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REPORT OF INVESTIGATIONS/1996

U.S. Bureau of Mines Final Report: Midnite Mine Water Treatment Studies

UNITED STATES DEPARTMENT OF THE INTERIOR

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UNITED STATES BUREAU OF MINES

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and E. J. Lahoda

UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary

BUREAU OF MINES
Rhea Lydia Graham, Director

This report has been technically reviewed, but it has not been copy edited because of the closure of the agency.

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

BVH	bed volumes per hour	mg	milligram
cm	centimeter	mg/g	milligram per gram
cm/sec	centimeter per second	mg/h	milligram per hour
cp	centipoise	min	minute
g	gram	mL	milliliter
gal	gallon	mL/min	milliliter per minute
g/L	gram per liter	mm	millimeter
h	hour	pCi/L	picocuries per liter
L	liter	pct	percent
lb	pound	ppb	part per billion
L/h	liter per hour	ppm	part per million
L/min	liter per minute	rpm	revolutions per second
M	molar concentration	sec	second
meq/mL	milliequivalent per milliliter	V	volt
		°C	degree Celsius

U.S. BUREAU OF MINES FINAL REPORT
MIDNITE MINE WATER TREATMENT STUDIES

By L. E. Schultze,[1] D. N. Nilsen,[2]
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ABSTRACT

The U.S. Bureau of Mines reviewed and evaluated options for treatment of the approximately 500 million gallons of contaminated water in flooded pits at the Midnite Mine on the Spokane Indian Reservation. While current lime treatment produces discharge quality water, the resultant sludges are radioactive, presenting a disposal problem. Of the 24 commercial processes and seven emerging technologies evaluated, none demonstrated a significant advantage over ion exchange using a strong base anion exchange resin in either laboratory or field tests. Uranium was lowered from 22 ppm to 0.2 ppb in treated water. Radium was lowered from 44 pCi/L to <1 pCi/L using a modified precipitation with $BaCl_2$. The natural zeolite, clinoptilolite, lowered radium to 6-8 pCi/L when used as an ion exchanger.

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INTRODUCTION

In 1993, the Congress directed the U.S. Bureau of Mines (USBM) to conduct a series of studies to provide information needed for technical and policy decisions for site reclamation at the Midnite Mine, an inactive uranium mine located on the Spokane Indian Reservation near Wellpinit, Washington. The Bureau of Land Management (BLM) is the lead agency for the Department of Interior (DOI) for the reclamation of the Midnite Mine. This report summarizes the results of the water treatment studies.

A major reclamation issue at the Midnite Mine is two pits containing approximately 500 million gal of water contaminated with U, Ra, Mn, and other heavy metals. The Dawn Mining Company, to comply with its National Pollutant Discharge Elimination Systems (NPDES) permit, is currently operating a water treatment plant at the Midnite Mine. The process uses a combination of lime and barium chloride additions to precipitate the radionuclides and other metals. While this process generates clean water for discharge, it produces a sludge that is classified as a source material by the Nuclear Regulatory Commission (NRC). The mining company trucks this sludge off the Indian Reservation to their mill in Ford, Washington. The sludge is treated at the mill to remove U and the remaining slurry is periodically pumped into the tailings impoundment located at the mill.

If the Dawn Mining Company becomes unable to meet the commitment to treat the contaminated water at the Midnite Mine, the Department of the Interior (DOI) may have to assume contingency treatment of the mine water. Since the DOI would not have access to the off site mill or tailings pond, this would require disposal of the sludge in a regulated landfill. Cost of commercial disposal is estimated to be $28 per 1,000 gal of mine water treated. At the current treatment rate of up to 500 gal per min, disposal costs would be approximately $5,400,000 per year. This cost is based on continuous operation of the plant over a 270 day period (the plant is closed during winter months due to freezing conditions and county road load restrictions) and does not include transportation, sludge drying, or applicable licenses and permits.

In order to provide cost effective options for contingency water treatment, six USBM technologies and one commercial technology were tested at the bench scale. In addition, a Request for Information was advertised in the Commerce Business Daily for innovative commercially available water treatment methods. Of the 23 submittals received and reviewed by the USBM, Diphonix resin manufactured by EIChroM Industries, Inc., a solid phase extractant manufactured by Chromato Chem, Inc., and the Westinghouse Modified Waterglass Process were determined to have potential application to the mine water. Since discharge quality water is currently being produced at the mine site, most of the technologies focused on pretreatment to remove U and Ra prior to the precipitation treatment. This would prevent the generation of an NRC source material and eliminate the need for expensive disposal. Recovered U could be sold, defraying part of the treatment costs and eliminating long term disposal concerns, and only a small quantity of Ra would require disposal.

The USBM technologies tested for U recovery were bioremediation, ion elutriation, liquid emulsion membrane (LEM), porous beads containing biological extractants, reduction using biogenic hydrogen sulfide, and supported liquid membrane (SLM). Also tested was a commercial strong base anion exchange resin. Comparison of test results demonstrated that ion exchange (IX) using a strong base anion exchange resin and LEM were the most effective based on a combination of costs and U removal. Preliminary cost estimates for the two techniques were $1.38/1,000 gal and $2.91/1,000 gal, respectively.

It has not been determined if separate Ra removal will be required for treating the water at the Midnite Mine. The Ra can be precipitated in conjunction with the alkaline neutralization and meet NPDES discharge limits. Allowable Ra concentrations in the resultant sludge is the unknown factor. The state of Washington is an agreement state, indicating that the Nuclear Regulatory Commission has granted authority to the state to regulate radioactive materials within its borders. The State of Washington is currently promulgating proposed regulations for governing Ra content in water treatment sludges. The EPA has suggested guidelines for disposal of drinking water treatment wastes containing radioactivity. Radium precipitation in conjunction with the alkaline precipitation results in a final Ra concentration in the sludge of 34 pCi/g on a dry weight basis. The suggested EPA guidelines for a sludge with a Ra concentration of 3 to 50 pCi Ra/g of dry weight is a physical barrier of 10 feet of earth or nonradioactive waste designed for long term stability plus institutional controls to avoid inappropriate use of the disposal site (*1*).

Since a separate Ra removal step could be needed, tests were also done to evaluate precipitation and adsorption techniques. The two most promising were adsorption on a natural zeolite and precipitation using a modified barium chloride precipitation procedure.

RESULTS AND DISCUSSION

Laboratory Tests

Diphonix Resin: As part of the request for information for techniques for removing U from Midnite Mine water, tests were done on Diphonix resin manufactured by Eichrome Industries; a resin developed to remove U from highly acidic solutions. Comparative flask tests were done between Diphonix and DOWEX 21K XLT, a commercially available ion exchange resin. Resin samples (0.5 g) were contacted with 200 mL of Midnite Mine water in shaken flasks and sampled at timed intervals. Sample volumes were 7 mL. No corrections were made for volume changes. Analyses of U remaining in solution are shown in table 1.

While Diphonix is capable of removing U from Midnite Mine water, the kinetics are much slower than is the case for DOWEX 21K XLT. Also, discussions with the manufacturer revealed that Diphonix is very difficult to strip. Since it is a strong enough chelating agent to pull UO_2^{2+} from SO_4^{2-}, it would require acid strengths of several molar concentrations to strip U. This excess acid would need to be neutralized in order to precipitate a U product, adding significantly to the reagent costs. No stripping tests were run since there was insufficient Midnite Mine water available to load a resin sample.

Table 1.--Comparison of resins

Time, h	Uranium in solution, ppm	
	Diphonix	DOWEX 21K XLT
1	22	14
2	18	13
5	17	7
22	7	<3

Ion Exchange: A drum of water from pit 3 at the Midnite Mine site was obtained and analyzed. The major components are shown in table 2.

Table 2.--Analysis of pit 3 water

Component	mg/L	Component	mg/L
Al . . .	55	Si . . .	10
Ca . . .	460	Sr . . .	1.9
Co . . .	1.6	Zn . . .	1.5
K	15	Cl^- . . .	3.2
Mg . . .	270	F^- . . .	8.1
Mn . . .	105	No_3^- . . .	18
Na . . .	55	SO_4^{2-} . .	2,430
Ni . . .	2.4	U	22

Tests were initiated using a strong base ion exchange resin (DOWEX 21K) known to have good characteristics for U recovery. All column tests used 1 by 30 cm columns with a 1-L feed reservoir attached to the top. Flow rates were controlled by adjusting a stopcock at the bottom of the column. The test column contained 25 g of resin and was operated at 1 mL/min. Analyses of effluent showed <0.2 ppm U through 4 L of treated water. No other metals were removed by the resin. Calculations based on resin loadings achieved at commercial U recovery plants (1.2 meq/mL) (*2*), a resin moisture content of 50 pct, and a specific gravity of 1.0 predict that the column would treat 81 L of Midnite Mine water. For verification, the remaining water (≈190 L) was treated at 1 L/h (17 mL/min) through three columns in series, each containing 25 g of resin. The flow rate is based on a 24 BVH treatment rate as recommended by Dow Chemical Company (*3*). Analyses of treated water demonstrated that the first of the three columns removed at least part of the U from 100 L of water. Any residual U, not removed in the first column, was removed to <0.2 ppm during treatment in the remaining two columns. Calculated loading for column 1 was 1.0 meq/g. This confirms that at least 83 pct of the theoretical ion exchange capacity of the first column can be utilized while still producing clean water from the three column train.

Screening tests were also done using DOWEX 21K XLT, a newer, more resilient formulation (*4*). Tests were done by contacting 0.5 g of resin with 200 mL of water in an Erlenmeyer flask placed in a laboratory shaker and removing 7 mL samples at timed intervals. Results, shown in table 3, show that the resin is more efficient in removing U from Midnite Mine water.

Table 3.--Comparison of resins

Time, h	Uranium in solution, ppm	
	DOWEX 21K	DOWEX 21K XLT
3	16	14
7	17	10

A second continuous column test was run using DOWEX 21K XLT resin. Three 1 cm diameter columns each containing 25 g of resin were used to treat 66 L of Midnite Mine water at 37 BVH. Column 1 showed breakthrough exceeding the detection limit of 3 ppm after 31 L (1,170 bed volumes) and continued to remove U through 41 L (1,550 bed volumes). Breakthrough on column 2 was not observed until 64 L had been treated and column 3 showed no breakthrough. Uranium loading was calculated to be 29 mg/g of resin, 24 pct of that obtained using DOWEX 21K. The lower loading is at least partly due to the 54 pct higher treatment rate. Analysis by ICP-MS detected less than 0.2 ppb U in treated effluent from column 3. The U loaded resin was stripped using 2*M* NaCl adjusted to pH 1 with HCl. More than 97 pct of the U was stripped in 10 bed volumes. Five bed volumes were sufficient to strip 85 pct of the U. The U was precipitated by addition of hydrogen peroxide.

Liquid Emulsion Membrane: Solvent extraction (SX) is an approach that has been used for years by industry for the recovery of U from a variety of solutions (*5*). A related technique, LEM, has been investigated (*6*) for the recovery of U from Wet Process Phosphoric Acid. The study indicated that the LEM technique was economically superior to SX in this application. Recent research by the Bureau of Mines (*6-9*) demonstrated the potential efficiency of the LEM technique for the selective removal and recovery of metals (such as copper) from dilute solutions.

In the LEM process, metal ions in the waste water are selectively removed through direct contact with an emulsion that is made from an organic phase and an aqueous internal phase. The internal phase is emulsified into the continuous organic phase. The organic phase contains a metal extraction reagent that selectively removes the desired metal from the waste water. In general, the main advantage of the LEM process over the SX process is that the metal ions entering the organic phase are quickly removed by the contained internal phase. Thus, the metal concentration in the organic phase in the LEM process remains very low and its ability to remove metals from water remains high even when the concentration of metals in the water drops to very low levels. Because of this, the extraction of metals from dilute solutions is very efficient. The extracted metals, transferred within the emulsion to the internal solution, can be concentrated to high levels for efficient metal recovery.

The scientific literature was searched to identify extractants, combinations of extractants, and related components that may be applicable for this situation. A number of extractants have shown some ability for the extraction of U. The following are the general chemical classes (or combinations) into which many of the identified extractants fell: dialkyl orthophosphoric acids, secondary or tertiary alkyl amines, dialkyl pyrophosphoric acids, synergistic combinations such as dialkyl orthophosphoric acids and trialkyl phosphine oxides, and tri-n-butyl phosphate (TBP). In order to formulate an emulsion membrane that could be used effectively for the selective removal of U from the Midnite Mine water, screening tests were conducted with many of the extractants that were identified by the literature search. Solvent extraction tests were used as a screening tool to evaluate these extractants, stripping agents, and phase modifiers. Results from these tests helped to identify several extractants and/or combinations that appeared to offer promise. Typical results from these tests are shown in Table 4.

Table 4.--Screening tests for selection of extractants for uranium extraction

Extractant(s)	Phase modifier/ diluent	Raffinate[1] analyses, ppm			Extraction[2], pct		
		U	Mn	Zn	U	Mn	Zn
D2EHPA + TOPO	None/ Kermac 470W	<1	20	<0.1	>97	81	98
D2EHPA + TBP	None/ Kermac 470W	<1	85	0.4	>97	19	90
TBP	None/ aromatic 100	27	105	4.1	13	0	0
Alamine 336	Isodecanol/ Kermac 470W	<1	105	4.1	>97	0	0

[1] Two phase contact (SX-type). Raffinate analyses after third contact with organic phase.

[2] Analyses of feed for these tests: 31 ppm U, 105 ppm Mn , and 4.1 ppm Zn.

Based upon the data in this table, Alamine 336 showed the best selectivity. However, based on the data from the intermediate raffinates in these tests (data not shown in this table), Alamine 336 needed all three contacts to reduce the U level to <1 ppm, whereas, the di-2-ethylhexyl phosphoric acid (D2EHPA) systems using TBP and tri-octyl phosphine oxide (TOPO) accomplished that feat in just one contact. Later tests demonstrated that when Alamine 336 was used in combination with a dilute H_2SO_4 internal solution in an emulsion membrane, excellent extraction of U resulted.

Results from stripping tests showed that U loaded on D2EHPA-TOPO or D2EHPA-TBP was quantitatively stripped by sodium carbonate (Na_2CO_3) solutions but not by any of the acidic solutions that were tested. In reviewing the data, it was evident that some separation of the metals loaded on these organic mixtures was possible through the choice of stripping solutions. It appeared to be possible to use an internal solution containing acid such as phosphoric acid (H_3PO_4) to remove loaded Mn and Zn in the emulsion membrane, and then, contact the separated organic phase with (Na_2CO_3) to remove the U from the organic phase prior to recycle. In the extraction tests with Alamine 336, it was found that only U was extracted from the Midnite Mine water. Stripping tests indicated that U was quantitatively stripped by both Na_2CO_3 and NaCl solutions. Therefore, relatively pure U containing solutions would likely be produced through the use of Alamine 336 with a single stripping step.

