solution (Station 2) compared to the 3500 mc/day at Station 34. The effect of the leaching process is illustrated between Stations 5 and 6 where the

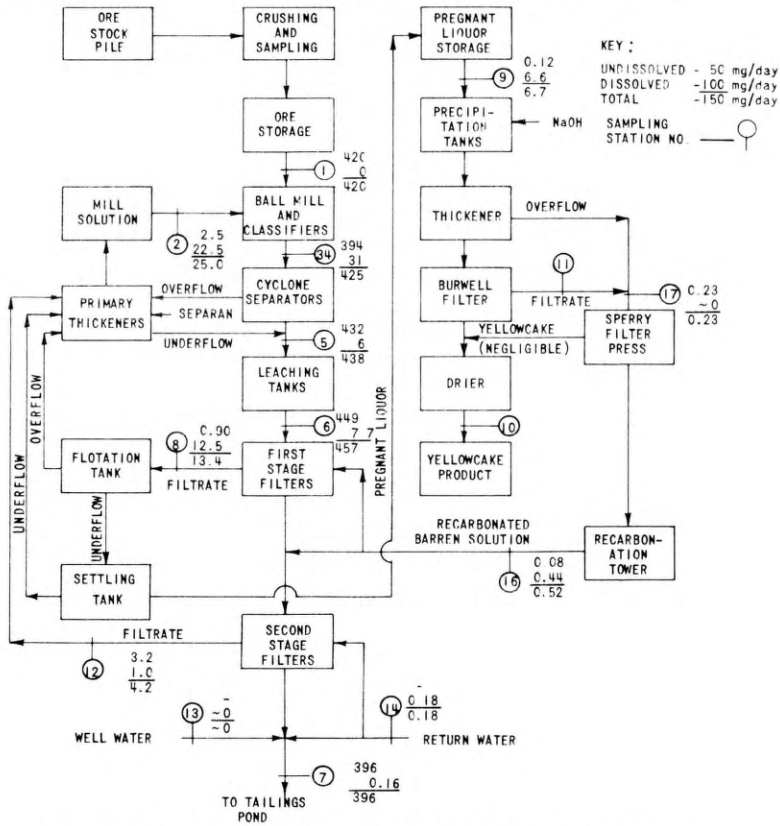


Figure 3. Schematic flow diagram for Radium-226 at the Homestake-New Mexico Partners mill, September 1959.

Table 7. RADIUM - 226 IN PROCESS STREAM

Station	Radium-226 mg/day		
	Undissolved	Dissolved	Total
1	420	a	420
2	2.5	22.5	25
34	394	31	425
5	432	6.0	438
6	449	7.7	457
7	396	0.16	396
8	0.90	12.5	13
9	0.12	6.6	6.7
10	6.4	a	6.4
12	3.2	~ 1.0	4.2
13	-	0	~ 0
14	-	0.18	0.18
16	0.08	0.44	0.52
17	0.23	~ 0	0.23

a Solid Sample

Table 6. RADIUM - 226 CONCENTRATIONS

Station	Radium - 226 in slurry, $\mu\mu\text{g}/\text{l}$		Radium - 226 in dry undissolved solids, $\mu\mu\text{g}/\text{g}$
	Undissolved	Dissolved	
1	a	a	530
2	890	8,160	3,450
34	124,000	9,820	490
5	427,000	5,620	540
6	463,000	7,880	570
7	225,000	100	490
8	1,410	19,600	2,150
9	270	15,200	740
10	a	a	3,490
11	2,800	2.4	26,400
12	7,900	2,400	4,250
13	b	0.4	-
14	b	160	-
16	170	990	390
17	530	5.4	2,260

a Solid Sample.

b Negligible Solids Content.

actual flow. The larger particles usually contain less activity per gram than the smaller particles, and we would, therefore, expect to find a discrepancy of the type involved. This was evident previously in Table 4. Thus, while the activity at Station 7 was calculated at 1741 mc/day, it was more probably in the neighborhood of 2200 mc/day. Table 5 also illustrates that the majority of the alpha activity remained undissolved through the process, and was discharged to the tailings pond with the solids.

Samples to be analyzed for Ra-226 were prepared at the Taft Center and forwarded to a private laboratory for these determinations. Preparation entailed separating the solids from the liquid with membrane filters, and grinding the solids portion to less than 100-mesh. The undissolved activity is in the solids remaining on the membrane filter; the dissolved activity is in the liquid portion of the sample passing through the filter. Table 6 presents the results of the laboratory analyses for radium per liter of slurry and per gram of dry undissolved solids. The finer particles apparently have a greater activity than the coarser particles.

When the laboratory results of Table 6 are combined with the flow balance of Table 2 a radium balance throughout the mill may be computed. This is shown in Table 7 and Figure 3. A balance

and milling, thus partially breaking the chain. As a result, the observed value of 2,630 mc/day in Table 5 is within the range that would be expected.

Of the 420 mg/day of Ra ²²⁶ entering the mill in the raw ore, 6.4 mg/day, or 1.5 per cent, leave with the yellowcake. This is substantially more than has been found in mills using the acid leach process.

Chemicals added to the process at the time of the survey are listed in Table 8. On a yearly basis, the plant uses caustic at a rate of 17 to 22 pounds per ton of ore processed and soda ash at a rate of 0 to 5 pounds per ton, with an average of 20 pounds and 1 pound per ton, respectively. In addition, the use in the recarbonization tower of carbon dioxide from the flue gas must be recognized as part of the chemical consumption. Analysis of the filtrate at Station 7 provided the following data in terms of mg/l of filtrate:

Arsenic	-	0.20 mg/l
Chlorida	-	275 mg/l Cl ⁻
Phenol Alkalinity	-	900 mg/l as CaCO ₃
Total Alkalinity	-	4050 mg/l as CaCO ₃
Sodium	-	2950 mg/l Na ⁺
pH	-	9.6

These figures, with the exception of pH, could be expressed in terms of slurry flow by reducing the concentrations by 20 per cent.

Waste Disposal

As the tabular data indicate, 285 gpm of slurry entered the tailings ponds during the survey period. Of this, 54 gpm were undissolved solids and the remaining 231 gpm were liquid. The solid portion contributed an estimated 396 milligrams of Ra ²²⁶ per day to the pond and the liquid phase only 0.16 mg/day. The return water from the pond (Station 14) was slightly higher in Ra-226 concentration, probably due to leaching and evaporation in the pond. As the flow diagrams indicate, the liquid returned at Station 7 is mainly a combination of repulping water from Station 14 and fresh water from Station 13.

The wastes are contained within the tailings pond and there are no surface waters within the vicinity; hence, surface water pollution is not a problem. The possibility of ground water pollution, however, cannot be ignored.

A number of private wells are in use in the area and ground water is used for domestic consumption, for livestock, and for irrigation. In addition, the towns of Milan and Grants, a few miles south of the mills, have municipal supply wells.

Three aquifers are present in the area: Silt, sand and gravel of the alluvium; interbedded clay, siltstone and sandstone beds in

Table 8. CHEMICAL CONSUMPTION

Chemical	Pounds added per ton of ore processed
Cyanide (50% CN^-)	0.82
Caustic (100% NaOH)	2.84
Soda Ash	2.65
Jaguar	0.052
Separan	0.023

was calculated for each cycle and then averaged at each station. Thus the figures represent the quantities of radium in the process while the mill was processing an average of 880 tons of ore per day.

