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Laboratory Evaluation of Limestone and Lime Neutralization of Acidic Uranium Mill Tailings Solution

Progress Report

Prepared by B. E. Opitz, M. E. Dodson, R. J. Serne

Pacific Northwest Laboratory
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PREVIOUS DOCUMENTS IN SERIES

This progress report is the fourth NUREG document prepared for this project, Tailings Neutralization, Alternatives for Immobilizing Toxic Material in Tailings (FIN B2370 Task 4). The project has three thrust areas, neutralization methods selection, laboratory analysis of selected neutralizing reagents and a field demonstration of the most effective neutralizing method as determined by the laboratory studies. The project was initiated in September, 1981. Other reports from this project are:

NUREG/CR-2938, "Tailings Treatment Techniques for Uranium Mill Waste: A Review of Existing Information," D. R. Sherwood, R. J. Serne, September 1982.

NUREG/CR-3030, "Evaluation of Selected Neutralizing Agents for the Treatment of Uranium Tailings Leachates: Laboratory Progress Report," D. R. Sherwood, R. J. Serne, February 1983.

PNL-4677, "Field Demonstration Plan for Verification of Uranium Mill Tailings Neutralization Technique," B. E. Opitz, R. J. Serne, March 1983.

ABSTRACT

Laboratory experiments were conducted to evaluate the performance of a two step neutralization scheme for treatment of acidic uranium mill tailings solutions. Tailings solutions from the Lucky Mc Mill and Exxon Highland Mill, both in Wyoming, were initially neutralized with limestone, CaCO_3 , to an intermediate pH of either 4.0 or 5.0, followed by lime, Ca(OH)_2 , neutralization to pH 7.3. On the basis of these combination limestone/lime treatment methods, CaCO_3 neutralization to pH 4 followed by further neutralization with Ca(OH)_2 to pH 7.3 resulted in the highest quality effluent solution with respect to EPA's water quality guidelines. Furthermore, this combination method is the most cost-effective treatment procedure tested in our studies over the last 2 yr.

Neutralization experiments to evaluate the optimum solution pH for contaminant removal were performed on the same two tailings solutions utilizing only lime Ca(OH)_2 as the neutralizing agent. The pH optimization data indicates solution neutralization above pH 7.3 does not significantly increase removal of pH dependent contaminants from solution.

Column leaching experiments were performed on the neutralized sludge material (the precipitated solid material which forms as the acidic tailings solutions are neutralized to pH 4 or above). The sludges from Lucky Mc and Exxon neutralized tailings solutions were packed into columns and then contacted with laboratory prepared synthetic ground water until several effluent pore volumes were collected. Effluent solutions were analyzed for macro ions, trace metals and radionuclides in an effort to evaluate the long term effectiveness of attenuating contaminants in sludges formed during solution neutralization. Neutralized sludge leaching experiments indicate that Ca, Na, Mg, Se, Cl, and SO_4 are the only constituents which show solution concentrations significantly higher than the synthetic ground water in the early pore volumes of long term leaching studies. Longer-term leaching studies are continuing.

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EXECUTIVE SUMMARY

Laboratory experiments were conducted to evaluate the performance of a two step neutralization procedure for treatment of acidic uranium mill tailings solution. The two step solution treatment, initial limestone neutralization to intermediate solution pH's of 4.0 or 5.0, followed by lime neutralization to $\approx$ pH 7.3, was identified in a previously completed literature review (see Sherwood and Serne 1982) as a potentially cost effective treatment to attenuate contaminants in tailings solution. Most applications of this type of solution treatment have been performed on acid mine drainage or coal pile runoff waters and have proven to be one of the least expensive treatment methods tested for those industries.

Studies examining the feasibility of combination limestone/lime neutralization were initiated this past year. Acidic tailings solutions from the Lucky Mc and Exxon Highland Mills, both in Wyoming, were neutralized to pH 4.0 or pH 5.0 in separate tests using limestone (CaCO_3), followed by further solution neutralization with lime (Ca(OH)_2), to pH 7.3.

Evaluations of the effectiveness of the combination limestone/lime treatment for neutralizing acidic uranium tailings solutions were based on two criteria: 1) treated effluent water quality, and 2) reagent cost. A third criteria, neutralized sludge handling properties, will be evaluated in future laboratory investigations.

Treated effluent water quality data suggest that initial solution neutralization with CaCO_3 to either pH 4 or pH 5 followed by lime neutralization to pH 7.3 is effective in reducing contaminant concentrations in tailings solution. Total dissolved solids contents were reduced by greater than 55% for the Lucky Mc tailings solution and greater than 57% for Exxon tailings solutions. Certain macro ions (Cl , NO_3 and SO_4), trace metals (Cd and Se) and one radionuclide (^{226}Ra) still show solution concentrations above EPA's maximum contaminant levels for various types of waters. Ions such as these will require some type of additional solution treatment such as specific ion removal techniques, to reduce their solution concentration to meet waste water quality guidelines.