A secondary objective of the water treatment effort was to produce a commercially valuable product containing U. In that way, no radiological wastes would be produced and a valuable resource would be recycled to the economy. In addition, the sale of the U byproduct would help to offset some of the costs of the remediation effort. With these objectives in mind, LEM, SX, and hybrid systems containing elements of both the LEM and SX approaches were investigated for possible field testing at the Midnite Mine.

Two flowsheets were developed based upon the results from the screening tests and both flowsheets were evaluated in batch tests. In the D2EHPA flowsheet, an emulsion membrane was made between the D2EHPA and a H_3PO_4 internal solution. The U and much of the Mn and Zn were extracted into the emulsion. Only the Mn and Zn reported to the internal solution; the U stayed in the organic phase. The resulting emulsion was broken and the recovered organic phase went to a stripping stage where the U was stripped with either a Na_2CO_3 solution or a H_3PO_4 solution containing a reductant such as Fe^{2+}. If Na_2CO_3 was used, the extractant was converted back to the H^+ form before recycle to the LEM extraction stage. The recovered internal solution containing just Mn and Zn could be processed for those metals using techniques such as pH adjustment and precipitation.

The second flowsheet was based on the Alamine 336 system. In that flowsheet, an emulsion membrane is made between Alamine 336 and a H_2SO_4 internal solution. The extractant reacts with the H_2SO_4 to form an Alamine salt which produces a much superior extractant for U from the Midnite Mine water. After contact with and separation from the mine water, the emulsion is broken and the recovered internal solution is recycled for further emulsion makeup. The extracted U is held in the organic phase. The recovered organic phase then goes to a stripping stage where the U is stripped with a Na_2CO_3 solution. The organic phase would then be recycled to the LEM extraction stage.

Based on the relative simplicity of the Alamine 336 system, only flowsheets pertaining to that system were investigated in a laboratory scale, continuous flow, LEM circuit. As a part of these continuous circuit investigations, appropriate equipment designs and operating parameters were developed for scale up to a pilot plant system. The results from the laboratory scale circuit were very encouraging. On the average, the U level in the Midnite Mine water was reduced to $\leq$150 ppb while producing a concentrated and pure U containing stripping solution. The target level for U in the effluent was ≤ 0.7 ppm (≤ 700 ppb).

Although four extraction stages were initially built into this circuit with a total residence time of about 20 min, only one stage having a residence time of 5 min was necessary to reduce the U concentration to <0.3 ppm. In these continuous circuit tests, the organic phase and the U bearing stripping solution were recycled to build up the levels of U to steady state values. The requirement for recovery of a commercially valuable U byproduct necessitated doing the U extraction selectively and concentrating the extracted U into a solution from which it could be efficiently recovered. A simplified flowsheet of the LEM system to be used at the Midnite Mine is shown in Figure 1.

The pertinent chemical reactions that apply to the main unit operations of the system are shown below.

Extraction Related:

$$UO_2^{+2} + nSO_4^{-2} \rightarrow UO_2(SO_4)_n^{2-2n}$$

$$2R_3N_{org} + H_2SO_4 \rightarrow (R_3NH)_2SO_{4\,org}$$

(for n = 2)

$$UO_2(SO_4)_2^{-2} + (R_3NH)_2SO_{4\,org} \rightarrow (R_3NH)_2UO_2(SO_4)_{2\,org} + SO_4^{-2}$$

Stripping Related:

$$(R_3NH)_2UO_2(SO_4)_{2\,org} + 4Na_2CO_3 \rightarrow 2(R_3N)_{org} + Na_4UO_2(CO_3)_3 + 2Na_2SO_4 + H_2CO_3$$

Precipitation Related:

$$Na_4UO_2(CO_3)_3 + 3H_2SO_4 \rightarrow UO_2SO_4 + 3CO_2\uparrow + 2Na_2SO_4 + 3H_2O$$

$$2UO_2SO_4 + 6NaOH \rightarrow Na_2U_2O_7 + 2Na_2SO_4 + 3H_2O$$

Radium Adsorption: Midnite Mine water from which the U had been removed using three columns of DOWEX 21K XLT was passed through a 1 cm column containing 20 g of a natural zeolite; clinoptilolite from Hector, CA. Treatment rate was 37 BVH. Analyses showed that Ra was lowered from 37 pCi/L to 6 pCi/L, close to the detection limit of ±2 pCi/L, in the first 38 bed volumes. Radium in treated effluent slowly increased to 13 pCi/L after 453 bed volumes representing removal of 65-84 pct. Since the NPDES calls for 3 pCi/L, a second column was added to the field test.

Radium Precipitation: A literature search revealed that although numerous technologies have been proposed for removing Ra from dilute solutions, the only technology which has been applied on a large scale is barium chloride addition. This involves adding sufficient amounts of barium chloride to precipitate insoluble barium sulfate using the sulfate naturally present in the water. The Ra precipitates in the barium sulfate matrix due to having similar chemistry to barium. Dawn Mining is currently using barium chloride addition to remove Ra in conjunction with the alkaline neutralization process. The approach taken during this field test separates the Ra precipitation from the alkaline precipitation of Mn and Zn from the water.

Once the Ra was precipitated in the barium sulfate matrix, the precipitate was separated from the water. The barium sulfate precipitation occurred rapidly, resulting in extremely fine particles. To enhance settling of these fine particles, a ferric chloride solution was added to precipitate ferric hydroxide to collect the barium sulfate precipitate and facilitate solid-liquid separation.

Solid Phase Extractant: A fast solid phase extractant developed by Chromato Chem, Inc. was examined for its ability to remove U. The process uses polyethylene glycol molecules covalently bonded to the surface of silica particles. The long polyethylene glycol molecule has a chelating agent attached to its end which binds U. Column tests utilizing this material were conducted at the Salt Lake City Research Center under a contract with ChromatoChem, Inc.

Results indicated that this material has potential for removing U. There was a strong indication that it also has some affinity for Mn and Zn. The amount of water processed appeared to be similar to that processed by conventional ion exchange. The major drawback of using this material was its cost. Because this is an emerging technology, cost for the extractant is about $10,000 per kilogram. This is approximately 40 times that of an ion exchange resin. If the cost of this material decreases, this technology warrants further examination.

Waterglass: This process involves adding dilute waterglass (sodium silicate) to a process stream to form a precipitate (see Figure 2) which captures the U and other heavy metals. The precipitate is removed from the process stream using a continuous pressure filter. The waterglass portion of the precipitate is then dissolved in NaOH solution leaving a concentrated heavy metal sludge. The dissolved waterglass is reused in the process stream precipitation operation while the U and other heavy metals in the residual sludge are reclaimed through dissolution or stabilized for disposal. Westinghouse is using this technology for the removal of U from the process wastewater stream at the Westinghouse Commercial Nuclear Fuels plant in Columbia, SC.

The overall objective of this program is the application and demonstration of the waterglass process for the removal of U from the Midnite Mine aqueous effluent. Specific objectives are to:

1. Demonstrate U removal to less than 0.5 ppm from actual samples of aqueous effluent from the Midnite Mine.
2. Demonstrate the re-dissolution of silica with NaOH and verify that the U is concentrated in the sludge.
3. Demonstrate the dissolution of the U from the NaOH leached sludge with H_2SO_4. Precipitate the U from the H_2SO_4 with hydrogen peroxide.

4. Determine the required concentration of waterglass and NaOH to meet required U removal and waterglass dissolution.
5. Determine uranium concentration in the following:
   - feed solution
   - treated solution
   - residual sludge before dissolution with NaOH
   - residual sludge after dissolution with NaOH
   - dissolved waterglass.
6. Determine metals (Zn, Cu, Mn, Fe, Cd, Ca, Mg, Si) and Ra concentration in the following:
   - feed solution
   - treated solution
   - dissolved waterglass
   - residual sludge after dissolution with H_2SO_4
   - H_2SO_4 after hydrogen peroxide precipitation.
7. Develop an overall and uranium mass balance around the process.

The above program objectives were delineated in three major tasks:

1. characterization of the feed water from the Midnite Mine
2. determination of the silicate dose
3. measurement of the waterglass dissolution.

Two additional tasks are included in the program as confirmatory and material balance tests and include optimum waterglass dose and waterglass sludge dissolution. The details of these tests are described in the experimental section of this report. All experiments were batch type carried out with standard laboratory glassware. Treated quantities of mine effluent ranged from 0.2 liters to 10 liters in a single operation. For the confirmatory tests in tasks 4 and 5, 30 liters of mine effluent in 10 liter increments were treated with waterglass and the solids and filtrates combined for subsequent processing with NaOH and H_2SO_4. Solids and suspended solids were determined according to Standard Methods for the Examination of Water and Wastewater, 16th edition, APHA, AWWA, WPCF publishers, pages 92-100, 1985. Chemical analyses were performed by Jordan Laboratories, Corpus Christi, TX. A listing of all analyses that were performed is shown in Table 10. Waterglass (sodium silicate, type N) was obtained from the PQ Corporation, Chester, PA. It was diluted with deionized water and used as a 6 w/o solution. The SiO_2/Na_2O ratio of the waterglass feed was 3.17 with SiO_2 being 28.66 pct and Na_2O being 9.03 pct.

A flowsheet illustrating the overall chemical process steps for Tasks 1 through 3 is shown in Figure 3 and the details of each step are presented below.

Task 1: The mine effluent in 5 gal cans was mixed by rolling and samples were immediately removed for analysis. The effluent was a clear colorless liquid with no discernible odor having a pH of 4. Total solids were measured at 0.53 pct with no measurable suspended solids. The elemental composition analysis is shown in Table 5.

Table 5.--Elemental composition of the Midnite Mine feed

Element	Concentration, ppm
Calcium	463
~~Cadmium~~	0.05
Copper	0.25
Iron	0.3
Magnesium	270
Manganese	100
Silicon	27
Uranium	25.4
Zinc	7.2
Ra	39 pCi/L

Task 2: Aliquot samples (200 mL) were removed from the 5 gal mine effluent containers. Various amounts of the 6 pct sodium silicate solution was added to each of the 200 mL mine effluent samples with mild stirring to obtain various concentrations of sodium silicate calculated as ppm Si. The sodium silicate was poured as a steady stream into the mine effluent. As soon as the silicate solution was added, the mine effluent turned milky and a precipitate began to form. The solids were filtered and the filtrate was analyzed for U. The solids were pink in color and very fine in particle size. The solids were gel like in physical form and slow to filter. Some of the solids passed through a 25 micron filter (#5 Whatman paper) so a 4 micron filter was used (#4 Whatman paper). The filtrate was clear and colorless and the pH of the filtrate varied as a function of the concentration of the sodium silicate. The results of the analysis are reported in Table 6.

The optimum concentration of sodium silicate appears to be between 700 and 1677 ppm Si. At a concentration of 1677 ppm Si, the U extraction is 99.6 pct (25.4 to 0.10 ppm) and well within the required maximum limit of 0.5 ppm U.

Table 6.--Optimization of the sodium silicate addition rate

Waterglass added, ppm Si	pH	U concentration, ppm U
0	4	25.4
419	7	2.06
700	8	0.46
1,677	9	0.10
1,739	9	0.17
3,359	10	1.37
6,955	10.5	4.40
70,000	11.5	3.21

Task 3: The solids obtained in Task 1 contain both heavy metal contaminants and excess silica. To separate the silica from the contaminants for possible recycling, the solids were contacted with NaOH to examine its effect on the removal of the silica. Sodium hydroxide (28 w/o) was used initially and added to the solids such that Na/Si ratios of 2 and 4 were obtained. Contact time was 30 min. A brown suspension was obtained after the 30 min stirring. The solid was filtered and a light brown solid was collected that formed a dark brown surface skin after exposure to the air. Underneath the surface skin the solids were light brown in color. This solid was difficult to filter because it had a tendency to plug the pores of the #4 Whatman paper. The brown solid would pass through the #5 Whatman paper. The brown solid also had a pasty texture which could have contributed to plugging of the pores on the filter paper, resulting in very slow filtration. The filtrate was a clear light brown color. Analysis of the filtration products show that the U is indeed concentrated in the solids. In order to facilitate silica dissolution, multiple contacts with warm NaOH may be required for waterglass redissolution. Additionally, a less concentrated NaOH solution (20 w/o) may also facilitate mixing, Si dissolution and filtration. The analytical results are shown in Table 7.

If the solids are dried at 100 °C for >2 h a hard fused mass is obtained that is insoluble in 50 pct H_2SO_4.

The second part of task 3 involves the extraction of U from the sludge with H_2SO_4. A 50 w/o H_2SO_4 was mixed with the sludge at acid:sludge ratios of 0.5:1, 1:1, 2:1, and 3:1 and stirred for 30 min before vacuum filtering to collect the solids and filtrate. An acid/sludge ratio of 3:1 appeared to be the optimum ratio to facilitate mixing. A dark brown solid and a dark pink/brown filtrate was obtained. The solid is hygroscopic. The solids were also washed four times with an equal volume of 25 w/o H_2SO_4. After washing the solid was medium brown color and the filtrate was clear light amber color. The analytical results are shown in Table 8.

Table 7.--Redissolution of waterglass, element concentrations in ppm

Element	Na/Si = 2		Na/Si = 4	
	Solids	Filtrate	Solids	Filtrate
Uranium	4,600	27	4,200	75
Silicon	246,000	15,100	278,000	2,380

Table 8.--Concentration of uranium and silicate in sulfuric acid washed solids, ppm

Number of washes	Solids		Filtrate	
	U	Si	U	Si
1	1,300	86,850	500	50
4	8	133,000	0	22

The final part of task 3 is the addition of hydrogen peroxide to the above filtrates to precipitate U. A 10 w/o hydrogen peroxide solution was added to the filtrate at a H_2O_2/U ratio up to 100:1. The only significant event was a decolorization of the filtrate. No visible precipitate was formed. The filtrate contained 6 ppm U and 30 ppm Si. The results of this test were inconclusive since the amount of U being removed was small and the difference between initial and final levels could have been within experimental error.