Table 7 and Figure 3 indicate the radium balance between stations is good in most cases. The 445 (420 + 25) mg/day of radium entering the ball mill with the raw ore and the mill solution agrees well with the 425 mg/day at Station 34. The uranium precipitation stage only contains a small amount of Ra^{226} ; the 6.7 mg/day entering at Station 9 are accounted for as 6.9 (6.4 + 0.5) mg/day in the yellowcake and the recarbonated barren solution. The 457 mg/day of Ra^{226} leaving the leaching stage at Station 6 is slightly higher than expected though still in line with the other stations having high solids content. A total of 442 (425 + 13 + 4.2) mg/day enter the thickener units from the classifiers and the filters as compared to the 470 (438 + 25 + 6.7) mg/day leaving these units for the leaching stage (Station 5) as mill solution (Station 2) and pregnant liquor solution (Station 9). The over-all plant balance shows 420 mg/day in the raw ore (Station 1) as against 402 (396 + 6.4) mg/day in the slurry to tails (Station 7) and the yellowcake product (Station 10). Because the Ra^{226} at Stations 13 and 14 is negligible for balancing purposes, again it would appear that Station 7 has less activity than would actually be expected. In all cases mentioned above the discrepancies in the radium balance were less than 10 per cent of the quantity being considered.

Most of the radium remains undissolved through the mill, although dissolved radium concentrations build up at several process locations, due to recycling of mill solution. If the ore entering the process at Station 1 is considered to be in radioactive equilibrium, the amount of radium entering with the ore each day can be computed from the assay for U_3O_8 . On the basis of the average assay of 0.186 per cent U_3O_8 during the survey period, the radium entering was calculated as 420 mc/day, in exact agreement with the value calculated from the radium analysis. On this same basis, if it could be assumed that all of the daughters of U^{238} are in radioactive equilibrium with the parent isotope, we would expect the gross alpha activity entering the process to be about 3,300 mc/day. Radon-222, however, is a gas; hence a portion of it will be lost to the atmosphere in the ore body during mining and handling

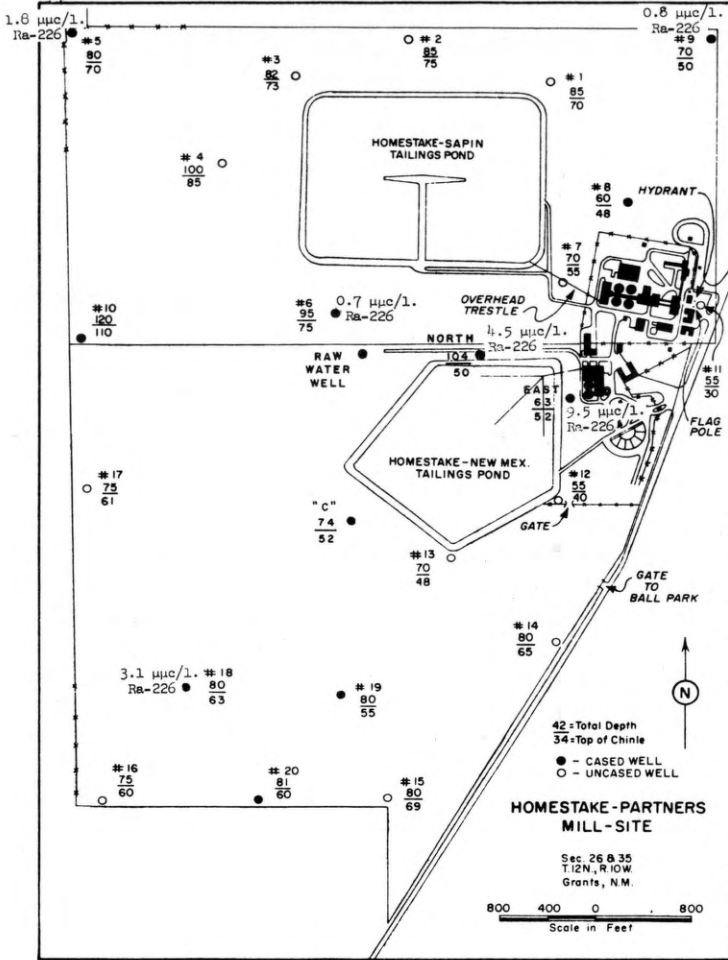


Figure 4. Radium-226 in water samples from test wells at Homestake-Partners mill-site.

the Chinle formation; and the San Andres limestone. Domestic and stock wells usually obtain sufficient water from the alluvium or from the Chinle formation. Water levels in the general area indicate that the water in the alluvium occurs under water table conditions and moves southwestward from the mill sites into the valley of the Rio San Jose. It then moves down the valley in a southeastward direction. The alluvium is in contact with the San Andres limestone along the southwest edge of the valley, west of Milan, and at these points water in the alluvium can enter the limestone formation. Water in the San Andres limestone is under artesian pressure and moves in a general easterly direction from the mills. The level and movement of water in the Chinle formation has not been determined definitely. At the mills the depth to water in the alluvium is thought to be about 80 feet. The depth to the San Andres limestone is 600 feet but the artesian pressure raises the water level in this formation to 130 feet below the land surface. ¹⁸

Samples from test wells in the vicinity of the mill were analyzed for radium-226. The results (0.8, 1.8, 0.7, 4.5, 9.5, and 3.1 $\mu\mu\text{c}/\text{l}$) are shown on Figure 4, a map of the area. Radioassays on the solids in the samples from the north and the east test wells indicated radium 226 concentrations of 551 and 1,685 $\mu\mu\text{g}/\text{g}$ of solids, respectively. These concentrations are higher than in the ore feed to the mill. Additional samples were analyzed from wells several miles to the west of the mills and from wells between Grants and San Rafael. Results of these analyses indicate a radium content of from 0.1 to 0.4 $\mu\mu\text{c}/\text{l}$, or the usually expected natural concentrations.

If monitoring of the test wells at the mill should indicate a buildup or spread of the radium-226 consideration may have to be given to ways and means of sealing the ponds and preventing further buildup. This is suggested in view of the facts that the radium concentration of the discharge to the pond (Station 7) was measured as 124 $\mu\mu\text{g}/\text{l}$ of liquid and, at the time the wells were sampled, the mill had been in operation less than two years.

Acknowledgment

The generous cooperation and technical assistance of the following are gratefully acknowledged: John Hernandez, New Mexico Department of Public Health; personnel of the Homestake-New Mexico Partners Mill; the U. S. Atomic Energy Commission; Charles E. Sponagle, Public Health Service, Region VIII, Denver, Colorado; E. A. Pash, Carl Hirth, Carl Shadix, and H. D. Nash, Public Health Service, Cincinnati, Ohio; and D. E. Rushing, Public Health Service, Salt Lake City, Utah. The technical advice and guidance of Dr. E. C. Tzivoglou, Public Health Service, Cincinnati, Ohio, was greatly appreciated. This study was supported by funds made available through the Environmental and Sanitary Engineering Branch, Division of Reactor Development, U. S. Atomic Energy Commission.

THE CARBONATE LEACH URANIUM EXTRACTION PROCESS

II. HOMESTAKE-SAPIN PARTNERS, GRANTS, NEW MEXICO

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Introduction

This report presents the results of a study conducted at a second uranium refinery employing the "carbonate leach extraction process. The study was performed by the U. S. Public Health Service and the New Mexico Department of Public Health during September 1959, with the cooperation of personnel of the Homestake-Sapin Partners mill and the U. S. Atomic Energy Commission.