Studies designed to determine the optimum final pH for solution neutralization were also conducted. The optimum final pH for tailings solution neutralization is defined as the pH where further addition of a neutralizing reagent no longer significantly increases the removal of contaminants from solution. Data from this study could result in significant solution treatment savings by preventing over-neutralization of the tailings solution through the addition of excess neutralizing reagents. Results of these experiments performed on the Lucky Mc and Exxon tailings solutions show neutralization of tailings solution above pH 7.3 does not significantly increased removal of contaminants. Tailings solution constituents such as Al , As , Ba , Cr , Fe , Si , V , ^{210}Pb , ^{238}U and ^{230}Th showed reductions in concentrations or activities in excess of 98% after neutralization to pH 7.3. Acid tailings constituents not

effectively removed by Ca(OH)_2 neutralization include the macro ions, Ca, Na, Mg, Cl, NO_3 and SO_4 and the trace metals, Co, Mo, and Se.

Of the original 15 constituents (including solution pH) in the low pH Lucky Mc tailings solution whose concentrations or activities exceeded the EPA recommended water quality maximum concentration limits, only two macro-ions, SO_4 and NO_3 , one trace metal, Se, and one radionuclide, ^{226}Ra , exceed the EPA standards after neutralization with Ca(OH)_2 . For the Exxon solution out of the original 10 constituents exceeding the limits, only one macro ion, SO_4 , one trace metal, Se, and one radionuclide, ^{226}Ra , exceed the limits after similar neutralization.

To evaluate the long term contaminant attenuation properties of the sludge material generated, column leaching studies were conducted. Laboratory prepared synthetic ground water was pumped at a constant flow rate through the sludge columns. Leaching data indicate that constituents such as Ca, Na, Mg, Se, Cl and SO_4 are readily leached from the sludge material during initial leachate contact. As leaching continues for several pore displacement volumes, the concentrations of these constituents decrease and approach those of the synthetic ground water. No significant contaminant release was detected for other macro ions, trace metals or any of the radionuclides after the initial contact with leach solution. These sludge leaching studies indicate the sludge end product, generated as neutralization occurs, remains as a chemically stable, low density precipitate. When leached with low ionic strength ground water, the sludge does not permit the dissolution and release of the pH dependent contaminants but does release those soluble salts previously mentioned. Tailings solution neutralization is an effective means of controlling many contaminants originally present in the untreated acid solution. Extended sludge leaching experiments will continue to be monitored to evaluate the effectiveness of tailings solution neutralization for long term contaminant attenuation.

Reagent cost data for the two step treatment show that initial solution neutralization to pH 4.0 with CaCO_3 followed by lime neutralization to pH 7.3 is the least costly method of neutralizing tailing solution examined to date. The reagent costs incurred in neutralizing acidic tailings solution using the combination limestone/lime treatment are predicted to be less than 2% of 1982 uranium (as U_3O_8) production costs and extrapolation of laboratory reagent cost data. Furthermore, if the costs of capital equipment and operation costs triple the cost of the reagents alone, the additional increase still remains below 4% of the fully burdened uranium production costs.

INTRODUCTION

Conventional(a) uranium mills account for most of the uranium produced in the United States (85 to 90% of the total U.S. production in 1979). A majority of United States (U.S.) uranium producers employ a sulfuric acid leaching process for uranium extraction. In addition to the extraction and purification of uranium, the milling process generates two waste forms for which disposal is necessary: the solid fraction of the ore material known as tailings and the solution fraction of the process waste sometimes called raffinate, tailings liquor or tailings solution. Over the course of one day an active mill may process greater than 1500 MT of uranium-bearing ore. Since many of the previously mined ore deposits and those currently being mined contain less than one half of 1% uranium by weight, every metric ton of ore material processed results in approximately one metric ton of solid waste tailings. Furthermore, for uranium recovery, every metric ton of processed ore produces ≈ 1 metric ton of acidic (pH 2.0 or less) waste tailings solution. This results in the generation of 1500 MT of solid tailings and 1500 MT (1.5×10^6 liters) of tailings solution each day.(1)

The untreated uranium mill tailings acidic waste solutions characteristically contain a high total dissolved solids content, high concentrations of macro cations (i.e., Al, Ca, Fe, Mg, Na) and anions (i.e., Cl, NO_3 , SO_4). In addition other contaminants in the solutions include trace metals (i.e., As, Cd, Cr, Cu, Mo, Ni, Pb, Se, etc.) and radionuclides (i.e., natural uranium, ^{210}Pb , ^{226}Ra , ^{230}Th). Many of these cations and anions are mining and milling additives to enhance uranium production. For instance, constituents such as ammonium and nitrate are added as blasting agents in the mining process. Others, such as Fe, Mn, Na, Cl, and SO_4 are process additives in the milling cycle used as oxidizing agents, or to aid in dissolution or precipitation reactions to recover the desired uranium. Many of the trace metal concentrations originate from two sources: 1) impurities arising from the use of industrial or commercial grade process chemicals and 2) dissolution of trace metals from the ore material. When the ore material is being processed with acidic leachate in the milling circuit, the trace metals can dissolve in the sulfuric acid solution (pH 2.0 or less) used for uranium extraction. This dissolution occurs since the solubility of many trace metals is pH dependent and results in higher solution concentrations as acid contact continues.