A listing of analytical results and a U material balance for each of the steps in Tasks 1 through 3 is presented in Table 11 of the Attachment. The multiplicity of the operations (i.e., feed transfers, solid and liquid separations, washings, combining of feed materials, NaOH and H_2SO_4 treatments) certainly affected these initial material balance numbers. Only in one step (see feed #4 in table 5) were the material balance values essentially non-existent. Nevertheless, the numbers do indicate that the chemistry works for U and heavy metal removal and decontamination of mine effluent with waterglass is a viable process. With this in mind the processes represented in tasks 1 through 3 were repeated in Tasks 4 and 5 using the optimum concentration of chemicals suggested by the results obtained in the first 3 tasks.

In a meeting with personnel from the USBM on October 4, 1995, the results of Tasks 1 through 3 were discussed. As a result of this meeting, it was decided to examine an additional pathway in the treatment process. This involved treating the waterglass captured contaminant solids directly with H_2SO_4, thereby eliminating the NaOH dissolution step. In addition, the peroxide step would also be eliminated since the results showed that it was ineffective. A process flowsheet for Tasks 4 and 5 is shown in Figure 4. The details of each step of the process are presented below.

Three 10,000 g portions of the mine effluent were treated individually with the waterglass at a Si concentration of 1700 ppm. The mine effluent was clear and colorless with a pH of 4. As soon as the waterglass was added, the mine effluent turned milky pink color. The mixture was stirred for 2 min and vacuum filtered through a #4 Whatman filter paper. There was some turbidity in the filtrate. It was refiltered. The pH of the filtrate was 8.9. The solid was pink colored and gelatinous. The filtrates and the solids from the three 10,000 g portions were combined to form one filtrate and one solid sample. The pink solid was washed 2X with warm (40 °C) 20 w/o NaOH at the optimum Na/Si = 3 ratio to facilitate stirring. The mixture was stirred 20 min and a light brown color suspension was obtained. This mixture was filtered through a #4 Whatman paper. The filtering was a very slow process. The light brown solid (which turned dark on the surface after exposure to air) was a viscous solid and plugged the pores of the filter paper. The filtrate was filtered 3X because the solid kept passing through the filter. The filtrate was a clear light brown color that turned dark brown overnight. It had a pH of 12.6. After the third filtration a white precipitate formed in the filtrate. This was filtered and a clear colorless filtrate was obtained along with the white solids. This filtered very easily.

The brown solid obtained from the filtration process was washed 2X with 10 w/o H_2SO_4 and vacuum filtered once. This too was a slow process. A brown solid and a clear pale amber filtrate were obtained.

The white solid obtained from the filtrate after the third filtration was also washed 2X with 10w/o H_2SO_4 and vacuum filtered once. It filtered very easily and a light brown solid and clear colorless filtrate were obtained.

A portion of the solids that were obtained from the waterglass treatment step was set aside for processing by another pathway. This pink solid was washed with 10w/o H_2SO_4 by stirring for 10 min. A dark brown suspension was obtained that was vacuum filtered. The filtering process was slow but not as slow as the NaOH filtration step. A dark brown solid and a clear pale amber filtrate were obtained.

A detailed description of the samples taken for analysis in Tasks 4 and 5 as per the flowsheet in Figure 4 is given in Table 12. The results of those analyses are summarized in Table 9 and Figure 4. These results indicate that the U effluent level of 0.5 ppm can be easily achieved since the level obtained in these tests was 0.012 ppm. In addition, about 70 pct of the silica can be recycled back to the waterglass process. After leaching with 10 pct H_2SO_4, residual solids are generated at the rate of about 1 part per 2,000 parts of original mine effluent. Furthermore, these solids contain about 130 ppm of U, making them an uncontrolled material.

Analyses for Ca, Mg, Mn, Zn, Cd, Fe, Cu and Ra indicated that Ca, Mg and Ra were not efficiently removed from the feed stream. The Zn, Cd, Fe and Cu were all removed with >90 pct efficiency. After washing the waterglass precipitate with caustic and leaching the residual solids with sulfuric acid, a non-hazardous, non-radioactive solid was produced and a sulfuric acid stream which contained most of the uranium and some of the hazardous elements was produced. The next step in the process would be the selective recovery of the uranium using peroxide precipitation and recycle of the sulfuric acid for additional leaching.

These tests demonstrated that:

1. Uranium levels in the waste effluent were reduced to about 0.01 ppm U from 25.4 ppm using the waterglass process.
2. The waterglass was re-dissolved in caustic, producing a uranium rich solid containing >4,000 ppm U and a waterglass recycle stream containing about 70 pct of the silica with between 2 and 200 ppm U.
3. The uranium was dissolved in sulfuric acid leaving a solids residue containing about 130 ppm U. The residual solids were generated at the rate of about 1 part per 2,000 parts of mine effluent treated.
4. The concentrations of reactants were as follows:
   - Silica concentration to achieve lowest uranium level is between 700 and 1,739 ppm Si.
   - The Na/Si ratio for silica recovery from the waterglass precipitate is 3.
5. The concentration of Zn, Cu, Mn, Fe and Cd were all reduced in the mine effluent along with the uranium. Residual levels were Cu and Fe <0.01 ppm; Cd = 0.0025 ppm; Zn = 0.02 ppm; and Mn = 0.14 ppm.
6. The leached solids were non-radioactive and non-hazardous. These solids were produced at the rate of 0.8 pct of the weight of the waste feed stream. The uranium recovery was over 95 pct.

Table 9.--Summary of uranium results from tasks 4 and 5

Stream	Uranium level, ppm
Mine effluent	25.4
Treated effluent	0.012
Waterglass solids	4,100
2X NaOH leached solids	2,100
Filtrate	178
2X H_2SO_4 leached solids	190
Filtrate	187
3X NaOH leached solids	3,000
Filtrate	3.21
2X H_2SO_4 solids	130
Filtrate	237
2X 10 pct H_2SO_4 leached solids	3,100
Filtrate	101

Table 10.--Sample Identification, Description and Requested Analysis

ID Number	Description	Analysis
212537-33	Mine effluent	U, Si, Ca, Mg, Mn, Zn, Cu, Cd, Fe, Ra
212537-82A	Filtrate after waterglass addition	U, Si, Ca, Mg, Mn, Zn, Cu, Cd, Fe, Ra
212537-82B	Solids after waterglass addition	U, Si, Ca, Mg, Mn, Zn, Cu, Cd, Fe, Ra
212537-83A	Solids after NaOH wash	U, Si
212537-83B	Filtrate after two NaOH washes	U, Si
212537-83C	Solids after two NaOH washes, three filtrations	U, Si
212537-83D	Filtrate after third filtration	U, Si
212537-84C	Filtrate after two H_2SO_4 washes	U, Si, Ca, Mg, Mn, Zn, Cu, Cd, Fe, Ra
212537-84D	Solid after two H_2SO_4 washes	U, Si, Ca, Mg, Mn, Zn, Cu, Cd, Fe, Ra, and TCLP
212537-84A	Filtrate after NaOH washes and two H_2SO_4 washes	U, Si, Ca, Mg, Mn, Zn, Cu, Cd, Fe, Ra
212537-84B	Solid after NaOH washes and two H_2SO_4 washes	U, Si, Ca, Mg, Mn, Zn, Cu, Cd, Fe, Ra, and TCLP
212537-85A	Solids after waterglass and H_2SO_4 treatment	U, Si, Ca, Mg, Mn, Zn, Cu, Cd, Fe, Ra, and TCLP
212537-85B	Filtrate after waterglass and H_2SO_4 treatment	U, Si, Ca, Mg, Mn, Zn, Cu, Cd, Fe, Ra

Table 11.--Summary of results from tasks 1 through 3

		Feed, grams, pct solids	Uranium, level, ppm	Total uranium, mg	Uranium recovery, pct
Feed 1	Mine effluent	10,000	25.4	254	
Treatment	$NaSiO_3$	622 (6 pct)			
	HCl	177			
Products	Solid	750 (4.5 pct)	*336	*252	
	Filtrate	10760	0.17	1.8	0.7
Feed 2	Solids from feed 1	750 (4.5 pct)	*336	*252	
Treatment	NaOH	63 (29 pct)			
Products	Solid	135 (27 pct)	4,400	163	65
	Filtrate	*678	50	*33.9	*13
Recovery, pct					78
Feed 3	Solids from feed 2	123 (27 pct)	4,400	146	
Treatment	H_2SO_4	96			
Products	Solids	128 (40 pct)	1,300	66	45
	Filtrate	137	500	68	46
Recovery, pct					92
Feed 4	Solids from feed 3	107 (40 pct)	1,300	56	
Treatment	H_2SO_4 wash 4X	400			
Products	4X Washed solids	205 (30 pct)	7.6	0.5	
	4X filtrate	89	8.9	0.8	
Feed 5	4X filtrate from feed 4	89	8.9	0.8	
Treatment	H_2O_2	40			
Products	Solids	none			
	Filtrate	120	6	0.7	91
Recovery, pct					91

*Note: These numbers were obtained by material balance.

Table 12.--Tasks 4 and 5 analytical results, concentration of metal, ppm

ID No.	U	Ca	Mg	Mn	Si	Zn	Cd	Fe	Cu	Ra	Moisture
212537-33	25.4	463	270	100	27	7.2	0.05	0.3	0.25	39*	
212537-82A	0.012	300	67	0.14	140	0.02	0.0025	<0.01	<0.01	12	
212537-82B	4,100	29,000	32,000	18,800	207,000	1,900	8.2	380	38	5.7	83 pct
212537-83A	2,100				218,000						72.2 pct
212537-83B	178				31,000						
212537-83C	3,000				254,000						78.3 pct
212537-83D	3.21				7,000						
212537-84C	237	540	1,700	680	660	90	0.38	76	2.6	3.6	
212537-84D	130	820	1,050	800	261,000	54	0.3	106	2.0	0.5	69.6
212537-84D TCLP	1.70	12	18	10	36	2.5	0.01	<0.1	0.06	2.0	
212537-84A	187	500	1,230	450	960	100	0.26	68	2.2	16	
212537-84B	190	22,800	1,030	3,600	239,000	65	0.3	180	2.4	8.0	68.5
212537-84B TCLP	1.74	360	16	16.5	92	1.5	0.01	<0.1	0.03	1.9	
212537-85A	3,100	25,100	43,800	18,500	83,900	2,300	12	590	39	5.0	76.5
212537-85A TCLP	0.798	0.7	<0.1	0.01	112	0.06	<0.01	<0.01	<0.01	0.2	
212537-85B	101	0.9	0.9	0.05	3,400	14	<0.01	<0.1	0.11	3.4	

*pCi/L = picocuries per liter.

Table 13.--Summary of uranium results and material balances from tasks 4 and 5

Item	Description	Feed, grams, pct solids	Uranium level, ppm	Total U, mg	U recovery, pct
Feed 1	Mine Effluent	30000	25.4	762	
	212537-33				
Treatment	6 pct NaSiO3	1827 (6 pct)			
Products	Solids 212537-82B	989 (17 pct)	4,100	689	90
	Filtrate 212537-82A	29940	0.012	0.359	0.04
Recovery, pct					90
Feed 2	Solids from feed 1	455 (17 pct)	4,100	317	
Treatment	20 pct NaOH	1195 (20 pct)			
Products	Solids 212537-83A	259 (28 pct)	2,100	152	48
	212537-83C	97 (22 pct)	3,000	64	20
	Filtrates 212537-83B	275	178	49	15
		805	3.21	3	1
	212537-83D				
Recovery, pct					84
Feed 3	Solids from feed 2, 212537-83A	225 (28 pct)	2,100	132	
Treatment	10 pct H_2SO_4	414			
Products	Solids 212537-84B	97 (32 pct)	190	6	
	Filtrate 212537-84A	430	187	81	
Feed 3	Solids from feed 2, 212537-83C	73 (22 pct)	3,000	48	
Treatment	10 pct H_2SO_4	180			
Products	Solids 212537-84D	40 (30 pct)	130	2	
	Filtrate 212537-84C	228	237	54	
Total Feed	-83A + 83C			180	
Total Solids	-84B + -84D			8	4
Total Filtrate	-84A + -84C			135	75
Recovery, pct					79
Feed 4	Solids from feed 1, 212537-82B	435 (17 pct)	4,100	303	
Treatment	10 pct H_2SO_4	400			
Products	Solids 212537-85A	380 (23 pct)	3,100	270	89
	Filtrate 212537-85B	618	101	62	20
Recovery, pct					99

*Dry basis.

Field Tests

Flowsheet: Water from pit 3 was obtained just prior to entering the lime treatment plant at the Midnite Mine site. Part of the water was treated for Ra precipitation by the modified $BaCl_2$ treatment and sent to IX train A and LEM (figure 5). Untreated pit 3 water was sent to IX train B. Treated water was returned to the plant.

Ion Exchange: Two column trains were employed; a 3 column set using water which had been treated with $BaCl_2$ for Ra removal (train A) and a 5 column train treating as received pit 3 water (train B). Each column was 2.5 by 90 cm and both trains were operated in series using a single peristaltic pump for each train. Train A treated water at 250 mL/min (31 BVH) using 325 g of DOWEX 21K XLT in each column. The higher flow rate was intended to test the kinetic limits of the resin for U removal. Train B treated water at 100 mL/min (12 BVH) using three columns each containing 325 g of resin and two columns each containing 300 g of clinoptilolite from Hector, CA.

Results for train A were difficult to evaluate since the pretreatment for Ra removal also removed as much as 80 pct of the U. Feed to train A occasionally contained <4 ppm U which would result in resin loadings of less than 2 mg U/g resin or about 7 pct of the loading achieved in laboratory tests. Effluent from train A contained 0.2 ppb U at the conclusion of the test demonstrating that low U levels are obtainable even at the higher flow rates.

Early in the test, the resin in the first column of train A began to turn black. The column was removed from the train and replaced with a fresh column. Later analysis found that the discoloration was only on the surface of the individual beads. This was the only column in which a Si based sealant was used to repair leaking fittings. All other leaks were repaired using an epoxy compound. Batch testing demonstrated that the discolored beads were still able to load U from Midnite Mine water. The discolored beads were found to contain higher levels of several metals, including Mn, than was found in beads from the column that were not discolored leading to speculation that some of the Mn in solution may have been oxidized to MnO_2 by components of the sealant causing precipitation to occur.