The Homestake-Sapin mill with a design capacity of 1500 tons of ore per day was placed in operation during the latter half of 1958. Located about ten miles northeast of Grants, New Mexico, (adjacent to the Homestake-New Mexico Partners mill) it lies in an arid area with no surface water in the near vicinity. At the time of the survey, the mill was processing about 1640 tons per day of dry ore, which assayed from 0.143 per cent to 0.235 per cent U_3O_8 . Recovery of U_3O_8 averaged 90 per cent with a yield of 5000 pounds per day of yellowcake. The plant effluents were discharged to a tailings pond, where all but a small liquid portion (recycled as process water) was retained for dissipation by evaporation and possibly seepage. Figure 1 is a detailed flow diagram of the refinery. The units are described in detail in the following section.

Process Description

ORE PREPARATION

Ore is brought from the mines by truck and is initially stored outdoors on a storage pad. A bulldozer transfers the ore to a feeder from which it is carried by belt conveyor to a jaw crusher. If the ore contains more than about 10 per cent moisture it is passed through a gas fired rotary kiln dryer; ores with less than 10 per cent moisture by-pass the dryer.

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LEACHING

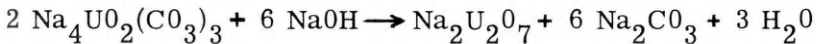
The underflow from the primary thickener is pumped by a diaphragm pump to the first of eight leach tanks in series. The retention time in each leach tank is about one hour. Under leaching conditions of approximately 225° F. and 60 pounds pressure, most of the uranium remaining in the solids is leached out.

Leaching solutions contain carbonate and bicarbonate ions, and under the process conditions, the soluble uranyl tricarbonate ion, $UO_2(CO_3)_3^{-4}$, is formed.

After leaching, the slurry flows to a 100-foot diameter secondary thickener where additional separan is added to aid in settling the suspended solids. The secondary thickener overflow, known as pregnant solution, from each circuit is combined. The pregnant solution is clarified by means of a rotary filter, and then is stored in the clarified-pregnant-solution storage tank. The small amount of solids removed by the filter is slurried and returned to the secondary thickener. Underflow the secondary thickeners is pumped to the tailings filtration area.

PRECIPITATION AND PREPARATION OF YELLOWCAKE

Clarified pregnant solution is pumped to the first of seven agitated precipitation tanks operated in series. Here, sodium hydroxide is added as a 50 per cent solution until the pregnant solution contains 8 grams of NaOH per liter. With the increase of pH, the uranium precipitates as sodium diuranate or yellowcake, as follows: ¹⁷



The yellowcake slurry is transferred to a thickener to which a solution of locust bean gum, a natural polysaccharide, is added to aid in settling the yellowcake. Overflow from the thickener is filtered through a plate and frame filter press to remove the small amount of yellowcake that is carried over, and the clarified barren solution is then passed through a recarbonation tower. Flue gas from the boiler plant is passed countercurrent to the barren solution in the tower, and the carbon dioxide in the flue gas neutralizes the caustic alkalinity and forms additional carbonate. The recarbonated barren solution is then available for re-use in the process.

Underflow from the thickener contains the yellowcake, which is filtered out with a rotary filter. The yellowcake is repulped with fresh, softened water and refiltered, and the filtrate is added to the yellowcake thickener. The resulting filter cake is washed, dried, pulverized and then drummed for shipment to plants of the U. S. Atomic Energy Commission. Yellowcake is filtered and packaged only during the day shift.

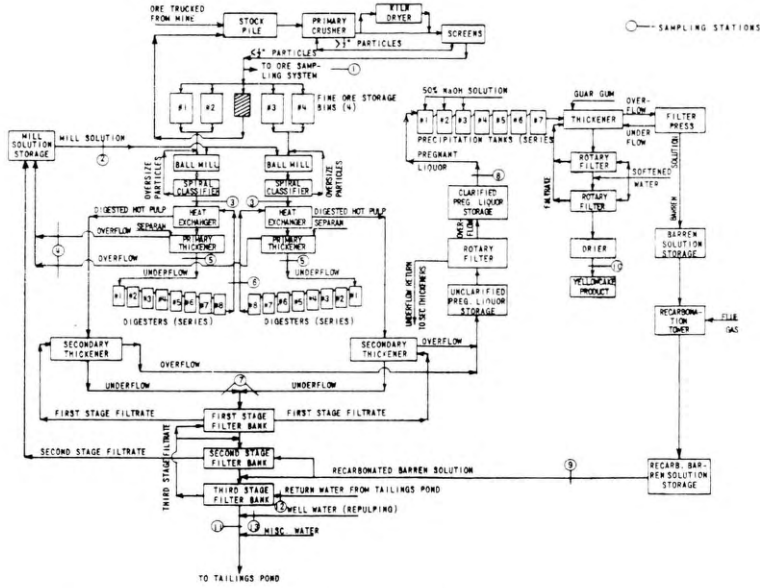


Figure 1. Flow diagram of Homestake-Sapin Partners uranium mill, Grants, New Mexico, September 1959.

Next, the ore is sampled to ascertain the uranium content for each lot. The ore passes through a sample cutter which diverts 10 per cent of the ore stream. The 10 per cent sample then passes through a second cutter which takes another 10 per cent sample. After four such cuts, a sample of 0.2 pounds per ton of ore processed is obtained. The balance of the ore is approximately equally distributed in four fine-ore bins of 1500 tons capacity each.

In the process following the fine ore storage there is a duplicate circuit through the plant. This duplication of facilities continues until the pregnant solution streams from each circuit are combined.

Two of the fine ore bins feed to each circuit. Ore fed to process is first weighed by an automatic weightometer and then is added to a ball mill along with mill solution to make a relatively thick slurry. Following this, the slurry flows to a spiral classifier where oversize material is separated and returned to the ball mill. Additional mill solution is added to the classifier to give an effluent with a specific gravity of 1.20. Approximately 45 per cent of the solids in the classifier effluent are minus 200 mesh and 12 per cent are plus 65 mesh.

The classifier effluent is pumped to a 100-foot diameter primary thickener where the solids are concentrated in the bottom and the overflow is returned to mill solution storage. Separan is added in a one per cent solution to facilitate settling.

matic sampler each day and composited the three equal portions for each cycle.

A 1-day lead time was used for the raw ore samples. A portion of the official sample from each ore lot was obtained from that collected by the plant sampling equipment before the ore was discharged to the fine ore storage bins. To make the composite sample for each cycle, the portion taken from each ore lot processed was weighted according to the tonnage of the lot. For the ore samples, the period from 8 AM Sept. 16 to 8 AM Sept. 19 was Cycle I and the period from 8 AM Sept. 19 to 8 AM Sept. 22 was Cycle II.

Composite yellowcake samples were obtained for each of two consecutive 3-day periods beginning September 18, thus giving a 1-day lag period. Representative samples of each day's production were weighted according to tonnage of production for the day and composited for the cycle. Yellowcake was not packaged on September 20, the third day of Cycle I. Thus, the production on September 21 was equally divided between both cycles to compensate for this variation.

As mentioned in the process description, there are duplicate circuits in the plant from the beginning of the process through the secondary thickener step. During the survey individual samples were obtained at significant points for both the north and south circuit. Samples from the same point in each circuit were then combined. A list of all the sampling stations is shown in Table 1.

Sample Processing

The samples collected during the survey were shipped to the Public Health Service's Robert A. Taft Sanitary Engineering Center, where all chemical and physical analyses were performed, except the analysis for radium-226.

Although the results presented in the following section are average values for Cycles I and II, analyses for dissolved and undissolved gross alpha and beta activity, dissolved and undissolved radium-226, sodium (Na^+), and pH were performed on individual samples from each cycle. Thus, each station is associated with two results for each applicable analysis. Supplementary analyses for arsenic, chloride, phenolphthalein alkalinity, and total alkalinity were performed on the liquid portions of Station 11 and 13 samples.