The acidic dissolution reactions also release the radionuclides present in the ore material. Since the milling extraction procedures are specific for uranium recovery, several of the radioactive daughter products, ^{230}Th , ^{226}Ra and ^{210}Pb remain in the acidic tailings solution throughout the milling process. Due to the long half-life of ^{230}Th ($\approx 80,000$ years) and ^{226}Ra (≈ 1600 years) the tailings and tailings solution can remain radioactive virtually indefinitely.

(a) Conventional uranium milling used here refers to the processes of mining, crushing, grinding and leaching of the ore primarily for uranium recovery. This would include chemical separation and concentration of uranium.(1)

Since the concentrations and activities of several elements in untreated tailings solutions often exceed the Environmental Protection Agency (EPA) water control guidelines by several orders of magnitude, several options have been developed for disposal of tailings solids and solutions. Options include evaporation ponds with synthetic or clay liners, unlined disposal ponds with underdrains for solution recycling, and mine shaft disposal. Regardless of the method chosen, if the acid waste is not contained in the designated disposal impoundment, the high concentration of the previously mentioned contaminants may present a potential environmental problem in terms of ground water or surface water contamination.

Several instances of surface or ground water contamination have occurred in the U.S.⁽²⁾ e.g., Canon City, Colorado (Cotter), Ford, Washington (Dawn Mining), Gas Hills, Wyoming (Union Carbide). (Details may be found in Minerals Resources Waste Management Team Report 1, 1980.) Such contamination may have been minimized or totally avoided if the waste solution had been treated prior to or during disposal.

Cumulative estimates through the year 2000 for uranium requirements for electrical power generation are greater than 500,000 MT of U_3O_8 .⁽¹⁾ Recent estimates show conventional mill processing would generate 4.6×10^8 MT of tailings.⁽³⁾ As a result of these predicted future uranium requirements and the previously mentioned environmental problems, the U.S. Nuclear Regulatory Commission (NRC) established a project to assess the effectiveness, benefits and costs of neutralizing tailings and tailings solutions to reduce the quantity of toxic and radioactive contaminants available for migration.

Presently very few, if any, U.S. mills neutralize uranium mill tailings or tailings solutions. Therefore, the data and experience for U.S. uranium mill treatment techniques is extremely limited. As part of the program a literature review was conducted⁽⁴⁾ to identify and to assess the effectiveness of current tailings treatment techniques for attenuating contaminants in tailings solutions and from the leaching of solid uranium mill tailings. While very little information was available on U.S. tailings treatment techniques considerable research has been performed on neutralizing acid mine drainage from other industries (i.e., metal plating or surface disposal of coal mine waste). In addition, substantial research has been performed on Canadian uranium mill tailings impoundments which have been neutralized. The Canadian information is very useful but not directly transferable to U.S. technology since Canadian ores contain a significantly higher content of sulfide-bearing minerals such as pyrite. Even though Canadian uranium producers are required to neutralize acidic tailings prior to disposal, over periods of time (1 to 20 years) the tailings can eventually reacidify due to oxidation of pyrite and subsequent generation of hydronium ions.^(5,6,7) Because U.S. tailings do not contain as much pyrite as Canadian tailings reacidification is not expected to be as troublesome as in Canada.

Three general treatment methods were identified in the literature review:⁽⁴⁾ neutralization, fixation and specific constituent removal. During neutralization, a reagent is added to the tailings solution to neutralize the

acidity and raise the pH, reducing the solubility of various pH-sensitive contaminants. In contrast, fixation processes add material such as lime, cement or asphalt to the waste to produce a physically stable composition that resists ground-water-induced leaching of hazardous constituents. Specific constituent removal encompasses varying techniques, such as alternate ore leaching processes, effluent treatment with sorption, or ion exchange agents or selected precipitation that reduce specific constituent concentrations in tailings solution.

Based on the literature review, neutralization appears to be better suited for treating uranium mill tailings than fixation processes or specific ion removal because neutralization:

1. limits the solution concentration of many contaminants
2. treats the solution at a reasonable cost and,
3. does not tremendously increase the volume of waste as do fixation processes.

However, the effectiveness of the neutralization process depends on the reagent used as well as the waste being treated. Furthermore, the selection of tailings solution neutralization as the most viable method of treatment was based, in part, upon results obtained from the neutralization of acid mine drainage and Canadian uranium mill wastes as opposed to actual observations on U.S. acid uranium mill wastes because few if any U.S. mills neutralize acidic waste tailings solutions.