Train B treated 345 L (704 bed volumes) and decreased U to less than 5 ppb. Breakthrough was not achieved. While the lack of breakthrough indicates that U loading was not at maximum, calculated U loading was 56 mg/g; 115 pct greater than that measured at breakthrough in the laboratory tests. This is partially attributable to the 71 pct lower treatment rate but may also be due to improved efficiency of scale up; a phenomenon known to occur in ion exchange processes due to improved contact and longer residence times. If DOWEX 21K XLT loads to 1.2 meq/g, a level reported for DOWEX 21K in industrial use (*3*), an additional 535 L (1090 bed volumes) could be treated. ICP-MS analysis detected <5 ppb U in the treated water.

One of the concerns over using unfiltered water was plugging of the column by suspended sediments. As a safeguard, an in line filter was placed in front of the first column. Over the course of the test, there was no detectible build up of sediments on the filter indicating that prefiltration would not be required.

The first column from train B was stripped using 6.5 bed volumes (3 L) of 2*M* NaCl adjusted to pH 1 with HCl. The stripping solution, containing 1.7 g/L U, was treated with hydrogen peroxide to precipitate the U. X-ray diffraction analysis did not detect any impurities in the product.

Liquid Emulsion Membrane: Based upon the laboratory investigations, an available continuous LEM system (small pilot plant-scale) was modified for use in field testing at the Midnite Mine. The available pilot plant (called a PDU) was a mobile unit that had been originally designed and used for the recovery of copper from dilute leach solutions and waste waters; therefore, some modifications were necessary before it could be used for U recovery. One of the major differences relates to the method of metal recovery. In the copper circuit, electrowinning was used as the recovery step, and in the U circuit, precipitation of yellow cake and filtration were to be used. The other major differences were related to the use of totally different emulsion membrane formulations in the two circuits. However, for the most part, the same equipment designs for the unit operations described in other publications (*7-9*) were used.

A flowsheet for the continuous circuit used in the field test is shown in Figure 6. All major equipment items are shown on this flowsheet. The equipment was mounted in a 24 ft long enclosed semi-trailer. Figures 7 and 8 show views of the LEM trailer and the PDU equipment. The design capacity of the unit was 2-4 L/min of aqueous feed (depending on feed composition). All components, with the exception of the emulsion generation vessel, were fabricated from clear acrylic plastic.

In the emulsion generation step, recycled organic phase and internal solution were combined in an emulsion premix stage at the desired organic/internal ratio (typically 4:1 organic to internal in most cases, but 2:1 with U extraction). The emulsion premix stage was a cylindrical baffled tank with a capacity of 6 L. This step generated a weak emulsion that flowed by gravity to the dispersion unit that generated the stable emulsion. The flow through dispersion unit was similar in design to industrial units used to generate emulsions. The residence time in this unit was about 12 sec. The generator consisted of a slotted stator and an internal rotor. This unit was operated at a speed of 5,000 rpm resulting in a tip speed of 730 cm/sec, to produce internal droplets in the organic phase with an average diam. of 5 microns.

The emulsion and feed solution were combined in a four stage cocurrent flow extraction unit. In addition to the four extraction stages, there is a small premix stage where the emulsion and aqueous feed solution are first combined. The unit was a cylindrical, baffled, tank with a capacity of 4 L, containing a turbine mixer near the inlet that served to break the emulsion into small globules. The emulsion/aqueous mixture flowed by gravity from the premix tank through the four extraction stages. The extraction stages had a working capacity of 15 L. They were fitted with a double set per shaft of relatively large, slow turning, 3 bladed propellers. The mixers were operated at 100 rpm resulting in a tip speed of 50 cm/sec. The objective was to generate globules of emulsion with an average diameter between 0.5 and 1 mm. The emulsion then was separated from the raffinate (aqueous feed depleted of U) in a cylindrical settler. The emulsion was sent to the emulsion breaking/product recovery circuit. The raffinate flowed by gravity from the primary settler to a secondary settler fitted with baffles where most of the entrained emulsion was separated. From the secondary settler, the raffinate flowed to a coalescer where the last remaining emulsion was removed with fabric material (polypropylene cloth) that collected the last traces of emulsion. The raffinate was then pumped back to the mine water treatment plant where the remaining metals were precipitated.

The emulsion was pumped to a small surge tank from which it flowed by gravity to an electrical coalescer where it was broken into the two original phases used to generate the emulsion. The coalescer was a rectangular vessel, similar in design to a SX settler. It was fitted with two horizontal electrodes. The bottom electrode was an uninsulated stainless steel screen that was in contact with the separated aqueous internal solution. This electrode was operated at ground potential. The upper electrode was a stainless steel wire that was formed into a rectangular shape and was covered with polyvinyl chloride tubing to insulate the wire. A 60 hertz ac potential of 5,000 to 10,000 V was applied across the electrodes. Essentially no current flowed between the electrodes because the "hot" electrode was insulated. The working volume of the coalescer was 6.7 L which provided a retention time of 11 min. The recovered organic phase from the coalescer was collected in a surge tank prior to being sent to the U recovery step. The recovered internal solution was collected in a surge tank where the acid level was adjusted back to the original level by the addition of concentrated H_2SO_4. After the acid level was adjusted in the internal solution, it was recycled back to the emulsion generation step.

The organic phase from the coalescer contained the U in the form of a uranyl complex. The organic phase was contacted with a Na_2CO_3 solution to strip the U. This was done in a cylindrical 6 L baffled tank. The mixing action in the stripping tank generated a weak emulsion between the organic phase and the Na_2CO_3 solution. This emulsion flowed into a second electrical coalescer similar in design to the first coalescer except the volume of the second coalescer was only 2 L. The separated organic phase flowed into a surge tank and then was pumped back to the emulsion premix tank to generate more emulsion. The Na_2CO_3 stripping solution was recycled until it built up a sufficient concentration of U to allow precipitation of the U as sodium diuranate (yellow cake). To replenish Na_2CO_3 consumed during U stripping, half of the stripping solution was being regenerated through the addition of solid Na_2CO_3 while the remainder was being recycled. Solid Na_2CO_3 was used to avoid dilution of the stripping solution even though dissolution of the solid was relatively slow. A bleed stream from the loaded stripping solution was sent to the U precipitation step. This was accomplished in two 4 L precipitation stages. In the first stage, H_2SO_4 was added to remove residual Na_2CO_3. In the second stage, NaOH was added to precipitate the U as yellow cake.

The primary parameters used in the LEM field test are shown in Table 14. These parameters were adapted from those used in the research with the laboratory scale circuits. The organic phase contained the indicated proportions of Alamine 336 (a tertiary amine extractant), P100 (Paranox 100, a non-ionic surfactant),

Table 14.--Summary of target operating parameters for LEM Midnite Mine field test

Nominal flow rates:	
AMD aqueous feed	2.7 L/min
Organic	424 mL/min
Internal solution	212 mL/min
Emulsion	636 mL/min
Strip solution	212 mL/min
Organic composition:	5.0 wt pct Alamine 336
	1.0 wt pct P100 surfactant
	4.0 vol pct Isodecanol
	Balance Isopar L kerosene
Organic viscosity	2.03 cp
Internal composition	50 g/L H_2SO_4
Strip composition	100 g/L Na_2CO_3

Isodecanol (a phase modifier), and Isopar L (an aliphatic kerosene). In addition to the organic phase, the emulsion contained an internal solution with a target acid level of 50 g/L H_2SO_4. In the emulsion, an organic to internal phase ratio of 2:1 was used. The ratio of aqueous feed to the emulsion phase was 4.25:1, and the organic to stripping phase ratio was 2:1. These ratios resulted in an overall ratio between the aqueous feed to the stripping phase of 12.74:1. Theoretically the U concentration in the stripping solution would increase by about 270 ppm on each cycle.

The LEM unit was operated for ten days on a continuous basis. A total of 17,800 L of mine water was processed. Both untreated mine water and water that was pretreated to precipitate Ra were processed in the system. The results indicate that the U level in the water was reduced from an initial level of 21 ppm to 120 ppb (0.12 ppm) in the effluent from the LEM unit. Raffinate analyses of <70 ppb (0.07 ppm) U were obtained during portions of the field test. Table 15 contains typical results from the continuous LEM circuit during the field test. Data in this table show that the U was reduced from 21 ppm in the Midnite AMD water to 0.1 ppm in the raffinate while the U level in the recycling stripping solution was built up to 9,400 ppm (9.4 g/L). The other major metal impurities in the AMD water (Mn and Zn) passed through the LEM system and exited with the raffinate. The extraction of U was quite selective based upon the low levels of metal impurities that collected in the stripping solutions. The recycling internal solution built up in levels of Mn and Zn through the entrainment of raffinate into the emulsion; however, very little U (<0.5 ppm) was contained in that solution. Excess internal solution caused by membrane swelling (transfer of water through the membrane) was removed and added to the raffinate stream being sent to the water treatment plant.

Table 15.--Typical results from continuous LEM system at Midnite Mine field test

Solution	Analyses							
	ppm				g/L			
	U	Fe	Mn	Zn	SO_4^{2-}	CO_3^{2-}	H_2O	H_2SO_4
Midnite AMD water	21.0	0.4	97.4	3.9	2.37	NAP	NAP	NA
Raffinate	0.1	NA	NA	NA	3.74	NAP	NAP	NA
Loaded organic	110	NA	NA	NA	NA	NAP	10	NAP
Loaded internal	<0.5	NA	41.0	2.0	NA	NAP	NAP	2.0
Recycled Internal	<0.5	NA	40.0	2.0	NA	NAP	NAP	24.6
Strip Feed	9,200	0.6	0.4	<0.1	34.4	46.5	NAP	NAP
Loaded strip	9,400	0.6	0.4	<0.1	35.2	43.0	NAP	NAP
Stripped organic	30	NA	NA	NA	NAP	NAP	5.5	NAP

Table 16.--Typical profile from LEM extraction unit

Solution	Analyses, U ppm
Midnite feed to extractor #1	21.0
Raffinate from extractor #1	0.38
Raffinate from extractor #2	0.21
Raffinate from extractor #3	0.14
Raffinate from extractor #4	0.14
Raffinate from settler	0.12

The extraction unit of the LEM circuit operated very efficiently. Table 16 shows data related to the amount of U at different points in the extraction unit. These data indicate that only one stage was necessary in order to reduce the U level to below the target value (<0.7 ppm U). Each extractor stage in the PDU had a superficial residence time of 5 min. The loss of organic phase from the LEM circuit was quite low. On the average, the raffinates contained between about 5 to 10 ppm (total) organic material. This amount includes both dissolved and entrained organic compounds from the LEM circuit.

The bleed stream removed from the recycling stripping solution was treated in the U recovery unit on a batch basis. Sulfuric acid was added to the stripping solution to lower the pH (range investigated was pH 3.2 to 4.6); destroying most of the carbonate. Then, 10*M* NaOH was added to precipitate the U. The pH range investigated was pH 9.9 to 11.8. The resultant slurry was filtered on a laboratory vacuum filtration unit. The resulting filtrate contained from 13 to 25 ppm U; therefore, this solution would be combined with the feed AMD water and sent to the LEM system before discharge to the existing precipitation plant.

The yellow cake produced in the field test was quite pure (table 17) and should be easily marketed to the nuclear industry.

One difficulty that was encountered during the field tests appeared to be related to the Ra precipitation process. Residual material (iron flocs and traces of flocculent) from the Ra removal circuit caused some phase disengagement problems in the primary settler of the LEM circuit. The secondary settler in the LEM circuit handled the situation; however, it is recommended that the LEM circuit should be located first in the process, then the Ra removal circuit.

Neutralization: After the field test was concluded, 10 liters of U and Ra free water were treated by alkaline precipitation to ensure the resulting sludge passes the EPA Toxic Characteristic Leach Procedure (TCLP) test. Failure to pass this test results in a material being classified a "hazardous waste" by the EPA, greatly increasing disposal costs. This water was fed to a 2 L reactor vessel with a residence time of 30 min. An electronic pH controller was used to maintain a proper feed rate of a 10 pct calcium hydroxide slurry to increase the solution pH to 11. This resulted in most of the metals in solution forming insoluble metal hydroxides and precipitating. The slurry containing the precipitated metals overflowed the reactor vessel into a vacuum filter. After the water had been treated, the precipitated sludge was subjected to the TCLP procedure and the treated effluent was analyzed to ensure it met the NPDES discharge limits.

Table 17.--Comparison of field-test produced yellow cake versus industrial specifications

	Standard concentration, pct	Maximum limit concentration, pct	LEM yellow cake, pct
Uranium	75	*65	69
Vanadium	0.10	0.75	<0.1
Phosphorus	0.10	1.00	<0.1
Halides	0.05	0.10	NA
Fluoride	0.01	0.10	NA
Molybdenum	0.10	0.30	<0.1
Sulfur	3.00	12.0	<1
Iron	0.15	1.00	<0.01
Arsenic	0.01	0.04	NA
Carbonate	0.20	0.50	NA
Calcium	0.05	1.00	<0.1
Sodium	0.50	7.50	5.7
Boron	0.005	0.10	<0.01
Potassium	0.20	3.00	<0.02
Titanium	0.01	0.05	<0.03
Zirconium	0.01	0.50	<0.01
Silica	0.50	2.50	<0.03
Magnesium	0.02	0.50	<0.003
Water	2.00	5.00	<2.0

* Minimum. NA Not analyzed.

Note: (1)Source of specifications in this table was Allied Signal, Inc. these specs are used to determine surcharges for use in their UF_6 conversion services. (2) The items that are reviewed for possible assessment surcharges are: vanadium, molybdenum, sodium, and potassium.

Table 18.--Effluent concentrations obtained after treating radionuclide-free Midnite Mine water with alkaline neutralization

	Analysis	NPDES standard
Ra, pCi/L	<1	3
U, mg/L	0.06	2
Zn, mg/L	<0.001	0.5
Mn, mg/L	<0.004	3

The alkaline precipitation proved effective in meeting the discharge standards for Mn and Zn and the sludge passed the TCLP test. Table 18 presents the effluent analysis and compares it to the NPDES standards. In addition to meeting TCLP standards, the sludge contained only 56 ppm U, well below the 0.05 pct criteria for classification as a nuclear source material by the Nuclear

Regulatory Commission. This indicates that the effluent from the Ra and U removal sections can be successfully treated with alkaline precipitation to produce an effluent that meets the NPDES standards and a sludge that passes TCLP testing.

Radium Adsorption: Radium analyses of effluent from the zeolite columns (train B of the ion exchange test) demonstrated that Ra was removed but that the kinetics were slower than anticipated. When flooded columns were left standing overnight, Ra levels decreased to 6-8 pCi/L. Effluent from the second column at the end of each day's operation contained 18 pCi/L. The head analysis was 44 pCi/L. Projection of the analyses of effluent from the first zeolite column indicate that each column could treat approximately 1100 bed volumes before replacement would be required. To lower Ra to the discharge level of 3 pCi/L would require 1-2 additional columns. Alternatively, $BaCl_2$ additions during lime treatment could be continued as a polishing step so long as there was insufficient Ra remaining to produce a hazardous waste.