The radium analyses were performed by a private laboratory under contract to the Public Health Service. Pretreatment of the samples by the Taft Center laboratory consisted of liquid-solid separation by filtration through a membrane filter, and grinding the dried suspended material to less than 100 mesh.

FILTRATION OF TAILINGS

The tailings filtration area consists of three stages of five rotary filters each. The combined underflow from the two secondary thickeners passes through the three filtration stages and the pregnant solution that carries over is separated from the solids before the solids are discharged to the tailings pond. Filtrate from the first stage filters is added to the secondary thickener, while filtrate from the second stage filters is pumped to the mill solution storage tank.

Filter cake from the first stage filters is washed by part of the third stage filtrate. The balance of the third stage filtrate is used to repulp the filter cake prior to the second stage filtration. About one-third of the recarbonated barren solution is used to wash the filter cake on the second stage filters. The remaining recarbonated barren solution is used for repulping between second and third stage filtration. Third stage filter cake is washed by reclaimed water from the tailings pond and, after removal from the filter drum, is repulped with unsoftened raw water. This slurry passes through an automatic sampler. After passing through the sampler, additional water is added before the slurry is pumped to the tailings pond. Mill personnel indicated that the additional water consisted of approximately 10 gpm from the reagent building, 40 gpm of cooling water from the vacuum pumps and 25 gpm of excess return water from the tailings pond.

Tailings Pond

The tailings pond is circular in shape and has 60 acres within the dikes. Water covered only 39 acres of this area at the time of the survey. In addition to the main pond there is a smaller pond used as a surge pond for the tailings pond water that is returned to process. Return water is decanted from the main pond. In addition to the process water, boiler plant blowdown water and the plant domestic sewage are added to the tailings pond. The sewage is first treated in a septic tank.

Sampling Procedures

Samples were obtained during two 72-hour cycles as follows:

- Cycle I - 8 AM Sept. 17, 1959, to 8 AM Sept. 20, 1959;
- Cycle II - 8 AM Sept. 20, 1959, to 8 AM Sept. 23, 1959

At all but three sampling stations, a sample was obtained for each cycle by compositing equal volumes every 2 hours for the duration of the cycle. Thus, 36 portions were used to make up the single composite sample.

The wastes going to the tailings pond were sampled by an automatic sampler operated by mill personnel. The Public Health Service obtained a portion of the sample collected by this auto-

Table 2. PROCESS STREAM CHARACTERISTICS ^a

Station (1)	Slurry flow, gpm (2)	Slurry specific gravity (3)	Dry suspended solids by weight % (4)	Specific gravity of dry solids (5)	Na mg/l in slurry (6)	pH (7)
1	b	-	-	-	-	-
2	1501	1.12	c	-	50.3 x 10 ³	10.5
3	1665	1.19	13.9	2.60	39.2 x 10 ³	10.4
4	1291	1.12	c	-	44.5 x 10 ³	10.3
5	357	1.50	51.2	2.46	24.2 x 10 ³	10.3
6	361	1.50	50.2	2.59	25.1 x 10 ³	10.2
7	316	1.56	54.6	2.50	23.6 x 10 ³	10.1
8	236	1.11	c	-	51.5 x 10 ³	10.1
9	241	1.13	c	-	59.3 x 10 ³	10.6
10	b	-	-	-	-	-
11	625	1.26 ^d	34.6 ^d	2.40	4.45 x 10 ³	10.1
12	60	1.01	c	-	5.15 x 10 ³	9.9
13	399	1.00	c	-	3.70 x 10 ³	7.5
14	3.5	1.00	c	-	4.45 x 10 ³	6.9

^a Average of Cycles I and II.

^b Solid sample.

^c Liquid sample (negligible solids).

^d Based on Cycle I only.

Table 3. CONCENTRATION OF SLURRY SOLIDS ^a

Station (1)	Dissolved solids, mg/1 slurry (2)	Suspended solids, mg/1 slurry (3)
1	b	b
2	138,000	850
3	126,000	165,000
4	137,000	780
5	87,900	765,000
6	94,500	752,000
7	91,300	854,000
8	159,000	145
9	162,000	50
10	b	b
11	12,200	435,000
12	14,800	198
13	1,880	8
14	1,700	56

^a Average of Cycles I and II.

^b Solid sample.

Table 1. SAMPLING STATIONS

Station Number	Description
1	Raw ore
2	Mill solution
3	Overflow from classifiers
4	Overflow from primary thickeners
5	Underflow from primary thickeners
6	Effluent from digesters
7	Underflow from secondary thickeners
8	Pregnant solution to precipitation tanks
9	Recarbonated barren solutions
10	Yellowcake product
11	Repulped third stage filter cake to tailings pond
12	Return water from tailings pond
13	Unsoftened well water
14	Softened water

Discussion of Results

Table 2 through 8 show average values obtained from the results of Cycle I and II. This technique of averaging over the two 72-hour periods was used because of the close agreement between analytical results for the two cycles, and to further minimize possible errors associated with representative sample collection and retention times, such as the 8-hour retention across the leaching circuit. The material balances were developed from a combination of field data (ore tonnage, yellowcake production, flows, etc.) extracted from mill records and laboratory analyses. The balances characterize each unit in the carbonate-leach process and form the basis for comparison between varying ore feed rates and ore quality.

Throughout the survey period, the mill operated somewhat in excess of design capacity. The ore was fed at the rate of 1590 dry tons per day during Cycle I, and 5130 pounds per day of yellowcake was packaged. Corresponding figures for Cycle II were 1686 dry tons per day and 4250 pounds, respective. The general physical characteristics and the concentration of sodium ion for the in-plant process streams, waste effluent, and raw water supply are presented in Table 2. Concentrations of dissolved and suspended solids are presented in Table 3.

In Table 2, the data in Columns (3) through (7) are laboratory determinations. The slurry flows (Column 2) except for Stations 8, 12, and 13, are calculated values. The flow at Station 9 was metered at an average value of 232 gpm for the survey period,

Figure 2 also indicates that material balances can be made across grouped process units. Proceeding from the ore storage bin, (Figure 2) the first balance quantitatively equates the input to the ball mill and classifier circuits of ore (Station 1) and mill solution (Station 2) with the output from the classifiers (Station 3). The output from the classifiers should also be accounted for in the overflow (Station 4) and in the underflow (Station 5) from the primary thickeners. Quantities present in the underflow from the primary thickener (Station 5) should be measurable in the effluent from the leaching circuit (Station 6). The recarbonated barren solution (Station 9) and yellowcake production (Station 10) should approximate the pregnant solution to the precipitation tanks (Station 8) and the caustic stream. As an over-all plant balance, the ore feed (Station 1), caustic stream, return water at the third-stage filters (Station 12), and untreated well water for tails repulping (Station 13) should approximate yellowcake production (Station 10) and the effluent to the tailings pond (Station 11).

Table 4. SOLIDS QUANTITIES ^a

Station ^b (1)	Dissolved solids, tons/day (2)	Suspended solids, tons/day (3)	Total solids, tons/day (4)
1	-	1,640	1,640
2	1,250	8.0	1,258
3	1,260	1,640	2,900
4	1,060	6.5	1,067
5	189	1,640	1,829
6	204	1,620	1,824
7	174	1,620	1,794
8	224	~ 0	224
9	235	~ 0	235
10	-	2.5	2.5
11	46	1,620	1,666
12	5.8	~ 0	5.8
13	5.0	~ 0	5.0
14	~ 0	~ 0	~ 0

^a Average of Cycles I and II.