The literature review revealed that little solution treatment data were available for potentially important radionuclides, toxic trace metals and certain macro ions. Therefore, controlled laboratory experiments comparing various neutralizing agents for treatment of acidic uranium mill tailings solutions from representative U.S. sites were initiated. The results of those controlled laboratory experiments were the subject of the first laboratory progress report entitled "Evaluation of Selected Neutralizing Agents for the Treatment of Uranium Tailings Leachates," by D. R. Sherwood and R. J. Serne.⁽⁸⁾ In that study six chemical reagents were chosen based on:

1. the literature review⁽⁴⁾
2. cost and
3. chemical availability information taken from issues of the Chemical Marketing Reporter

The reagents chosen were: coal fly ash, calcium carbonate (CaCO_3), hydrated lime (Ca(OH)_2), magnesia (MgO), soda ash (Na_2CO_3), and caustic soda (NaOH). Within the literature review, evaluations of the strengths and weaknesses of four of these reagents (limestone, lime, soda ash and caustic soda) were obtained. All four were confirmed as candidates for laboratory study with the lime tentatively selected as the most desirable. As magnesia is very similar to lime it was included in the list for laboratory investigation. Finally coal fly ash was studied because of its alkaline nature, its low cost and to evaluate whether the waste from one industry could provide a useful resource to another industry.

Preliminary evaluation of the effectiveness of the treatment of uranium tailings solutions by the selected neutralizing agents under controlled laboratory conditions was based on three criteria. The criteria were: treated effluent water quality, neutralized sludge handling and hydraulic properties, and reagent costs and efficiency. Water quality considers the total dissolved solids content but emphasizes the removal of radionuclides and potentially toxic trace metals. Sludge handling considers the mass of sludge produced and its attendant water content and drainage characteristics. Efficiency considers the actual amount of reagent used to raise the pH of the tailings solution to pH 7 versus the theoretical amount of reagent needed based on its equivalent weight.

The results of those initial laboratory experiments suggested hydrated lime as the best potential neutralizing agent. While the other neutralizing agents studied were effective in reducing the concentrations of many contaminants in tailings solutions, there was not one reagent effective for all of the contaminants investigated. (Details may be found in the first laboratory progress report.)⁽⁸⁾ Furthermore, the sludge associated with hydrated lime treatment had more desirable properties than the sludges from other neutralizing agents tested. Reagent usage and cost results have shown that hydrated lime neutralizes solution acidity with an efficiency of approximately 90%, and yields reagent costs equivalent to that of the most economical single reagent tested.

Based on the results of the initial laboratory screening studies additional hydrated lime/tailings solution interaction experiments were performed to further assess the effectiveness of this reagent in attenuating the contaminants associated with uranium mill tailings solution. Results from these further studies are discussed in this report. These hydrated lime [$\text{Ca}(\text{OH})_2$] experiments included studies to evaluate the optimum pH for solution neutralization. The optimum pH is defined as the solution pH where further addition of a neutralizing reagent no longer significantly removes contaminants. Also, column leaching studies were performed on the neutralization reaction precipitates, referred to as sludge. The sludge material was leached with a laboratory prepared synthetic ground water to evaluate the long term control of contaminants after precipitation from solution. Furthermore, new tailings solution neutralization experiments were initiated on a two component acid solution treatment which has been effective in treating acid mine drainage. The two component treatment utilizes calcium carbonate (CaCO_3) as the initial neutralizing reagent to pH 4.0 or 5.0 followed by hydrated lime [$\text{Ca}(\text{OH})_2$] neutralization to the desired pH of ≈ 7.3 . The results of these laboratory experiments completed through June 1983 are the subject of this progress report.

After completion of laboratory experiments in 1984 and with concurrence of NRC, a field demonstration project using the best neutralization process(es) determined from the available literature and laboratory studies will be performed. Field demonstration results would verify laboratory findings and provide large-scale cost and contaminant migration data that would be helpful in evaluating and promulgating NRC regulations on neutralization of uranium mill wastes. Furthermore, the data may substantiate that treatment of uranium

mill wastes as they are generated may prove to be more cost effective than future remedial action measures necessary at many sites to ensure contaminant immobilization.

METHODS AND MATERIALS

SAMPLE CDLLECTION

In November 1982, PNL scientists visited the Pathfinder (Lucky Mc) Gas Hills Mill outside of Riverton, Wyoming and the Exxon Highland Mill near Glenrock, Wyoming. Samples of acidic tailings liquors, solid tailings, and undisturbed overburden sediments were collected from each mill site for experiments in the tailings neutralization project and other companion projects.

Lucky Mc tailings liquors and solid tailings were collected from pond 2A at the location shown in Figure 1. Tailings liquor was sampled from the east side of pond 2A, 100 meters north of where the tailings solution/slurry was currently being discharged into the evaporation pond. In addition, approximately 95 liters of tailings solution were collected at the same location, and neutralized in the field to pH 10 with hydrated lime, Ca(OH)_2 . The large volume of sludge material produced via precipitation reactions are being physically and chemically characterized for long term contaminant attenuation properties. The tailings solution neutralization process consisted of filling each of two 115 liters barrels with approximately 95 liters of tailings liquor at the pond edge. Next, 2000 grams of Ca(OH)_2 were added to each barrel. The solution was then stirred vigorously and allowed to settle for 1 hour, after which the supernate in the top 1/2 of each barrel was disposed of and the remaining solution/slurry saved. Using the total acidity values for Lucky Mc tailings solution given in the initial neutralization laboratory report,⁽⁷⁾ it was calculated that 2000 grams of lime would be enough neutralizing reagent to raise the pH of the tailings liquor above 8.0. Initial onsite pH readings of the untreated tailings liquor and neutralized solution showed pH $\approx$ 2 and pH $\approx$ 10, respectively.