Radium Precipitation: The equipment consisted of 4 precipitation tanks, a rapid mix tank, 2 aging tanks and a thickener for solid-liquid separation (Fig. 9). Midnite Mine water was fed to the precipitation tank at 3.1 L/min. Simultaneously, a 7.6 g/L $BaCl_2$ solution was metered into the first precipitation tank at 3.5 mL/min. The residence time in each precipitation tank was 10 min. The water containing the precipitated Ra was then fed to the rapid mix tank and the 2 aging tanks in series. The retention time in the rapid mix tank was 3 min and in each aging tank is 40 min. A 11.6 g/L $FeCL_3$ solution was fed to the rapid mix tank at 3 mL/min to precipitate ferric hydroxide as a collector for the Ra precipitate. The slurry was then fed to a thickener to produce an underflow containing about 3 pct solids and a clarified overflow. The clarified overflow was filtered with a sand filter to remove any unsettled precipitate and then fed to either the LEM or IX circuits or disposed of directly into the Dawn Mining Company water treatment plant. The slurry containing the precipitated Ra in a barium sulfate/ferric hydroxide matrix was disposed of by feeding it to the first alkaline precipitation tank in the existing Dawn Mining Company water treatment plant.

The flocculent (Nalco 9708-PULV) used by Dawn Mining Company in their water treatment plant was used during the field test to flocculate the ferric hydroxide. This necessitated raising the solution pH to 5. A 10 pct calcium hydroxide slurry was used to increase the pH.

The $BaCl_2$ precipitation proved effective at decreasing the Ra concentration in Midnite Mine water to less than 1 pCi/L. Table 19 details typical analysis of the various streams in the Ra precipitation section. Because the barium sulfate precipitation reaction is extremely rapid, it was assumed any precipitation would occur in the four precipitation tanks. Therefore, the aging tanks were not sampled, although the sand filter effluent was sampled to ensure discharge standards were met. The Ra concentration was consistently below the 3 pCi/L discharge limit after the third precipitation tank.

Increasing the solution pH for effective flocculation precipitated some of the U in the water. The U concentration dropped from 23 mg/L to approximately 5 mg/L. This could be remedied by removing the U prior Ra removal. An additional advantage would be that the two precipitation operations, Ra and alkaline for the other metals, would operate as sequential steps. Therefore, operational difficulties in the precipitation operations would have little chance of upsetting the U removal section, which is more sensitive to process upsets such as suspended solids.

Table 19.--Typical radium concentrations in various streams during the field test

Stage	Radium, pCi/L
Feed	48
Precipitation 1	7
Precipitation 2	4
Precipitation 3	<1
Precipitation 4	2
Rapid Mix	<1
Sand Filter	<1

Interestingly, analysis of these results and comparison to conducting the Ra precipitation in conjunction with the alkaline precipitation indicates there may not be an advantage to separating the Ra from the alkaline precipitation. This is contingent on the final rules for disposing of Ra containing sludges formulated by the State of Washington.

Research at the USBM Salt Lake City Research Center indicated that the Ra concentration in a dried alkaline neutralization sludge would be 34 pCi/g of dried sludge. The sludge generated by the Ra precipitation during the water treatment field test contained 109 pCi Ra/g of dried sludge. The sludge currently being produced by Dawn Mining Company, containing approximately 35 pCi/g Ra is being disposed of at the off site tailings pond. The USEPA has suggested guidelines for disposing of drinking water sludges or sludges containing 50 to 2,000 pCi/g of Ra. These guidelines suggest disposal to be determined on a case-by-case basis and that methods used for disposing of U mill tailings be considered (40 CFR 192). Unless the State of Washington drastically alters current acceptable practice with the new regulations, it is preferable to precipitate the Ra in conjunction with the alkaline precipitation process. If the amount of Ra allowable in a sludge is drastically lowered, then a separate Ra precipitation process could be installed.

Cost Estimates

Where sufficient information was available, cost estimates were made. The assumptions used and breakdowns of capital and operating cost estimates are listed in tables 20-35.

Ion Exchange:

Table 20.--Estimated capital cost, uranium ion exchange

Fixed capital:	
Ion exchange treatment section	$ 640,490
Uranium recovery section	12,350
Subtotal	652,840
Plant facilities, 10 pct of above subtotal	65,280
Plant utilities, 12 pct of above subtotal	78,340
Total plant cost	796,460
Land cost	0
Subtotal	796,460
Interest during construction period	13,390
Fixed capital cost	809,850
Working capital:	
Raw material and supplies	2,320
Product and in-process inventory	0
Accounts receivable	0
Available cash	14,480
Working capital cost	16,800
Capitalized startup costs	8,100
Subtotal	24,900
Total capital cost	834,750

Table 21.--Estimated annual operating cost, uranium ion exchange

	Annual cost	Cost per thousand gallons drainage
Direct cost:		
Raw materials:		
50 pct sodium hydroxide at $300.00 per ton . .	$ 2,590	$ 0.013
30 pct hydrogen peroxide at $500.00 per ton . .	6,750	0.035
Resin make up cost at $3.20 per lb	700	0.004
Drums and liners at $20.00 per drum	10,800	0.056
Total	20,840	0.108
Utilities:		
Electric power at $0.041 per kW·h	12,260	0.063
Total	12,260	0.063
Direct labor:		
Labor at $11.00 per hour	68,640	0.353
Supervision, 0 pct of labor	0	0.000
Total	68,640	0.353
Plant maintenance:		
Labor	18,330	0.094
Materials	18,320	0.094
Total	36,650	0.188
Payroll overhead, 35 pct of above payroll	30,440	0.157
Operating supplies, 20 pct of plant maintenance .	7,330	0.038
Total direct cost	176,160	0.907
Indirect cost, 40 pct of direct labor and maintenance	42,120	0.217
Fixed cost:		
Taxes, 1.0 pct of total plant cost	7,960	0.041
Insurance, 1.0 pct of total plant cost	7,960	0.041
Depreciation, 20-yr life	40,490	0.208
Total operating cost	274,690	1.414

Table 22.--Equipment cost summary, ion exchange treatment section, uranium ion exchange

(Third quarter, 1995 prices)

Item	Equipment	Labor	Total
Pumps	$ 10,290	$ 680	$ 10,970
Ion exchange columns	24,100	1,100	25,200
Column pumps	34,420	2,320	36,740
Strip sol surge tank	2,710	490	3,200
Strip sol feed pumps	2,430	220	2,650
Strip liq col trans pump	2,650	220	2,870
Hydrogen peroxide tank	100	10	110
Transfer pumps	3,040	220	3,260
Caustic soda tank	2,960	500	3,460
Transfer pumps	1,600	220	1,820
Uranium prec tank	3,290	410	3,700
Filters	134,660	8,590	143,250
Filtrate receiver tank	210	30	240
Pumps	2,650	220	2,870
Total	225,110	15,230	240,340
Resin cost			25,490
Total equipment cost x factor indicated:			
Foundations, x 0.234			52,570
Structures, x 0.050			11,260
Instrumentation, x 0.050			11,260
Electrical, x 0.151			34,080
Piping, x 0.250			56,280
Painting, x 0.020			4,500
Miscellaneous, x 0.100			22,510
Total			192,460
Total direct cost			458,290
Field indirect, 10.0 pct of total direct cost			45,830
Total construction cost			504,120
Engineering, 5.0 pct of total construction cost			25,210
Administration and overhead, 5.0 pct of total construction cost			25,210
Subtotal			554,540
Contingency, 10.0 pct of above subtotal			55,450
Subtotal			609,990
Contractor's fee, 5.0 pct of above subtotal			30,500
Section cost			640,490

Table 23.--Equipment cost summary, uranium recovery section, uranium ion exchange

(Third quarter, 1995 prices)

Item	Equipment	Labor	Total
Wash water tank	$ 150	$ 20	$ 170
Transfer pumps	3,790	220	4,010
Cake receiving hopper	100	10	110
Roller conveyor	550	40	590
Total	4,590	290	4,880
Total equipment cost x factor indicated:			
Foundations, x 0.098			450
Structures, x 0.050			230
Instrumentation, x 0.050			230
Electrical, x 0.392			1,800
Piping, x 0.150			690
Painting, x 0.020			90
Miscellaneous, x 0.100			460
Total			3,950
Total direct cost			8,830
Field indirect, 10.0 pct of total direct cost			880
Total construction cost			9,710
Engineering, 5.0 pct of total construction cost			490
Administration and overhead, 5.0 pct of total construction cost			490
Subtotal			10,690
Contingency, 10.0 pct of above subtotal			1,070
Subtotal			11,760
Contractor's fee, 5.0 pct of above subtotal			590
Section cost			12,350

Table 24.--Estimated capital cost

(Third quarter, 1995 basis)

Fixed capital:	
Uranium LEM Process section	$ 590,629
Subtotal	590,629
Plant facilities, 10 pct of above subtotal	59,063
Plant utilities, 12 pct of above subtotal	70,875
Total plant cost	720,567
Land cost	0
Subtotal	720,567
Interest during construction period	12,111
Fixed capital cost	732,678
Working capital:	
Raw material and supplies	17,240
Product and in-process inventory	0
Accounts receivable	0
Available cash	38,620
Working capital cost	55,860
Capitalized startup costs	17,400
Subtotal	73,260
Total capital cost	805,938

Table 25.--Estimated annual operating cost

	Annual cost	Cost per thousand gallons water
Direct cost:		
Raw materials:		
Alamine 336 at $2.61 per pound.......	$ 210	$ 0.001
Isodecanol at $0.70 per pound........	60	0.001
Isopar"L" at $1.05 per gallon........	740	0.004
Paranox 100 at $1.60 per pound.......	140	0.001
Sulfuric Acid at $20.00 per ton......	38,536	0.198
Sodium Carbonate at $0.26 per pound..	1,830	0.009
Sodium Hydroxide at $1.13 per pound..	8,450	0.043
Steel Drums at $30.00 per each.......	8,100	0.042
Total..........................	189,090	0.299
Utilities:		
Electric power at $0.041 per kW•h....	45,960	0.236
Total..........................	45,960	0.236
Direct labor:		
Labor at $11.00 per hour.............	68,640	0.353
Supervision, 0 pct of labor.........	0	0.000
Total..........................	68,640	0.353
Plant maintenance:		
Labor...............................	51,700	0.266
Materials...........................	51,700	0.266
Total..........................	103,400	0.532
Payroll overhead, 35 pct of above payroll.............................	42,120	0.217
Operating supplies, 20 pct of plant maintenance..........................	20,680	0.106
Total direct cost................	469,890	1.743
Indirect cost, 40 pct of direct labor and maintenance........................	68,820	0.354
Fixed cost:		
Taxes, 1.0 pct of total plant cost.....	17,110	0.088
Insurance, 1.0 pct of total plant cost.	17,110	0.088
Depreciation, 20-yr life..............	87,000	0.448
Total operating cost.............	659,930	2.721

Liquid Emulsion Membrane:

Table 26.--Equipment cost summary, uranium LEM Process section

(Third quarter, 1995 prices)

Item	Equipment	Labor	Total
Feed Pump	$ 6,100	$ 390	$ 6,490
Mixers-2	14,770	1,440	16,210
Settler	11,100	1,250	12,350
Raffinate Pump	4,860	330	5,190
Coalescer	4,550	1,150	5,700
Emulsion Pump	2,850	120	2,970
Emulsion Surge Tank	8,140	910	9,050
Electrical Coalescer #1	2,720	1,150	3,870
Transformer	910	170	1,080
Internal Solution Pump	2,430	120	2,550
Internal Bleed Pump	1,900	120	2,020
Sulfuric Acid Make-up Pump	5,560	120	5,680
Sulfuric Acid Storage Tank	3,550	630	4,180
Internal Solution Surge Tank	3,770	420	4,190
Pre-Mix Tank	5,470	580	6,050
Dispersion Unit	2,400	320	2,720
Organic for Start-up	14,890	50	14,940
Organic Pumps-3	9,220	460	9,680
Stripping Mixer	3,100	420	3,520
Electrical Coalescer #2	2,380	80	2,460
Transformer	910	170	1,080
Organic Surge Tank	6,060	680	6,740
Organic Addition Pump	1,360	120	1,480
Organic Addition Tank	1,680	320	2,000
Sodium Carbonate Surge Tank	3,770	420	4,190
Sodium Carbonate Pump	3,150	120	3,270
Sodium Carbonate Tank	16,250	1,690	17,940
Barren Strip Pump	2,460	120	2,580
Enriched Strip Pump	2,460	120	2,580
Strip Bleed Pump	1,800	120	1,920
Carbonate Neutralization Tan.	1,480	290	1,770
Sulfuric Acid Storage Tank	1,880	330	2,210
Acid Pump	3,720	120	3,840
Precipitation Tank	1,360	290	1,650
Sodium Hydroxide Pump	1,360	120	1,480
Sodium Hydroxide Tank	3,230	420	3,650
Precipitate Filter	62,150	1,660	63,810
Roller Conveyer	550	50	600
Filtrate Pump	1,800	120	1,920
Total	228,100	17,510	245,610

Table 26.--Equipment cost summary, uranium LEM Process section--Continued

Total equipment cost x factor indicated:	
Foundations, x 0.133	30,280
Structures, x 0.050	11,410
Instrumentation, x 0.050	11,410
Electrical, x 0.124	28,180
Piping, x 0.300	68,430
Painting, x 0.020	4,560
Miscellaneous, x 0.100	22,810
Total	177,080
Total direct cost	422,610
Field indirect, 10.0 pct of total direct cost	42,269
Total construction cost	464,879
Engineering, 5.0 pct of total construction cost	23,244
Administration and overhead, 5.0 pct of total construction cost	23,244
Subtotal	511,367
Contingency, 10.0 pct of above subtotal	51,137
Subtotal	562,504
Contractor's fee, 5.0 pct of above subtotal	28,125
Section cost	590,629

Neutralization: Note that 41 pct of the operating cost is disposal of the sludge (table 28). If the sludge is rendered non-hazardous by removal of the radionuclides as demonstrated by the field tests of neutralization, on site disposal could significantly lower this cost.