^b Approximately 18 tons per day of dissolved solids are added to the precipitation tanks (caustic stream)

Table 4 presents the average solids quantities of both cycles. If the balance points listed above are used, it is apparent that the materials balance (Figure 3) is quite good. The raw ore feed (Station 1) and mill solution (Station 2) comprise an input of 2,898 (1,258 + 1,640) tons per day to the classifier circuit as compared

which is in good agreement with the calculated value of 241 gpm. The field notes indicated, however, that the average metered flow would probably be low because of marked fluctuations in line flow for a period of about 8 hours during Cycle II. In the same 8-hour period softened water was added to the recarbonation barren tank to maintain suction. Fresh water was substituted for recycled water (Station 12) during the last half of Cycle II.

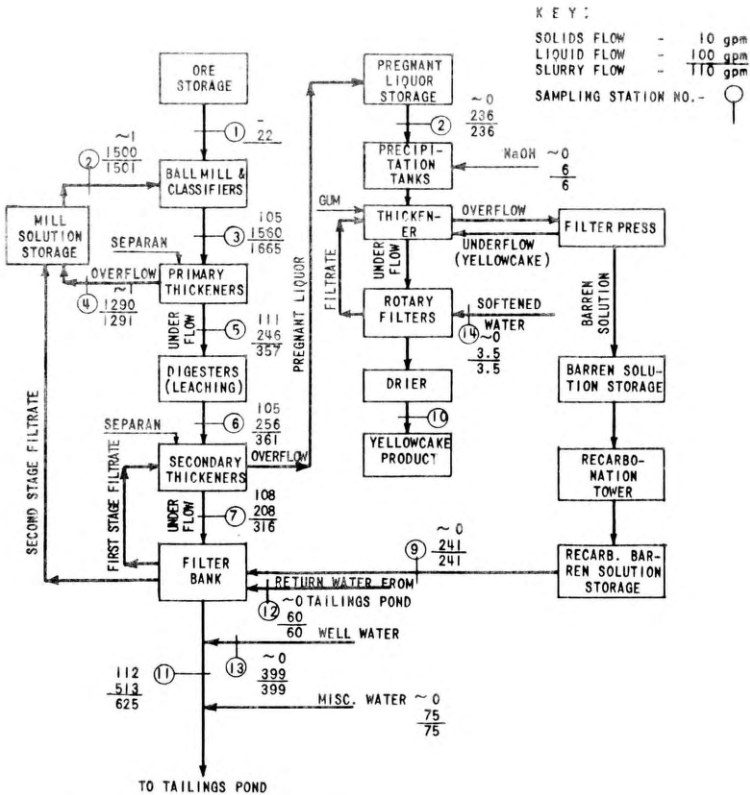


Figure 2. Schematic flow diagram of the Homestake-Sapin mill, September 1959.

Figure 2 illustrates the basic flow diagram of the mill in schematic form. The small differences in estimated slurry flows across process units are considered to be insignificant. The relatively small discrepancies in solids flow across a unit probably resulted from the limits of sensitivity of the dry-solids specific gravity analysis. Theoretically, if a constant feed rate and a steady state process throughout the mill are assumed the solids flow would be expected to remain unchanged throughout the mill because the decrease in undissolved solid tonnage is slight. Discrepancies in slurry flow are the result of the experimental errors that entered into the total weight and solid balances in the laboratory determinations. As will be seen, these discrepancies are not of major importance in this study.

Table 5. GROSS RADIOACTIVITY CONCENTRATIONS ^a

Station (1)	Suspended		Dissolved		Dry suspended solids	
	Alpha $\mu\mu\text{c/l}$ slurry (2)	Beta $\mu\mu\text{c/l}$ slurry (3)	Alpha, $\mu\mu\text{c/l}$ slurry (4)	Beta $\mu\mu\text{c/l}$ slurry (5)	Alpha $\mu\mu\text{c/g}$ (6)	Beta $\mu\mu\text{c/g}$ (7)
1	-	-	-	-	3,070	3,340
2	3,810	6,410	191,000	575,000	4,480	7,540
3	428,000	546,000	227,000	562,000	2,590	3,310
4	7,550	9,240	217,000	555,000	9,680	11,800
5	1,840,000	2,050,000	111,000	341,000	2,400	2,670
6	1,710,000	1,700,000	226,000	768,000	2,280	2,260
7	1,640,000	1,710,000	327,000	776,000	1,920	2,000
8	850	2,150	359,000	1,030,000	5,870 ^c	14,800 ^c
9	b	b	59,400	183,000	b	b
10	-	-	-	-	317,000	420,000
11	718,000	842,000	7,900	22,100	1,650	1,930
12	420	740	8,500	23,100	2,120	3,720 ^c
13	0.5	0.7	5.8	30	b	b
14	1.3	2.5	4.5	20	23 ^c	45 ^c

^a Average of Cycles I and II.

^b Not determined.

^c One cycle value, not average.

Gross radioactivity concentrations are presented in Table 5. These data show a consistent decrease in the gross alpha activity of one gram of undissolved ore solids as it moves from the ore storage bins through the digesters and ultimately to the tailings pond. Leaching of the uranium from the ore solids at the digesters is illustrated by the twofold increase in dissolved alpha activity between Stations 5 and 6 and the small decrease in the suspended solids radioactivity. The comparison of the alpha activity ($\mu\mu\text{c/g}$) of the heavy settleable solids (Stations 3, 5, 6, 7, and 11) with that of the smaller size suspended particles that are characteristic of thickener overflows (Stations 2, 4, and 8) was in agreement with observations from previous mill surveys; that is, the alpha activity of the smaller particles (slimes) exceeded that of the sands by factors of about 2 to 4.

If radioactive equilibrium in the ore among uranium-238, radium-226 and the other daughter products is assumed, the alpha activity of the dry suspended solids should remain constant across the ball mill and classifier circuit. The observed decrease at Station 3 compared to Station 1 may be due in part to leaching and a resulting loss of the third member in the decay chain, radon-222, to the atmosphere as a gas. That further leaching occurs as far as the secondary thickener is illustrated by the increase in the dissolved alpha activity of the pregnant liquor (Station 8) in comparison to the dissolved alpha activity of the digester effluent (Station 6)

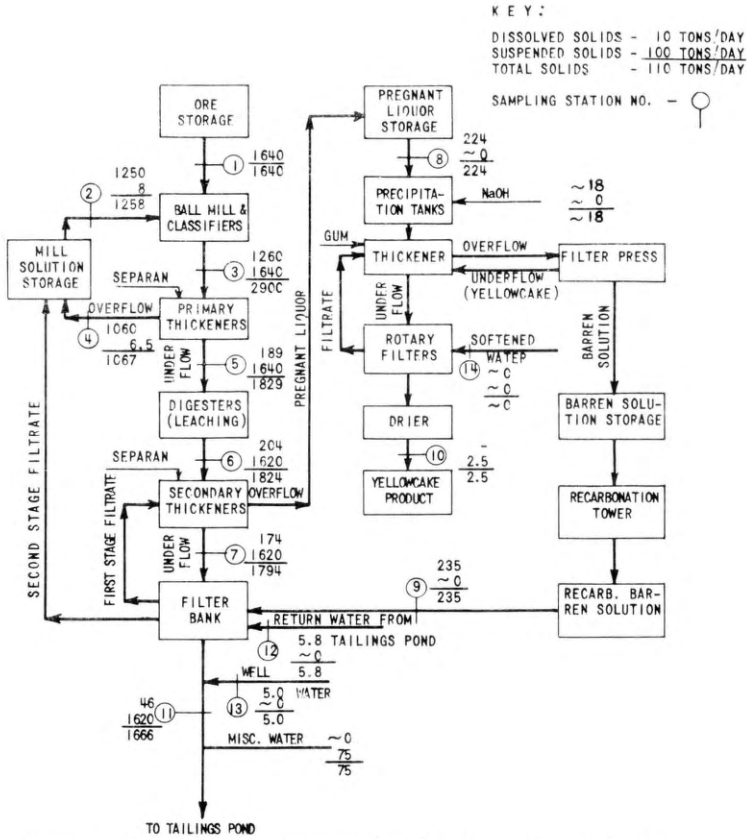


Figure 3. Schematic flow diagram of solids balance, Homestake-Sapin mill, September 1959.

to the measured output of 2,900 tons per day (Station 3). The output of 2,900 tons per day from the classifiers is also balanced by 2,896 (1,067 + 1,829) tons per day from the primary thickener overflow (Station 4) and underflow (Station 5).