Exxon Highland Mills tailings liquor and solid tailings were sampled in November 1982 from the north side of the present tailings pond, opposite the area where the slurry pipeline was located as shown in Figure 2. This location was also used to collect Exxon tailings liquor for the field neutralization process and is designated as sampling point 1.

The procedure used to collect the field neutralized solution/slurry for the Exxon Highland Mill tailings liquor was identical to that employed at the Lucky Mc mill. Due to the lower total acidity of the Exxon solution, 1500 grams of lime were used per 95 liters of acidic tailings solution.

Solid tailings and overburden samples were collected from both the Lucky Mc and Exxon Highland mills. The Lucky Mc tailings were collected from material near the edge of the embankment along the dam face on the west end of the tailings impoundment. Exxon tailings were collected from sampling point 2 as shown in Figure 2. Overburden material from the Lucky Mc mill was collected from the surface in an area just south of Pond #4. Exxon overburden samples were collected south of the tailings pond dam outside the existing embankment

FIGURE 1. Lucky Mc Mill Site and Sampling Locations

FIGURE 2. Exxon Highland Mill Site and Sampling Locations

and below the existing solution level of the tailings evaporation pond at sampling point 3 in Figure 2. The overburden and tailings samples from both mills are currently being used in a companion study, the results of which will be presented in the next laboratory progress report.

CHEMICAL REAGENTS

Laboratory-grade calcium carbonate (limestone) and calcium hydroxide (lime), were obtained from a local supply house. Finely-ground chemicals (<200 mesh) were used in all experiments requiring neutralizing reagents, to ensure faster solution/reagent reaction rates and to facilitate mixing.

LABORATORY PREPARED SYNTHETIC GROUND WATER MAKEUP

Laboratory prepared ground water was produced for use in all column leaching studies. The procedure used to formulate this synthetic ground water was derived from the chemical characterization data presented for Exxon Highland Mill process water (local groundwater).⁽⁹⁾ The groundwater sample was collected in April 1979 from inside the Exxon Highland Mill and it is used throughout Exxon's uranium extraction and purification process.

Laboratory prepared ground water was produced in 20 l batches by the addition of measured amounts of reagent grade chemicals. These reagents were chosen to provide cations and anions in amounts to produce concentrations matching those quoted for actual Exxon Highland Mill process water. Upon addition of all reagents to 20 l of warm distilled water, solution pH was adjusted from pH $\approx$ 9.0 to pH = 7.6 with the addition of small aliquots of concentrated sulfuric acid.

The reagents and amounts of each reagent needed to produce 20l of laboratory prepared ground water are given in Table 1.

Chemical characterization data for the laboratory prepared ground water used in leaching studies are presented in Table 2. Also included are the characterization results from the actual (April 1979) Exxon Highland Mill process water.⁽⁹⁾

TAILINGS SOLUTION CHARACTERIZATION

Detailed analysis of the untreated acid tailings liquors and the treated effluents from the neutralization experiments were performed for the solutions collected from both the Lucky Mc and Exxon Highland Mills. Macro-cations (Al, Ca, Fe, Mg, Mn, Si, Na, and Sr) present in the tailings solution and treated effluents were determined using a Jarrell-Ash emission spectrometer with an inductively coupled plasma source (ICP). Macro-anions (SO_4 , NO_3 , and Cl) were determined by ion chromatography on a Dionex Model 16 ion chromatograph. Trace metal constituents were determined either with the ICP (Cu and Zn) or by graphite furnace atomic absorption (Ag, As, Ba, Cd, Co, Cr, Pb, Mo, Se, and V) using a Perkin Elmer Model 5000 and HGA-5000 graphite furnace. The various methods of analyses for the specified elements are shown in Table 3. The neutralized effluents for cation and radionuclide analyses were preserved by

TABLE 1. Laboratory Prepared Ground Water Constituents

<u>Reagent</u>	<u>Grams of Reagent/20 L</u>
MgSO ₄	1.088
NaSO ₄	4.091
NaCl	1.169
NaNO ₃	0.075
CaCO ₃	2.647

TABLE 2. Laboratory Groundwater Chemical Composition

<u>Parameter</u>	<u>Exxon Highland⁽⁹⁾ Mill Process Water</u>	<u>Laboratory Prepared Ground Water</u>
Al	<0.1	<0.1
As	<0.02	<0.02
Ca	53	69
Cr	<0.05	<0.01
Fe	<0.1	<0.1
Li	<0.05	<0.05
Mg	11.0	11.0
Mo	0.5	<0.01
Na	91	105
P	<0.01	<0.1
Pb	<0.01	<0.02
Se	<1.0	0.34 ^(a)
Si	3.5	0.54
Sr	0.9	0.03
Zn	0.05	<0.02
Cl	36	44
NO ₃	3.5	3.3
SO ₄	181	300
EC (mmhos/cm)	0.82	0.76
pH (units)	8.2	7.6

(a) Analysis performed by ICP.