Table 27.--Estimated capital cost, lime precipitation

Fixed capital:	
Lime treatment section	$ 545,180
Subtotal	545,180
Plant facilities, 10 pct of above subtotal	54,520
Plant utilities, 12 pct of above subtotal	65,420
Total plant cost	665,120
Land cost	0
Subtotal	665,120
Interest during construction period	11,180
Fixed capital cost	676,300
Working capital:	
Raw material and supplies	31,440
Product and in-process inventory	0
Accounts receivable	0
Available cash	50,710
Working capital cost	82,150
Capitalized startup costs	6,760
Subtotal	88,910
Total capital cost	765,210

Table 28.--Estimated annual operating cost, lime precipitation

	Annual cost	Cost per thousand gallons drainage
Direct cost:		
Raw materials:		
Lime at $100.00 per ton	$ 62,100	$ 0.319
Sulfuric acid at $85.00 per ton	11,480	0.059
Flocculent at $3,700.00 per ton	5,990	0.031
Lime sludge disposal at $50.00 per ton	297,000	1.528
Total	376,570	1.937
Utilities:		
Electric power at $0.041 per kW·h	14,240	0.073
Total	14,240	0.073
Direct labor:		
Labor at $11.00 per hour	137,280	0.706
Supervision, 0 pct of labor	0	0.000
Total	137,280	0.706
Plant maintenance:		
Labor	14,850	0.076
Materials	14,850	0.076
Total	29,700	0.152
Payroll overhead, 35 pct of above payroll	53,250	0.274
Operating supplies, 20 pct of plant maintenance	5,940	0.031
Total direct cost	616,980	3.173
Indirect cost, 40 pct of direct labor and maintenance	66,790	0.344
Fixed cost:		
Taxes, 1.0 pct of total plant cost	6,650	0.034
Insurance, 1.0 pct of total plant cost	6,650	0.034
Depreciation, 20-yr life	33,820	0.174
Total operating cost	730,890	3.759

Table 29.--Equipment cost summary, lime treatment section, lime precipitation

(Third quarter, 1995 prices)

Item	Equipment	Labor	Total
Lime precipitation tank	$ 15,280	$ 2,590	$ 17,870
Transfer pumps	6,220	630	6,850
Lime-mix tank	13,470	2,270	15,740
Slurry pumps	8,280	220	8,500
Polymer mix tank	3,180	740	3,920
Polymer feed pumps	3,710	220	3,930
Clarifier	51,370	4,150	55,520
Slurry feed pumps	9,760	220	9,980
Centrifuge	5,770	2,520	8,290
Filtrate receiver tank	260	40	300
Filtrate transfer pumps	2,650	220	2,870
Clean effluent tran pumps	8,610	580	9,190
pH adjustment tank	15,830	850	16,680
Sulfuric acid feed tank	14,920	600	15,520
Acid pumps	4,700	220	4,920
Effluent tran pumps	12,180	740	12,920
Wet-cake receiving hopper	100	10	110
Conveyer	26,210	1,270	27,480
Hopper	100	10	110
Total	202,600	18,100	220,700
Total equipment cost x factor indicated:			
Foundations, x 0.167			33,930
Structures, x 0.050			10,130
Instrumentation, x 0.050			10,130
Electrical, x 0.199			40,240
Piping, x 0.250			50,650
Painting, x 0.020			4,050
Miscellaneous, x 0.100			20,260
Total			169,390
Total direct cost			390,090
Field indirect, 10.0 pct of total direct cost			39,010
Total construction cost			429,100
Engineering, 5.0 pct of total construction cost			21,460
Administration and overhead, 5.0 pct of total construction cost			21,460
Subtotal			472,020
Contingency, 10.0 pct of above subtotal			47,200
Subtotal			519,220
Contractor's fee, 5.0 pct of above subtotal			25,960
Section cost			545,180

Radium Adsorption: While insufficient data was obtained to make a cost estimate, the costs should be similar to those of the ion exchange process without the U recovery costs. Using that assumption, the following estimates were made.

Table 30.--Estimated capital cost, radium adsorption

(Third quarter, 1995 basis)

Fixed capital:	
Ion exchange treatment section	$ 640,490
Subtotal	640,490
Plant facilities, 10 pct of above subtotal	64,050
Plant utilities, 12 pct of above subtotal	76,860
Total plant cost	781,400
Land cost	0
Subtotal	781,400
Interest during construction period	13,130
Fixed capital cost	794,530
Working capital:	
Raw material and supplies	590
Product and in-process inventory	0
Accounts receivable	0
Available cash	12,690
Working capital cost	13,280
Capitalized startup costs	7,950
Subtotal	21,230
Total capital cost	815,760

Table 31.--Estimated annual operating cost, radium adsorption

	Annual cost	Cost per thousand gallons drainage
Direct cost:		
Utilities:		
Electric power at $0.041 per kW·h	$ 12,210	$ 0.063
Total	12,210	0.063
Direct labor:		
Labor at $11.00 per hour	68,640	0.353
Supervision, 0 pct of labor	0	0.000
Total	68,640	0.353
Plant maintenance:		
Labor	17,990	0.093
Materials	18,000	0.093
Total	35,990	0.186
Payroll overhead, 35 pct of above payroll	30,320	0.156
Operating supplies, 20 pct of plant maintenance	7,200	0.037
Total direct cost	154,360	0.795
Indirect cost, 40 pct of direct labor and maintenance	41,850	0.215
Fixed cost:		
Taxes, 1.0 pct of total plant cost	7,810	0.040
Insurance, 1.0 pct of total plant cost	7,810	0.040
Depreciation, 20-yr life	39,730	0.204
Total operating cost	251,560	1.294

Table 32.--Equipment cost summary, ion exchange treatment section, radium adsorption

(Third quarter, 1995 prices)

Item	Equipment	Labor	Total
Pumps	$ 10,290	$ 680	$ 10,970
Ion exchange columns	24,100	1,100	25,200
Column pumps	34,420	2,320	36,740
Strip sol surge tank	2,710	490	3,200
Strip sol feed pumps	2,430	220	2,650
Strip liq col trans pump	2,650	220	2,870
Hydrogen peroxide tank	100	10	110
Transfer pumps	3,040	220	3,260
Caustic soda tank	2,960	500	3,460
Transfer pumps	1,600	220	1,820
Uranium prec tank	3,290	410	3,700
Filters	134,660	8,590	143,250
Filtrate receiver tank	210	30	240
Pumps	2,650	220	2,870
Total	225,110	15,230	240,340
Resin cost			25,490
Total equipment cost x factor indicated:			
Foundations, x 0.234			52,570
Structures, x 0.050			11,260
Instrumentation, x 0.050			11,260
Electrical, x 0.151			34,080
Piping, x 0.250			56,280
Painting, x 0.020			4,500
Miscellaneous, x 0.100			22,510
Total			192,460
Total direct cost			458,290
Field indirect, 10.0 pct of total direct cost			45,830
Total construction cost			504,120
Engineering, 5.0 pct of total construction cost			25,210
Administration and overhead, 5.0 pct of total construction cost			25,210
Subtotal			554,540
Contingency, 10.0 pct of above subtotal			55,450
Subtotal			609,990
Contractor's fee, 5.0 pct of above subtotal			30,500
Section cost			640,490

Radium Precipitation: A cost evaluation for a plant processing 500 gpm was conducted based upon the results obtained during the field test. Several minor changes were made to the flowsheet as a result of the field test. These included decreasing the number of precipitation tanks from 4 to 3 and adding a centrifuge to further dewater the Ra precipitate prior to disposal.

Table 33.--Estimated capital cost,
Midnite Mine process, uranium removal, 500 g/min
(Third quarter, 1995 basis)

Fixed capital:	
Radium removal section	$ 1,696,140
Subtotal	1,696,140
Plant facilities, 10 pct of above subtotal	169,610
Plant utilities, 12 pct of above subtotal	203,540
Total plant cost	2,069,290
Land cost	0
Subtotal	2,069,290
Interest during construction period	34,760
Fixed capital cost	2,104,050
Working capital:	
Raw material and supplies	2,350
Product and in-process inventory	0
Accounts receivable	0
Available cash	17,360
Working capital cost	19,710
Capitalized startup costs	21,040
Subtotal	40,750
Total capital cost	2,144,800

Table 34.--Estimated annual operating cost, Midnite Mine process, radium removal, 500 g/min

	Annual cost	Cost per thousand gallons drainage
Direct cost:		
Raw materials:		
Barium chloride at $0.31 per pound	$ 2,590	$ 0.013
Radium sludge disposal cost at $0.33 per pound	3,080	0.016
Steel barrels at $30.00 each	320	0.002
Total	5,990	0.031
Utilities:		
Electric power at $0.041 per kW·h	19,110	0.098
Total	19,110	0.098
Direct labor:		
Labor at $11.00 per hour	22,880	0.118
Supervision, 0 pct of labor	0	0.000
Total	22,880	0.118
Plant maintenance:		
Labor	56,440	0.290
Materials	56,440	0.290
Total	112,880	0.580
Payroll overhead, 35 pct of above payroll	27,760	0.143
Operating supplies, 20 pct of plant maintenance	22,580	0.116
Total direct cost	211,200	1.086
Indirect cost, 40 pct of direct labor and maintenance	54,300	0.279
Fixed cost:		
Taxes, 1.0 pct of total plant cost	20,690	0.106
Insurance, 1.0 pct of total plant cost	20,690	0.106
Depreciation, 20-yr life	105,200	0.541
Total operating cost	412,080	2.118

Table 35.--Equipment cost summary,
Midnite Mine process, radium removal, 500 g/min

(Third quarter, 1995 prices)

Item	Equipment	Labor	Total
Feed pumps	$ 9,710	$ 630	$ 10,340
Radium precipitation tank	15,580	1,730	17,310
Transfer pumps	12,180	740	12,920
Barium chloride mix tanks	8,060	1,020	9,080
Transfer pumps	2,880	220	3,100
Filter	545,990	17,410	563,400
Filtrate receiver tank	4,920	400	5,320
Total	599,320	22,150	621,470
Total equipment cost x factor indicated:			
Foundations, x 0.063			37,610
Buildings, x 0.404			242,180
Structures, x 0.050			29,970
Instrumentation, x 0.050			29,970
Electrical, x 0.051			30,700
Piping, x 0.250			149,830
Painting, x 0.020			11,990
Miscellaneous, x 0.100			59,930
Total			592,180
Total direct cost			1,213,650
Field indirect, 10.0 pct of total direct cost			121,370
Total construction cost			1,335,020
Engineering, 5.0 pct of total construction cost			66,750
Administration and overhead, 5.0 pct of total construction cost			66,750
Subtotal			1,468,520
Contingency, 10.0 pct of above subtotal			146,850
Subtotal			1,615,370
Contractor's feed, 5.0 pct of above subtotal			80,770
Section cost			1,696,140

Waterglass: Compression of the time frame due to closure of USBM limited the ability to do a detailed cost analysis. Enough data was obtained, however, to do a simple calculation of reagent consumption. If one assumes addition of 1000 ppm Si based on data in table 6, then 7,500 ppm of waterglass containing 28.66 pct SiO_2 (13.4 pct Si) is required. This calculates to be 62 lb/1000 gal. Based on a cost of $9.54/100 lbs (*10*), the reagent cost would be $5.94/1000 gal. While 70 pct of the reagent can reportedly be recovered for recycle, this still represents a reagent cost of $1.78/1000 gal. Other cost estimates indicate that reagent costs are from 3 to 50 pct of the total. Other factors that would increase the cost of this process are the filtration steps. Every filtration discussed in the results section was reported to be slow with material passing through the filter. While this process would replace both the neutralization and U removal processes, it consumes NaOH in place of lime; a condition that has not proven to be cost effective at other locations.

SUMMARY AND RECOMMENDATIONS

Utilizing its water treatment expertise, the U.S. Bureau of Mines reviewed and evaluated options for treatment of the approximately 500 million gal of contaminated water in flooded pits at the Midnite Mine on the Spokane Indian Reservation. Dawn Mining is currently treating the water by lime neutralization and processing the resultant sludge at their off site mill in Ford, Washington. If Dawn Mining Company becomes unable to meet the commitment to treat the contaminated water at the Midnite Mine, the Department of the Interior (DOI) may have to assume contingency treatment of the mine water. Since the DOI would not have access to the off site mill or tailings pond, this would require disposal of the sludge in a regulated landfill. Cost of commercial disposal is estimated to be $28 per 1,000 gal of mine water treated. At the current treatment rate of up to 500 gal per min, disposal costs would be approximately $5,400,000 per year.

The best option was determined to be to continue to use lime neutralization as the final treatment but to remove the radionuclides in pretreatment steps so that the resultant sludge would be nonhazardous. Review and evaluation of existing water treatment technologies, including a Request for Information (RFI) advertised in the Commerce Business Daily, identified two techniques each for removing each uranium and radium that were tested on site. Three other techniques, identified through the RFI, were subjected to laboratory tests.

Results of the field tests demonstrated that treatment with either a strong base anion exchange resin or liquid emulsion membrane will decrease uranium to less than 0.7 ppm; the level required to avoid generation of a low level radioactive waste during lime neutralization. Uranium removal by pretreatment would be cost effective since cost estimates are $1.41 per 1,000 gallons using ion exchange or $2.72 per 1,000 gallon using liquid emulsion membrane for savings of $5,100,000 and $4,900,000 per year respectively. Laboratory testing of the techniques identified through the RFI demonstrated that all three were capable of removing uranium. None of them, however, were found to have any significant advantage over ion exchange using a strong base resin. Since there is commercial scale information available for uranium recovery using strong base ion exchange resins, this would be the preferred technique. A summary of estimates for both capital and operating costs is shown below:

Process	Total Capital Cost	Operating Cost, per thousand gal
IX	$834,000	$1.41
LEM	$806,000	$2.72
Neutralization	$765,000	$3.76
Radium Adsorption	$835,000	$1.29
Radium Precipitation	$2,145,000	$2.12
Waterglass	NA	NA

Less information is available on the impact of radium in the lime sludges. Removal of uranium may be sufficient to produce a nonhazardous waste and radium discharge limits could continue to be met using the current barium chloride addition during lime neutralization. If radium removal is also required, barium chloride treatment can be done prior to lime treatment. This would increase treatment costs by $2.12 per 1,000 gallons or $410,000 per year. Based on the results of the field tests, barium chloride treatment should not be done prior to uranium removal since it removes part of the U. If removal of 60-75 percent of the radium is sufficient, treatment using natural zeolites would be a practical option. Treatment costs would be approximately 60 pct that of the barium chloride treatment; $250,000 per year. Removal of both uranium and radium in separate pretreatment steps would still save $4,500,000 to $4,900,000 per year.