In good agreement with the 1,829 tons of solids per day in the slurry to the digesters (Station 5) is the 1,824 tons per day leaving the leaching circuits (Station 6). Further examination of the data shows an increase in dissolved solids of 15 tons per day across the leaching circuit and a corresponding decrease in suspended or undissolved solids of 20 tons per day. Pregnant solution (Station 8) and caustic at the precipitation tanks yield 242 (224 + 18) tons of solids per day as compared to 238 (235 + 2.5) tons per day in the recarbonated barren liquor (Station 9) and yellowcake product (Station 10). For the process as a whole, 1,669 (1,640 + 18 + 5.8 + 5.0) tons of solids per day enter the refinery as raw ore (Station 1), caustic, return water (Station 12), and well water (Station 13) in that order. This is in exact agreement with the 1,669 + (1,666 + 2.5) tons per day leaving the refinery as waste to the tailings pond (Station 11) and yellowcake product (Station 10).

Table 7. RADIUM-226 CONCENTRATIONS ^a

Station (1)	Radium-226 in slurry, $\mu\mu\text{g/l}$		Radium-226 in dry suspended solids, $\mu\mu\text{R/g}$ (4)
	Dissolved (2)	Suspended (3)	
1	-	-	497
2	9,560	1,220	1,440
3	13,200 (8,300) ^c	83,900	508
4	8,790	b	b
5	5,160	328,000	429 (500) ^c
6	6,620	370,000	492
7	5,280	380,000	445
8	18,900	286	1,970
9	59	5.4	107
10	-	-	7,190
11	34	222,000	510
12	35	bb	b
13	5.4	b	b
14	4.2	b	b

^a Average of Cycles I and II.

^b Not determined (negligible solids).

^c The parenthetical result is most probable. See discussion in text.

The over-all plant balance also showed considerable disagreement; 4,573 (4,570 + 3) mc/day entered the process as ore (Station 1) and recycled process water (Station 12), whereas the effluent to the tailings pond (Station 11) and the yellowcake product (Station 10) accounted for only 69 per cent of the input, or 3,138 mc/day. The over-all plant balance in the similar Homestake-New Mexico Partners Company mill showed a 77 per cent accounting. In that case it was suspected that the semiautomatic sampling device for collecting a tailings sample actually collected a non-representative excess quantity of large versus fine solids, thereby lowering the gross alpha activity; this may in part explain the discrepancy noted above. It appears probable that the alpha activity of representative dry suspended solids at Station 11 was within the range of 1,900 to 2,300 $\mu\mu\text{c/g}$ (Stations 7 and 6) as compared to the 1,650 $\mu\mu\text{c/g}$ determined for the sample obtained. Based on 2,100 $\mu\mu\text{c/g}$, the alpha activity at Station 11 would be increased to about 3,100 mc/day and the over-all recovery to about 83 per cent.

Concentrations of radium-226 per liter of slurry and per gram of suspended matter are presented in Table 7. The dissolved radium concentrations reflect those solids passing through a membrane filter, and the suspended concentrations, that portion retained on

The gross alpha concentrations of Table 5 and the balanced slurry flows of Table 2 form the basis for the gross alpha quantities presented in Table 6. If previously mentioned balance points are used, the gross alpha balance appears to be adequate. The 6,170 (4,570 + 1,600) mc/day input to the classifiers from the ore (Station 1) and mill solution (Station 2) is in good agreement with

Table 6. GROSS ALPHA QUANTITIES^a

Station (1)	Gross Alpha Radioactivity, mc/day		
	Dissolved (2)	Suspended (3)	Total (4)
1	b	4,570	4,570
2	1,570	30	1,600
3	2,070	3,860	5,930
4	1,550	53	1,603
5	216	3,570	3,786
6	445	3,340	3,785
7	562	2,830	3,392
8	456	~ 0	456
9	78	c	78
10	b	681	681
11	27	2,430	2,457
12	3	~ 0	3
13	d	d	d
14	d	d	d

^a Average of Cycles I and II.

^b Solid sample.

^c Not determined.

^d Negligible.

the 5,930 mc/day leaving the classifiers (Station 3). The output of 5,389 (1,603 + 3,786) mc/day from the primary thickeners is split between the overflow (Station 4) and underflow (Station 5). This agrees sufficiently well with the 5,930 mc/day input to the thickeners (Station 3), although a definite loss of alpha activity is noted. The balance across the digesters is excellent; 3,786 mc/day enter at Station 5 and the same amount leave at Station 6. Gross alpha activity in the recarbonated barren solution (Station 9) that leaves the process as yellowcake product (Station 10) totaled 759 (78 + 681) mc/day. This does not agree well with the 456 mc/day in the pregnant liquor (Station 8) and the negligible amount contributed by the caustic. The explanation for this discrepancy is not readily apparent, especially in view of the fact that the balances for solids and slurry flows at these stations were very good.

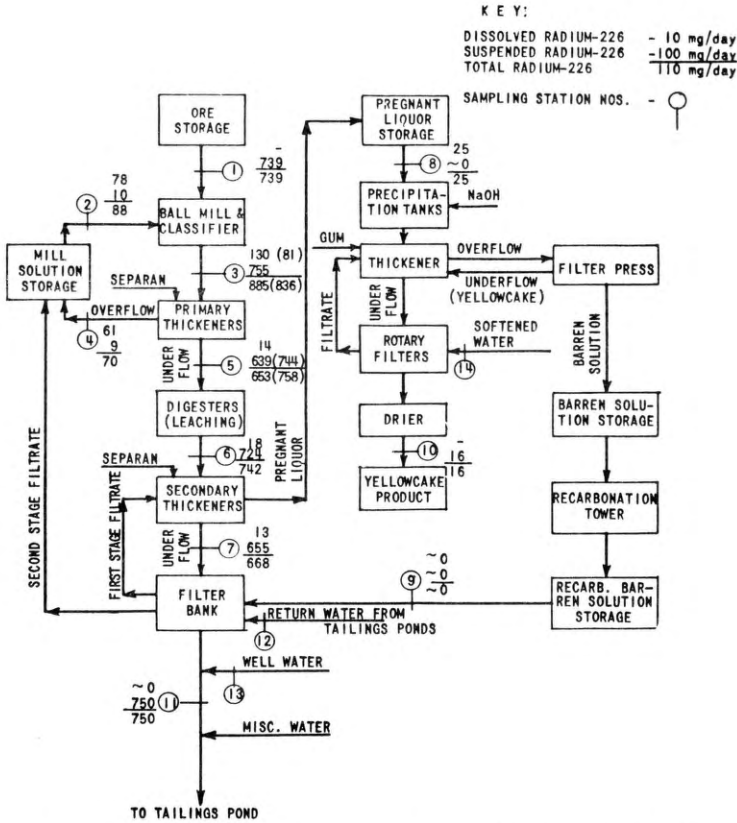


Figure 4. Schematic flow diagram of Radium-226, Homestake-Sapin mill, September 1959.