TABLE 3. Elements/Anions Considered and Proposed Analytical Methods

<u>Elements/Anions</u>	<u>ICP</u>	<u>Ness</u>	<u>IC</u>	<u>Tritrate</u>	<u>AA-GF</u>	<u>Intrinsic</u>
<u>Macro Cations</u>						
Al	X					
B	X					
Ca	X					
Fe	X					
Mg	X					
Mn	X					
Si	X					
Na	X					
Sr	X					
<u>Trace Metals</u>						
As					X	
Ba					X	
Cd					X	
Cr					X	
Cu	X					
Pb					X	
Mo					X	
Se					X(a)	
Ag					X	
V					X	
Zn	X				X	
<u>Radionuclides</u>						
²¹⁰ Pb						X
²³⁰ Th						X
²²⁶ Ra						X
U						X
<u>Anions</u>						
NO ₃			X			
PO ₄			X			
SO ₄			X			
Cl			X			

(a) AA hydride

acidification to pH <2 with ultra-pure nitric acid. The neutralized effluent samples used for anion analysis were preserved by storing the samples in sealed, air-tight containers.

Radionuclide concentrations in the tailings liquors and treated effluents were determined using high-resolution gamma spectroscopy. For these analyses, a volume of solution (250 ml) is evaporated leaving the residual evaporites. These salts are mixed with a cellulose binder and pressed into a pellet of fixed geometry. A Princeton Gamma-Tech intrinsic germanium diode coupled with a Nuclear Data ND6620 Nuclear Analyzer was used to analyze for uranium-238 and three of its daughter products. Lead-210, uranium-238, thorium-230, and radium-226 concentrations were determined over a counting time of seven hours using gamma intensities of 46.5, 63.3, 67.7, and 185.8 KeV, respectively. The ^{238}U activity is actually based on counting a gamma ray (63.3 KeV) of its daughter product ^{234}Th . The radium-226 activity is calculated after correction of the count rate of the 185.8 KeV peak for a contribution from uranium-235 which also has a gamma ray (183.7 KeV) nearby. The correction factor is based on the ratio of $^{238}\text{U}/^{235}\text{U}$ activity found in natural ore deposits (~21.5). Thus, upon calculation of the ^{238}U content an activity for ^{235}U may be calculated and subtracted from the total activity in the region of 185 KeV to yield an estimate of the radium-226 content. Detector efficiencies were determined on NBS traceable uranium bearing sediments pressed into pellets identical to those used for evaporite analyses.

The pH, Eh and electrical conductivity of the tailing liquors and treated effluents were measured. Solution pH and Eh were determined using a Corning model 130 pH/Eh meter and a combination pH electrode or a platinum banded redox electrode. Electrical conductivity was measured using a Markson Model 10 portable conductivity meter.

The Salotto method of total acidity⁽¹⁰⁾ was used to determine the total acidity of the Lucky Mc and Exxon tailing liquors. Briefly, the procedure is to titrate the acid solution with sodium hydroxide to a pH of 7.3 and calculate the total acidity as mg/l of CaCO_3 by the number of equivalents of NaOH added. The total dissolved solids (TDS) content of the tailings solutions and treated effluents was calculated in milligrams/liter by summation of the concentration values of the macrocations and anions that were determined by the methods described earlier.

SOLID SLUDGE CHARACTERIZATION

Samples of the solid sludge generated during the field neutralization of Lucky Mc and Exxon Highland acidic tailings liquors with calcium hydroxide, were analyzed for radiological properties by using similar procedures as those listed in the solution chemical analysis section. The only difference in the procedure is that a 10 gram oven-dried subsample of the solid material was utilized rather than the residual evaporites used for radionuclide determination in liquid samples.

pH OPTIMIZATION

For the purpose of this study, the optimum pH for acidic uranium mill tailings solution neutralization has been defined as the solution pH where further addition of a neutralizing agent no longer significantly increases removal of contaminants. To determine the optimum pH of neutralized tailings solution, samples of both Lucky Mc and Exxon Highland Mill acidic tailings liquors were neutralized from pH $\approx$ 2 to pH values of approximately 5.0, 6.5, 7.2 and 8.0 using reagent grade Ca(OH)_2 . After samples of each acidic tailings liquor had reached the desired solution pH, they were centrifuged, filtered and analyzed for solution quality. The neutralized solution chemical composition was then compared to solution data for the untreated liquors.

Duplicate samples containing 400 mL of either Lucky Mc or Exxon Highland Mill acidic tailings solution were placed in 0.5 liter pre-rinsed polyethylene bottles. Based on the theoretical equivalent weight of reagent grade Ca(OH)_2 , and the measured total acidity of the two tailings solutions, enough reagent was added to each sample to raise the pH to a desired level. Desired pH levels were pH = 5.0, 6.5, 7.2 and 8.0. After reagent addition, the bottles were placed on a oscillating shaker for 48 hrs to facilitate mixing. Upon completion of the 48 hr contact period, the pH of each sample was measured. If the pH of the supernate was at the desired level, the experiment was stopped at that point. If a supernate's pH was above or below a desired pH level, additional portions of acidic tailings liquor or reagent were added to the slurry and the above process repeated until the desired pH's were reached.