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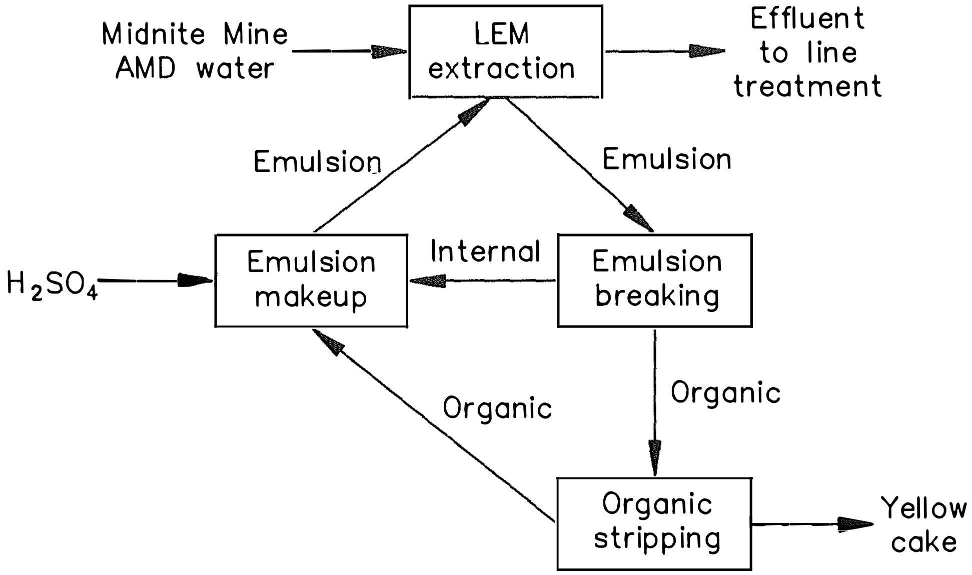

Figure 1. Simplified flowsheet of LEM system.

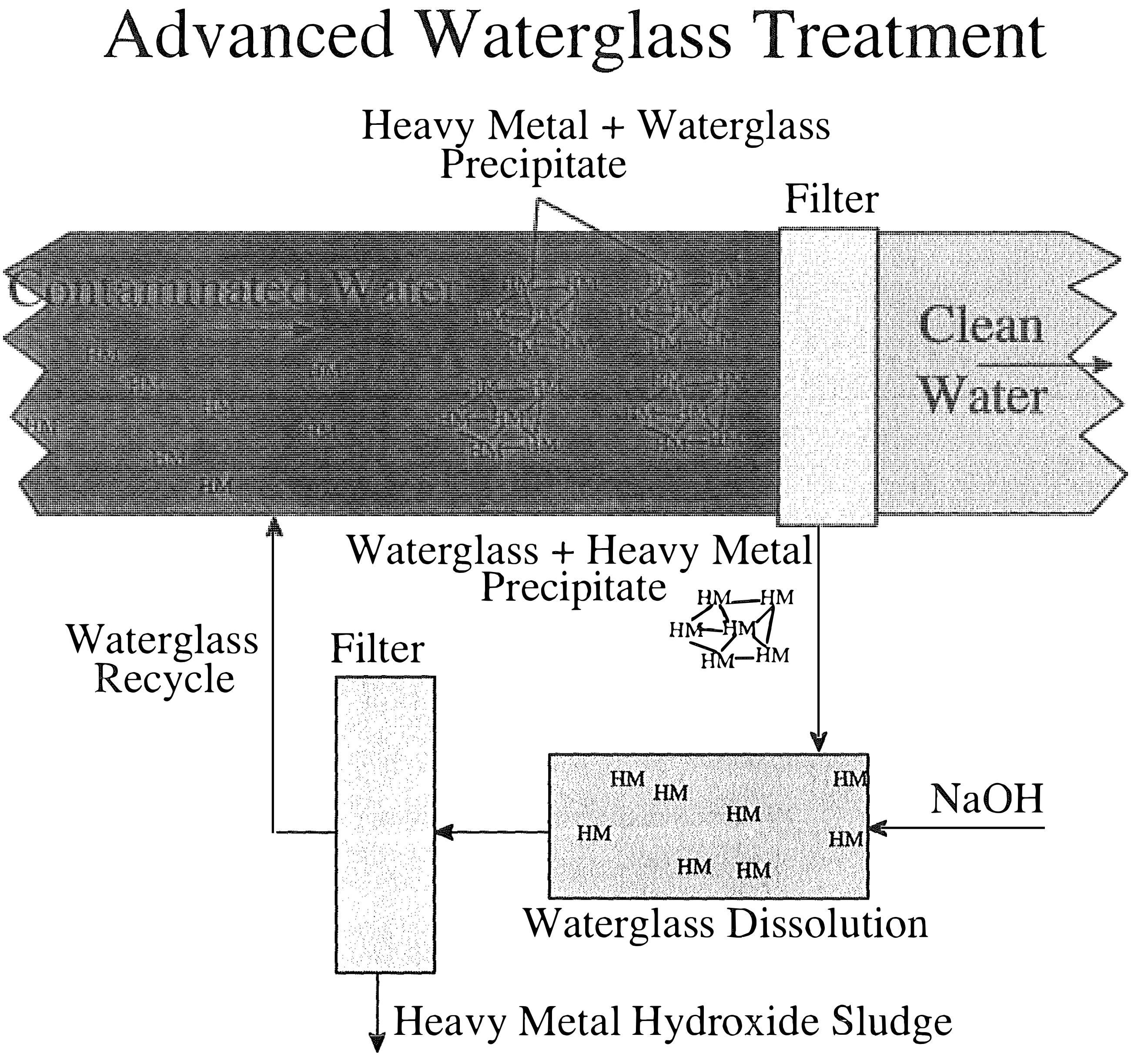

Figure 2. Waterglass process flowsheet.

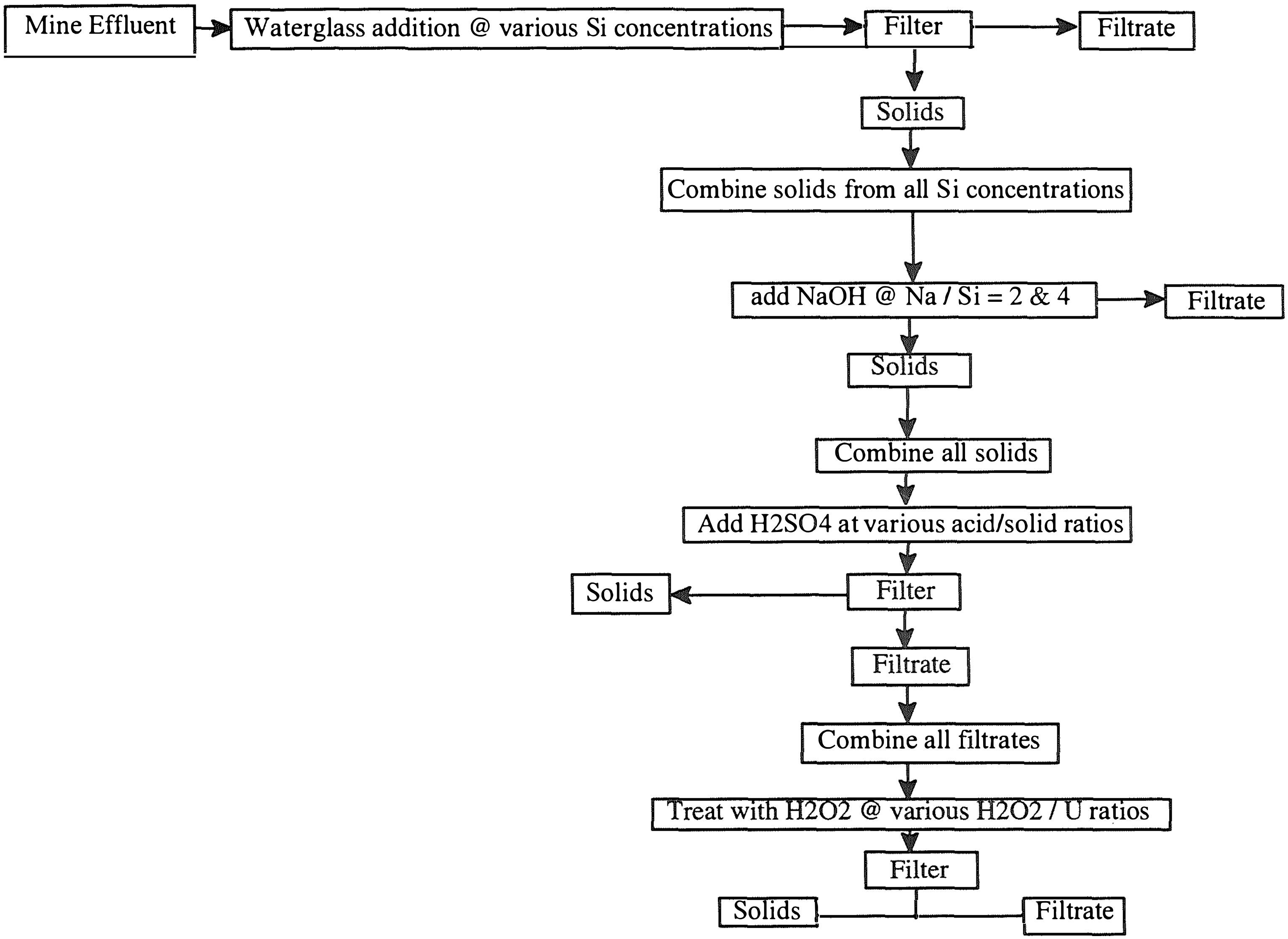

Figure 3. Flowsheet for tasks 1 to 3.

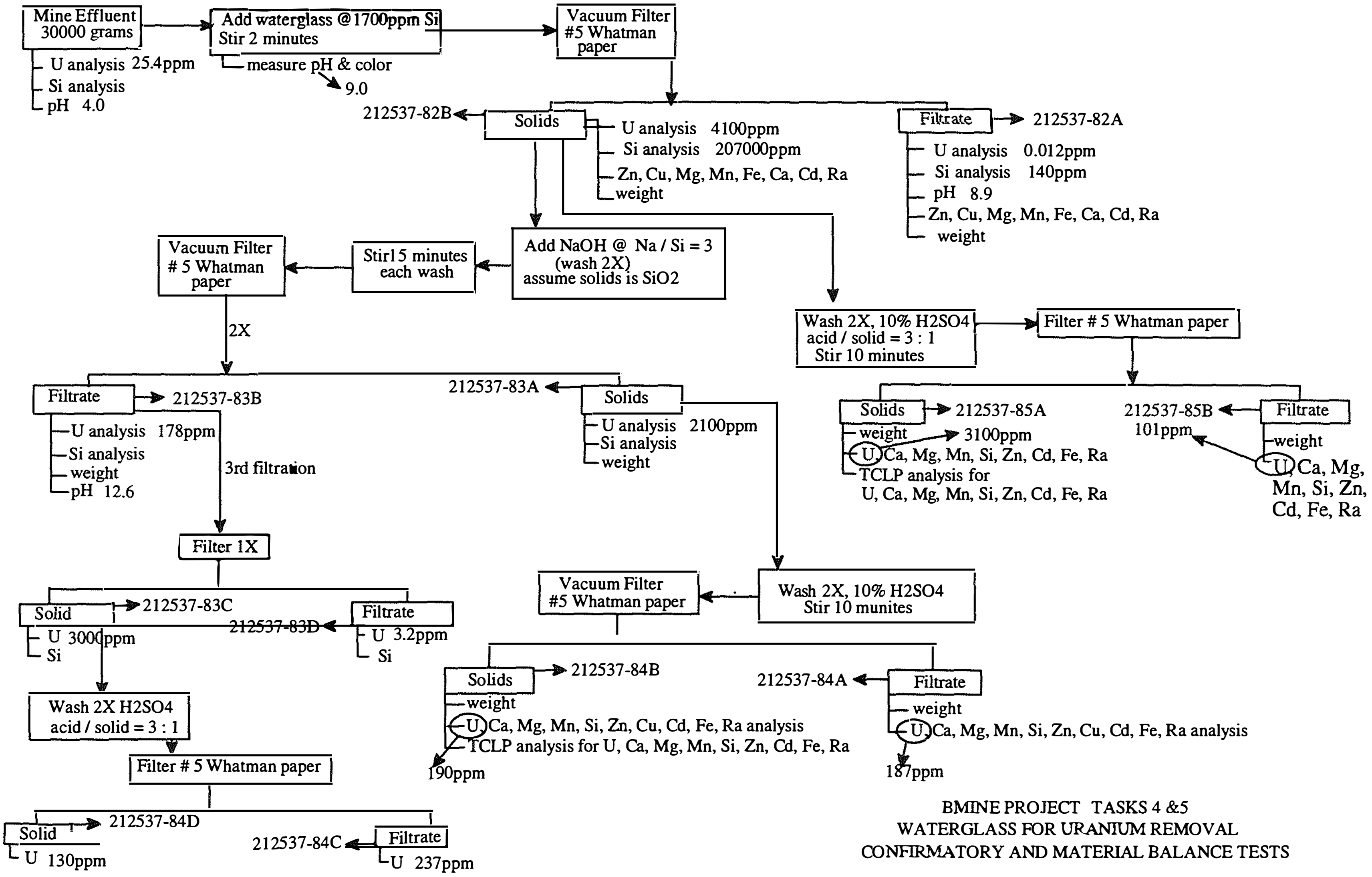

Figure 4. Flowsheet for tasks 4 and 5.