slurry leaving the primary thickeners (Station 5). In contrast, a value was reported of 15,300 micromicrograms of radium-226 per liter of liquid in the slurry leaving the classifiers (Station 3) prior to entering the primary thickeners. This latter value is clearly inconsistent with the surrounding data; between 8,800 and 10,100 $\mu\mu\text{g}/\text{l}$ of liquid are required for Station 3. As will be seen, a mean value of 9,600 $\mu\mu\text{g}/\text{l}$ of liquid, as against the reported 15,300 $\mu\mu\text{g}/\text{l}$, also perfects the quantitative radium-226 balance at this point. On a slurry basis, this gives a dissolved radium-226 concentration at Station 3 of 8,300 $\mu\mu\text{g}/\text{l}$ as compared to the reported 13,200.

Similarly, if the ore solids are followed through the process a somewhat lesser discrepancy at Station 5 and possibly at Station 7 is indicated. Proceeding in order through the mill 1 gram of ore solids contained 497 $\mu\mu\text{g}$ of radium-226 initially (Station 1), 508 $\mu\mu\text{g}$ at Station 3, 429 $\mu\mu\text{g}$ at Station 5, 492 $\mu\mu\text{g}$ at Station 6, 445 $\mu\mu\text{g}$ at Station 7, and 510 $\mu\mu\text{g}$ in the tails at Station 11. Of these data, a value between 492 and 510 $\mu\mu\text{g}/\text{g}$ is consistent at four locations, while the value at Station 3 (429 $\mu\mu\text{g}/\text{g}$) is quite low compared to the surrounding data for Stations 1 and 5. The value for Station 7 also appears

the filter. From the data for dry suspended solids, it is apparent that most of the radium remained in the undissolved form throughout the process; $497 \mu\mu\text{g/g}$ entered in the ore feed and about the same concentration left in the spent ore solids (Station 11). At intermediate steps in the process (Stations 3, 5, 6, and 7) the range of observed concentrations in the ore solids varied between 429 and $508 \mu\mu\text{g/g}$. As was the case with gross alpha activity, the fine-grained particles exhibited the highest activity.

Table 8. RADIUM-226 QUANTITIES ^a

Station (1)	Radium-226 mg/day		
	Dissolved (2)	Suspended (3)	Total (4)
1	b	739	739
2	78	10	88
3	130 (81) ^e	755	885 (836) ^e
4	61	9	70
5	14	639 (744) ^e	653 (748) ^e
6	18	724	742
7	13	655	668
8	25	~ 0	25
9	~ 0	~ 0	~ 0
10	b	16	16
11	~ 0	750	750
12	c	d	c
13	c	d	c
14	c	d	c

^a Average of Cycles I and II.

^b Solid sample.

^c Negligible.

^d Not determined.

^e The parenthetical result is more probable. See discussion in text.

Table 7 also indicates certain discrepancies that are important to interpretation. The concentration of dissolved radium-226 at Station 3 (overflow from the classifiers) is clearly not consistent with the dissolved radium-226 data for Station 2 (mill solution added at the classifiers) or with the data for Stations 4 and 5, while are locations immediately following Station 3. Specifically, the average dissolved radium was $9,560 \mu\mu\text{g/l}$ of liquid in mill solution entering the classifiers (Station 2), $8,800 \mu\mu\text{g/l}$ in the overflow from the primary thickeners (Station 4) that follow the classifiers, and $10,100 \mu\mu\text{g/l}$ in the liquid portion of the underflow

the leaching circuit consists of an estimated 758 mg/day entering at Station 5 and 742 mg/day leaving at Station 6. In comparison to the 836 mg/day at Station 3 is the 812 (70 + 742) mg/day from the primary thickener overflow (Station 4) and the digester effluent (Station 6). Pregnant liquor carries 25 mg/day to the precipitation circuit. This is in acceptable agreement with the 16 (16 + 0) mg/day accounted for as yellowcake product (Station 10) and re-carbonated barren solution (Station 9).

The total plant balance shows 739 mg/day entering as raw ore (Station 1) and 766 leaving via the waste effluent to the tailings pond (Station 11) and as yellowcake product (Station 10); plant input is in good agreement with plant output.

Based on the 739 mg/day of radium-226 entering the mill in the raw ore, 16 mg/day, or 2.2 per cent leave with the yellowcake product. This percentage is in general agreement with the 1.5 per cent for the Homestake-New Mexico mill but in substantially higher than that found in mills using the acid leach process and other ores.

To delineate further the characteristics of the main plant effluent to the tailings pond and the raw well water, a series of five chemical tests was run on the filtrate portions from Stations 11 and 13. The average values based on 1 liter of slurry, are tabulated in Table 9.

The rate of consumption of chemical additives as reported by mill personnel is presented in Table 10. Carbon dioxide, which was used to partially neutralize the caustic alkalinity in the re-carbonation tower, was not listed because it was generated within the process as flue gas. Oxidizing agents were not added during the survey and had not been added to the digesters for 3 months preceding the survey. In addition to the products listed in Table 10, lime, a small amount of soda ash, and sulphuric acid were used in the treatment of the mill's raw water supply.

Waste Disposal

Slurry flow to the tailings pond, as shown in Figure 2, averaged about 700 gpm, of which 112 gpm was solid flow, and 588 gpm, liquid. The spent ore solids are retained in the tailings pond, but the liquid phase, in addition to being retained for concentration by evaporation, may be recycled as return filter wash water or may drain by seepage. The opinion of mill personnel was that the soil at this location provided an excellent seal, thereby minimizing the problem of seepage into the ground water.

The 0.12 mg/day of dissolved radium entering the tailings pond at a concentration of $35\mu\mu\text{c}/\text{l}$ does not constitute the only source of possible ground water contamination. The insoluble radium accumulating at the rate of 750 mg/day provides a radium reservoir for leaching which, if coupled with seepage, could also produce a

Table 9. CHEMICAL CHARACTERISTICS OF THE FILTRATE AT STATIONS 11 AND 13

Station	Arsenic mg/l	Chlorides ₁ mg/l Cl	Phenolphthalein alkalinity mg/l as CaCO ₃	Total alkalinity mg/l as CaCO ₃
11	0.49	286	1,720	3,560
13	-	250	5	690

somewhat low, although this is less directly interpretable because of the side-routes between Station 6 and 7 (see Figure 2). As a result, the radium-226 concentration of undissolved solids at Station 5 was probably about 500 $\mu\mu\text{g/g}$, rather than the reported value of 429 $\mu\mu\text{g/g}$. This would also perfect the radium-226 quantity balance, as noted below.

No explanation for the foregoing two discrepancies can be offered at this time, although they appear to be quite definite.

The assumption of equilibrium in the ore between uranium-238 and its daughter, radium-226, allows a separate check to be made on the concentration in the raw ore. If the average ore assay of 0.167 per cent U_3O_8 for the survey period is used, a concentration of 474 micromicrograms of radium-226 per gram of ore is derived. This agrees quite favorably with the analyses average of 497 $\mu\mu\text{g/g}$. If the possibility of Radon-222 loss did not exist, it could be assumed that all the daughters of uranium-238 were in equilibrium with the parent during the survey period.