Once the samples had reached the desired pH levels, they were centrifuged, and the supernates were drawn off and filtered through a 0.45 micron membrane. The filtered solutions were preserved appropriately and then analyzed by the methods described in the tailings solution characterization section.

LIMESTONE/LIME BATCH CONTACT NEUTRALIZATION TESTS

Four hundred milliliters of each acid tailings solution were placed in pre-rinsed 0.5 liter polyethylene bottles. Based on the equivalent weight of limestone, the total acidity of the tailings solution and results of previous laboratory studies enough dry limestone was added to the bottles to raise the solution/slurry pH to $\approx$ 4.0 in one test and pH 5.0 in another. After reagent addition, the samples were placed in a linear oscillating shaker for 48 hr to ensure adequate mixing.

After the 48 hr contact period, the sample pH was measured. If the solution pH above the slurry had reached the desired pH of 4.0 or 5.0 depending on the test, the experiment was temporarily stopped. If the pH was less than desired an additional portion of limestone was weighed and added to the bottle and the bottle was placed on the shaker for an additional two days. The pH was then re-measured and the cycle continued until the initial desired pH was attained. Once each sample had reached the desired pH it was centrifuged, and the supernate solution filtered through a 0.45 micron membrane. The filtered solutions were subsampled, preserved (dependent on the analysis to be

performed) and then analyzed for anions, cations, and radionuclides by the techniques described in the solution chemical analysis section.

The remaining pH 4.0 and 5.0 filtered solutions then had weighed portions of calcium hydroxide added to the bottle and the bottle again placed on the shaker for 48 hours. The pH was re-measured and the cycle continued until a solution pH of ≈ 7.2 was achieved. Once the sample achieved the desired pH it was centrifuged, the supernate was again filtered, subsampled, and preserved for analyses as described earlier. The known weights of the two reagents added in each step were used to evaluate the cost of neutralizing acidic uranium mill tailings solution using the two component scheme. Tables presented in the results section show the average constituent concentrations and reagent costs obtained from duplicate tests.

COLUMN LEACHING EXPERIMENTS

Column leaching experiments were conducted on the sludge material which forms during the neutralization process. The sludge, collected as a field neutralized solution/slurry from the Lucky Mc and Exxon Highland mill sites, had the excess solution removed by filtration through a 0.45 micron filter and the remaining solid residue was dried in a convective oven at 105°C for 24 hr. The oven dried sludge from each mill site was placed in a ball mill crusher and disaggregated. Known weights of the <150 mesh sample were packed into four columns of known volume. Characteristics of the columns from each mill site are listed in Table 4. Clear acrylic tubing and end caps were used in constructing the columns for the experiments.

Laboratory prepared ground water, with elemental composition shown in Table 1, was used as the leachate. Flow through the columns was from the bottom to the top to ensure complete column saturation. Constant flow rates were maintained throughout the experiment with Buchler multistatic pumps (Model 426-2000) adjusted to 0.11 ml/min. Flow rates were monitored daily and samples were collected every 36 hr. Sample pH's and Eh's were taken after collection and then subsamples for anion, cation and radionuclide determinations were

TABLE 4. Column Parameters

	<u>Sample Identification</u>	
	<u>Lucky Mc</u>	<u>Exxon</u>
	<u>Sludge</u>	<u>Sludge</u>
Length (cm)	8.9	8.9
Inner Diameter (cm)	8.9	8.9
Bulk Density (g/cm ³)	0.80	0.87
Pore Displacement Volume (mL)	387	373
Flow Rate mL/min	0.11	0.11

prepared. Samples used for cation and radionuclide analyses were preserved by adding concentrated ultra-pure nitric acid to drop the pH to less than pH 2.0.⁽¹¹⁾ Samples for anion analyses were not treated and were analyzed as soon as possible after collection. All chemical analyses were performed as described in the solution characterization section.

RESULTS AND DISCUSSION

UNTREATED TAILINGS SOLUTION CHARACTERIZATION

The results of uranium mill tailings solution characterization from the Lucky Mc and Exxon Mills are shown in Table 5. The Lucky Mc Mill tailings solution had a low pH (1.7), high total acidity (15,700 mg/L as CaCO_3) and high total dissolved solids content (34.2 g/L). The total acidity content of 15,700 mg/L corresponds to a total acid content of greater than 300 milliequivalents per liter. In comparison, the Exxon uranium mill tailings solution had a slightly higher pH (2.0), a total dissolved solids content of 12.5 g/L and a total acidity of 105 mg/L as CaCO_3 . The difference in solution composition that may account for the Exxon tailings solution being more "dilute" than the Lucky Mc tailings solution may be due to the addition of mine dewatering solution in order to move the tailings to the pond. Further additional mine drainage is pumped directly into the pond so that samples collected from the evaporation pond include acidic tailings liquors diluted with several drainage solutions. Solution properties such as these illustrate how tailings solutions from two uranium mills can vary in solution composition even though both mills employ a sulfuric acid leaching process for uranium extraction.