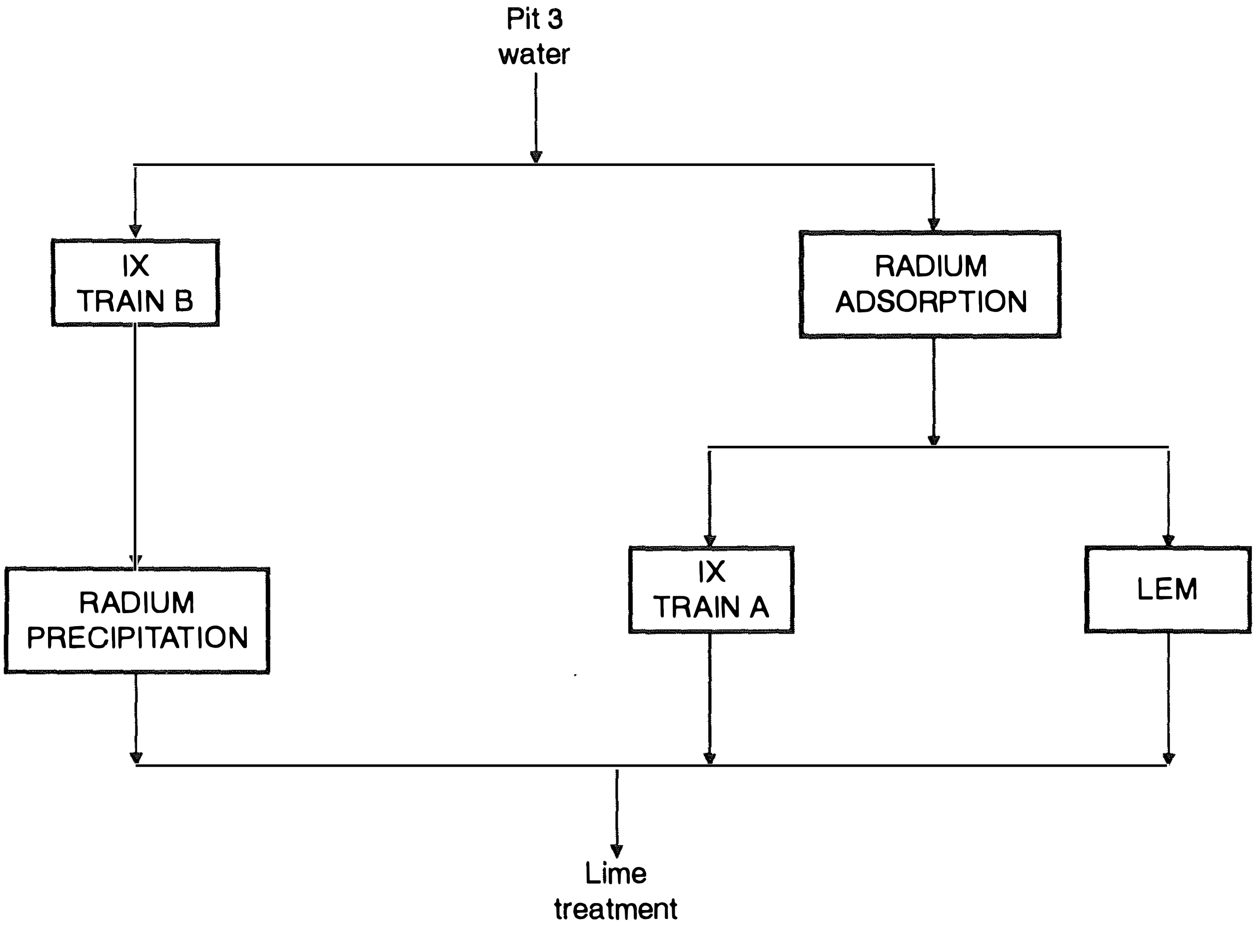

Figure 5. Field test treatment flowsheet.

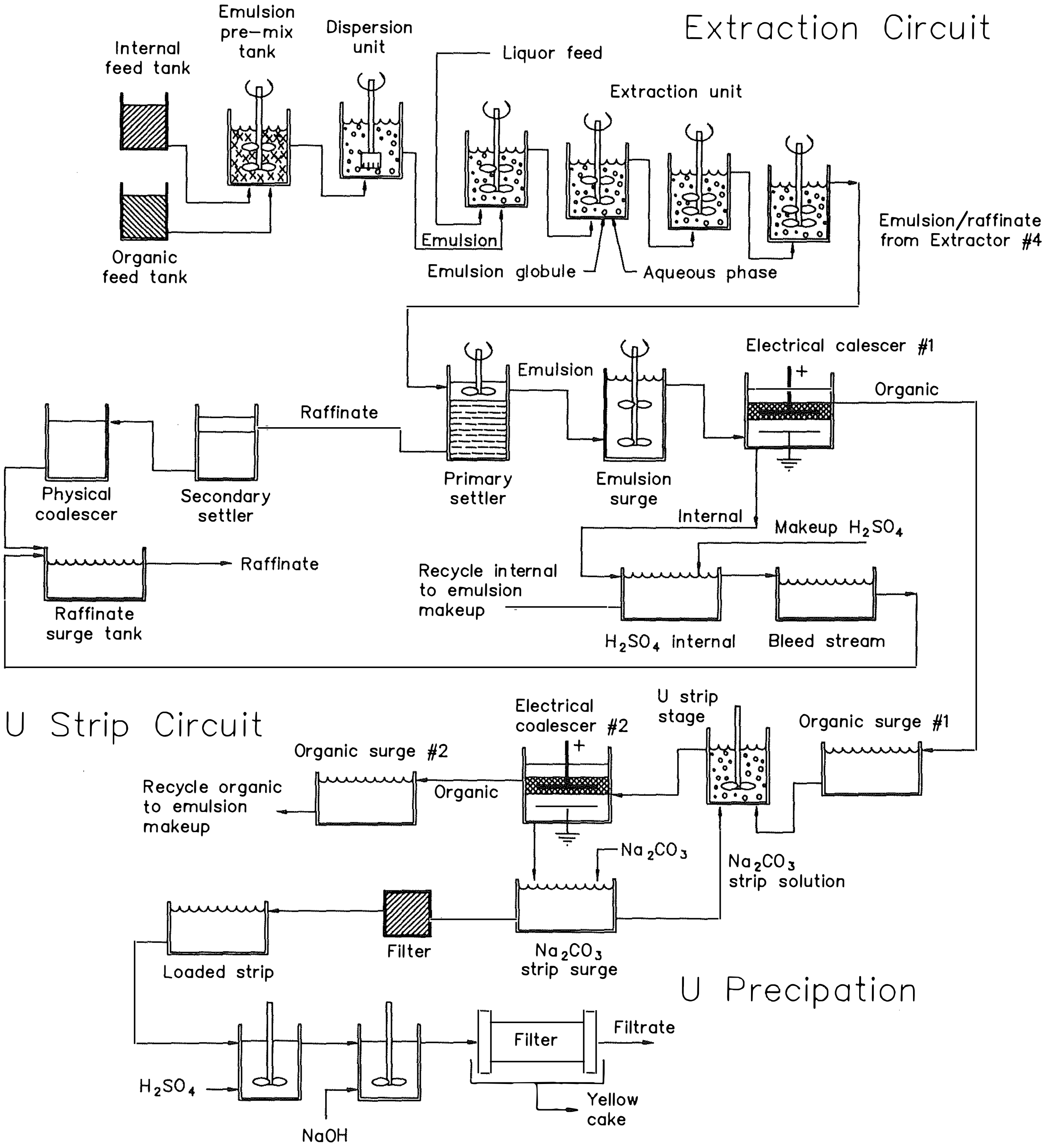

Figure 6. Optimization of the sodium silicate addition rate.

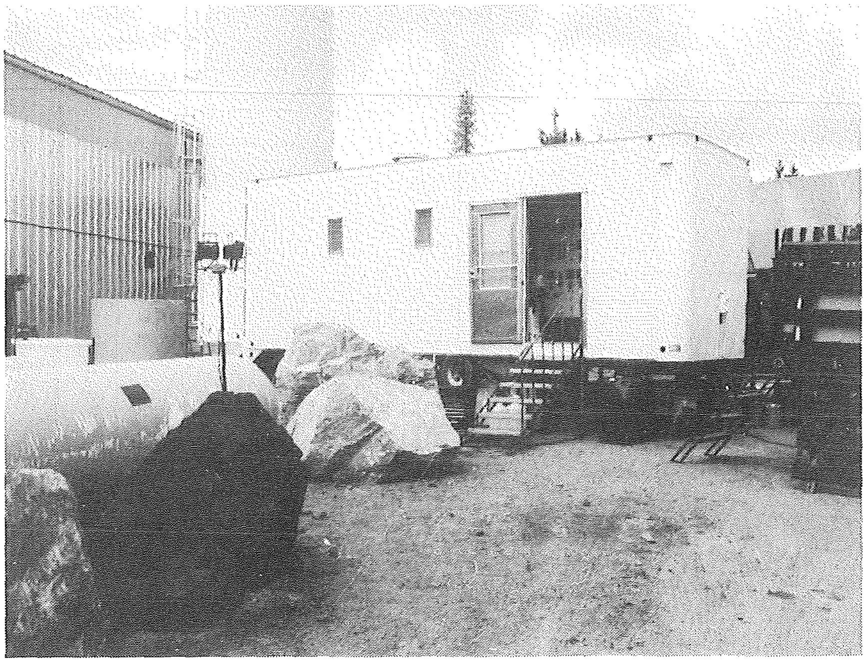

Figure 7. Twenty-four foot trailer at Midnite Mine site.

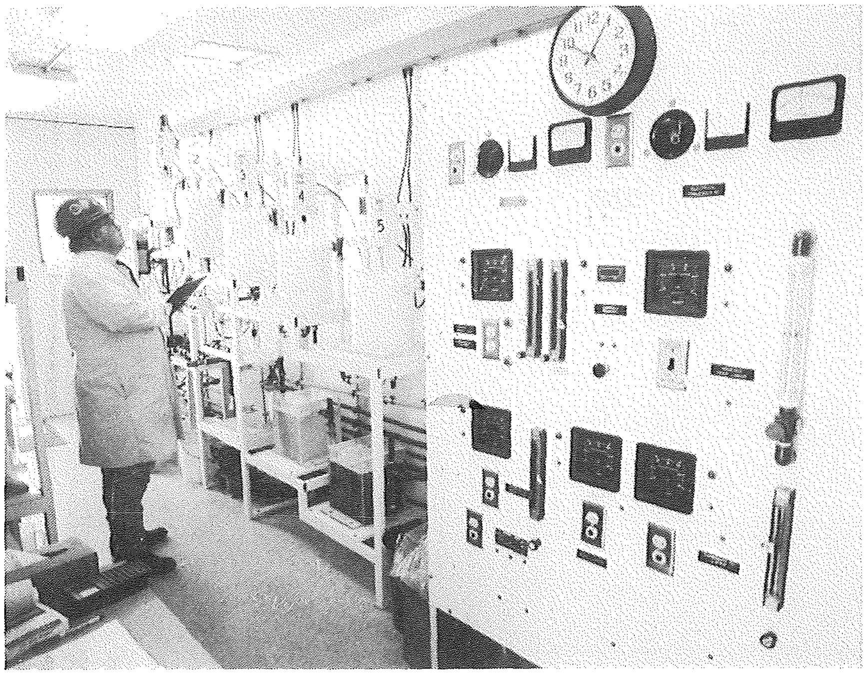

Figure 8. Interior of LEM trailer during Midnite Mine field test.

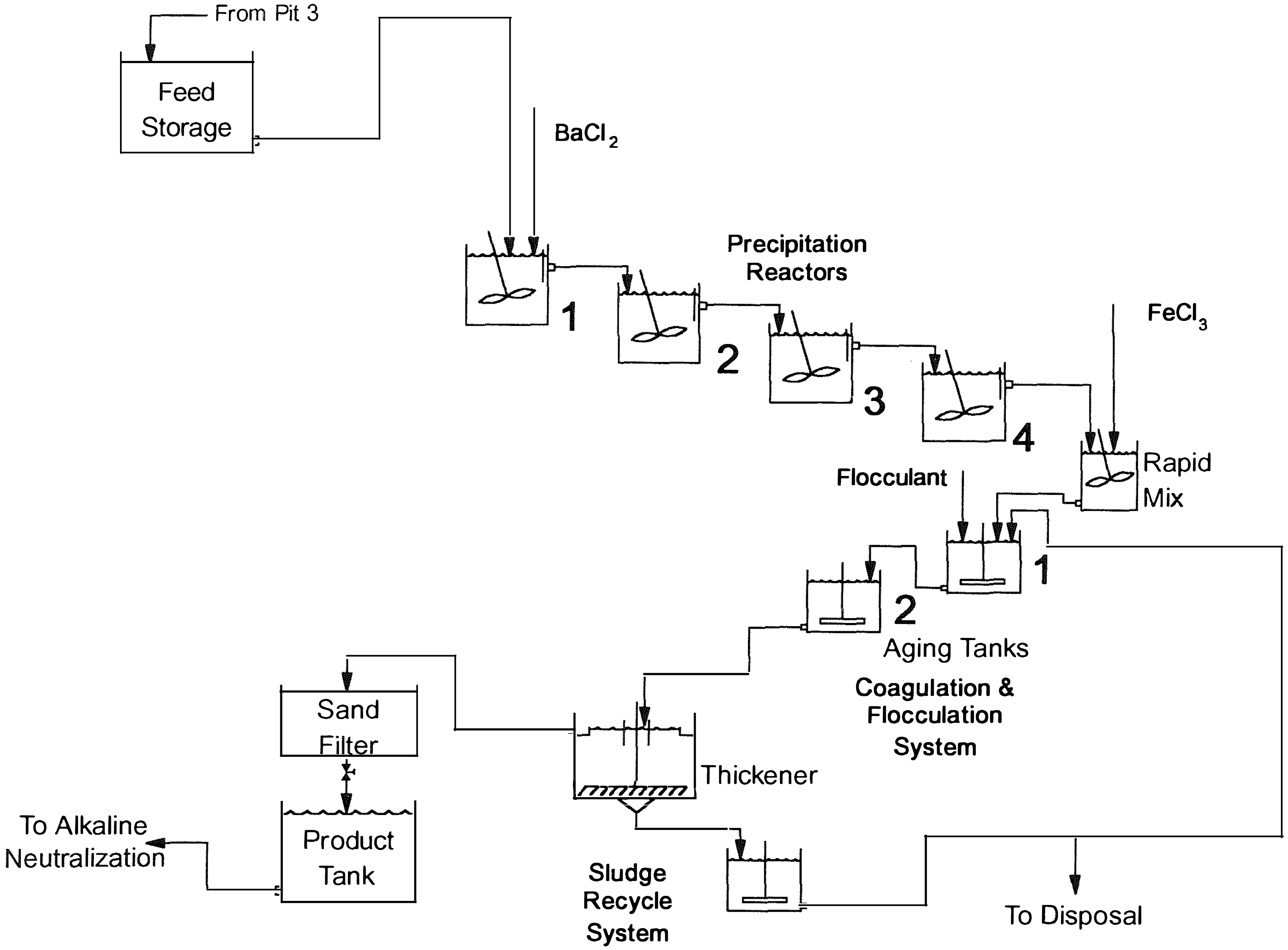

Figure 9. Flowsheet for radium precipitation circuit.