Table 10. CHEMICAL CONSUMPTION

Product	Quantity
Guar Gum	25 lbs/each three days
NaOH (100%)	30.82 lbs/ton of ore processed
Separan	0.05 lbs/ton of ore processed

Table 8 presents the radium quantities at the various process stations at an ore processing rate of 1,640 tons per day. The values in Table 8 were obtained with the concentrations of Table 7 and the slurry flows of Table 2. As indicated earlier, the reported dissolved radium-226 concentration at Station 3 and the undissolved radium-226 concentration for Station 5 are probably erroneous. The more probable results are given as parenthetical figures in Tables 7 and 8. If these figures are used, the radium balance throughout the process (Figure 4) is generally quite good, as follows:

Mill solution combines with the raw ore feed for 827 (88 + 739) mg/day of radium-226 entering the ball mill and classifiers. This is in good agreement with the estimated 836 mg/day at Station 3. Overflow (Station 4) and underflow (Station 5) from the primary thickeners account for 828 (70 + 758) mg/day. The balance across

Acknowledgment

The generous cooperation and technical assistance of the following are gratefully acknowledged: Personnel of the Homestake-Sapin Partners Mill; the U. S. Atomic Energy Commission; Charles E. E. Sponagle, Public Health Service, Region VIII, Denver, Colorado; E. A. Pash, Carl Hirth, Carl Shadix and H. D. Nash, Public Health Service, Cincinnati, Ohio; and D. E. Rushing, Public Health Service, Salt Lake City, Utah. The technical advice and guidance of Dr. E. C. Tsivoglou, Public Health Service, Cincinnati, Ohio, was greatly appreciate. This study was supported by funds made available through the Environmental and Sanitary Engineering Branch, Division of Reactor Development, U. S. Atomic Energy Commission.

significant ground water contamination problem. That leaching of radium from spent ore solids does occur has been discussed in the reports on the study of the Animas River by the U. S. Public Health Service, 10, 12

Table 11. RADIUM CONCENTRATIONS IN SAMPLES FROM TEST WELLS ON HOMESTAKE - SAPIN MILL PROPERTY.

Depth of well, ft.	Description	Dissolved Radium - 226, $\mu\mu\text{c}/1$	
		1959	1961
70	Cased	0.8	0.22
80	Cased	1.8	0.18
95	Cased	0.7	0.24
-	Observation Well	0.2	-
60	Cased	1	1.79

The Homestake-New Mexico Partners report points out the need for considering ground water contamination inasmuch as ranchers in the general area of the mills use well supplies for domestic consumption, for watering livestock, and for irrigation. In addition, the communities of Milan and Grants, located a few miles south of the mills, take their domestic supplies from wells. The Homestake-New Mexico Partners report also describes the water-bearing strata in the area, and the direction of ground water movement, and summarized the radium results for numerous well samples. Table 11 presents the radium concentrations found in samples from test wells located around the periphery of the tailings pond on the Homestake-Sapin mill property. These were collected in 1959 and 1961.

These results may be compared to the radium content of wells located several miles to the west of the mills and that of wells between Grants and San Rafael. The concentration range for these wells is 0.1 to 0.4 $\mu\mu\text{c}/1$, a natural background concentration range.

An evaluation of the Homestake-Sapin pond must take into account the presence of the Homestake-New Mexico Partners pond and their combined effect. Therefore, it seems advisable, in view of the reservoir of radium in both tailings ponds and the variability of results to date, that the monitoring of well supplies, particularly in the near-vicinity of the ponds, be continued until a firm conclusion on the presence or absence of seepage can be reached. If a significant buildup of radium in the test wells is observed over a period of time, remedial measures may be necessary. The need for such measures should be based on the observed rate of buildup, the possibility of peaking at a given concentration, and the human exposure potential in accordance with applicable radiation protection criteria.

Bibliography

1. Tsivoglou, E. C., Bartsch, A. F., Rushing, D. E., and Holaday, D. A. Effects of Uranium Ore Refinery Wastes on Receiving Waters. Proc. 1958 Nuclear Science and Engrg. Conf., Reprint 40, Am. Inst. Chem. Engrs., New York, N.Y. (March 17, 1958).
2. National Bureau of Standards. Maximum Permissible Amounts of Radioisotopes in the Human Body and Maximum Permissible Concentrations in Air and Water. Handbook 52, U. S. Gov't. Printing Office, Washington, D. C. (1953).
3. Dayton, S. U₃₋₈ Processing Made More Efficient by Plant-Controls at Edgemont Mill. Mining World, 19, No. 1, 36-43 (January 1957).
4. Public Health Service. Determination of Gross Radioactivity in Water, Silt, and Biological Materials. Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. (1957).
5. Standard Methods for the Examination of Water, Sewage and Industrial Wastes. Am. Publ. Hlth. Assn., New York, N.Y., 522 p., 10th Ed. (1955).
6. Part 20 - Standards for Protection Against Radiation. U. S. At. Energy Comm., Federal Register, 22, No. 19. (Tuesday, Jan. 29, 1957).
7. Public Health Service. Report on an Investigation of Ground Water Pollution, Grants-Bluewater, New Mexico. Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio. (Aug. 1957).
8. Velz, C. J., Graphical Approach to Statistics. Water and Sewage Works, 97. (1950).
9. Recommendations of the International Commission on Radiological Protection. Main Commission Report, Sept. 9, 1958; Pergamon Press, London, England. (1959).
10. Tsivoglou, E. C. Shearer, S. D., Shaw, R.M., Jr., Jones, J. D., Anderson, J. B., Sponagle, C. E., and Clark, D. A., Survey of Interstate Pollution of the Animas River, Colorado-New Mexico. U. S. Public Health Service, Robt. A. Taft San. Engrg. Ctr., Cincinnati, Ohio. (May 1959).
11. Public Health Service Drinking Water Standards, 1946. Public Health Reports, 61, No. 11, 371-384; Reprint No. 2697. (March 15, 1946; revised March 1956).

12. Tsivoglou, E. C., Shearer, S. D., Jones, J. D. Sponagle, C. E., Pahren, H. R., Anderson, J. B., and Clark, D. A. Survey of Interstate Pollution of the Animas River, Colorado-New Mexico. II. 1959 Surveys. U. S. Public Health Service, Robt. A. Taft San. Engrg. Ctr., Cincinnati, Ohio. (Jan. 1960).
13. Knott, Woodrow, The Processing of Uranium Ores of the Colorado Plateau by the Climax Uranium Company. The Mines Magazine, p. 29. (January 1955).
14. Survey of the Colorado and Gunnison Rivers in the Vicinity of Grand Junction, Colorado. Technical Report No. 2, Colorado River Basin Water Quality Control Project, U. S. Public Health Service. (May 1961).
15. National Bureau of Standards. Maximum Fermissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and Water for Occupational Exposure. Handbook 69, U. S. Gov't. Printing Office, Washington, D.C. (June 5 1959).
16. McClaine, L. A., Bullwinkel, E. P., and Huggins, J. C. The Carbonate Chemistry of Uranium: Theory and Applications. Internat. Conf. of Peaseful Uses of Atomic Energy, A/CONF. 8/P/525, USA. (July 18, 1955).
17. Clegg, J. W., and Foley, D. D. Uranium Ore Processing. Atoms for Peace, USA, Geneva 1958. Prepared for USAEC. Addison-Wesley Publ. Co., Reading, Mass. (Sept. 1958).
18. Review of Waste Disposal Problem at Homestake-Partners Mill-site (N.M.) Communication from the New Mexico Department of Public Health.