The dissolved constituents shown in Table 5 originate from one of two sources: 1) from process additives and 2) as by-products of the ore dissolution process. Process additives used in uranium milling include sulfuric acid (H_2SO_4), sodium perchlorate (NaClO_4), ammonium nitrate (NH_4NO_3) and ferrous carbonate (FeCO_3). These additives account for most of the high solution content of sulfate, chloride, nitrate, iron and the low pH. Other constituents in the tailings solution result from dissolution of the ore grade rocks and sediments during the leaching process or impurities contained in industrial grade chemical additives.

Reviewing the Environmental Protection Agency's maximum concentration levels shown in Table 6 and the results of the tailings solution characterization shown in Table 5, the Lucky Mc tailings solution contains four macro-ions, Fe, Mn, NO_3 , and SO_4 , seven trace metals, As, Cd, Cr, Cu, Pb, Se, and Zn, and three radionuclides, ^{210}Pb , ^{230}Th and ^{226}Ra , whose concentrations in solution exceed the set limits. Similarly for the Exxon tailings solutions, three macro ions, Fe, Mn, and SO_4 , four trace metals As, Cd, Cr and Se, and three radionuclides ^{210}Pb , ^{230}Th and ^{226}Ra , also exceed the water quality limits in Table 6.

Uranium mill tailings solutions containing high concentrations of these macro ions, trace elements and radionuclides, present a potential source of environmental contamination to surrounding sediments, ground water and surface water.

TABLE 5. Solution Chemistry of Lucky Mc and Exxon Highland Mill Tailings Liquors and Field Neutralized Tailings Liquor

Parameter	Lucky Mc Untreated Solution	Lucky Mc Neutralized Solution	Exxon Untreated Solution	Exxon Neutralized Solution
pH (Units)	1.7	9.4	2.0	12.5
Eh (mv)	785	231	807	162
Conductivity ($\mu\text{mho/cm}$)	32,300	11,900	10,400	4,950
Total Suspended Solids (mg/L)	50	10	20	20
Total Dissolved Solids (g/L)	34.2	6.4	12.5	3.7
Total Acidity (as mg/L CaCO_3)	15,735	ND(a)	5,269	ND
<u>Macro ions (mg/L)</u>				
Al	1,100	0.6	440	0.6
B	1.1	0.19	0.4	0.08
Ca	600	520	560	870
Fe	3,000	<0.5	1000	<0.5
K	160	170	44	55
Mg	1,250	6.4	540	0.7
Mn	160	<0.2	50	<0.2
Na	1,600	1,570	340	330
Si	300	10	310	1.1
Sr	14	1.6	8.5	7.8
SO_4	25,000	3,940	9,300	1,730
Cl	1,190	1,280	300	303
NO_3	302	247	9	<1
<u>Trace Metals (mg/L)</u>				
Ag	<0.02	<0.02	<0.02	<0.02
As	15.50	0.02	0.21	<0.01
Ba	0.07	<0.05	<0.05	0.11
Cd	0.25	<0.01	0.03	<0.01
Co	4.93	<0.02	1.31	<0.02
Cr	2.09	<0.01	1.25	<0.01
Cu	1.45	<0.02	0.97	<0.02
Mo	7.74	4.1	<0.02	<0.02
Pb	0.85	<0.02	<0.02	<0.02
Se	1.10	0.78	1.35	0.82
V	19.17	<0.02	10.71	<0.02
Zn	16	<0.2	4.5	<0.2
<u>Radionuclides (pCi/L)</u>				
^{210}Pb	12,300	<50	2,100	<50
^{238}U	15,550	70	2,100	<50
^{230}Th	185,400	<400	97,140	<400
^{226}Ra	4,020	55	758	81

(a) ND = Not Determined

TABLE 6. Maximum Concentration Levels for Specified Water

Constituent	Standard EPA-Inactive Tailings ^(a) mg/L	EPA-Interim Primary Drinking Water ^(b) mg/L	EPA-Secondary Drinking Water ^(c) mg/L	EPA Livestock Consumption ^(d) mg/L	Radiation Protection ^(e) pCi/L
Al	---	---	---	5	
As	0.05	0.05	---	0.2	
Ba	1.0	1.00	---	---	
Cd	0.01	0.01	---	0.05	
Cr	0.05	0.05	---	1.00	
Pb	0.05	0.05	---	0.1	
Hg	0.002	0.002	---	0.010	
Mo	0.05	---	---	uncertain ^(g)	
N in NO ₃	10.0	10.0	---	23	
Se	0.01	0.01	---	0.05	
Ag	0.05	0.05	---	---	
F	---	1.4-2.4 ^(f)	---	2.0	
Cl	---	---	250	---	
Cu	---	---	1.0	0.5	
Fe	---	---	0.3	No limit	
Mn	---	---	0.05	No limit	
SO ₄	---	---	250	---	
Zn	---	---	5.0	2.5	
B	---	---	---	5.0	
V	---	---	---	0.1	
TDS	---	---	500	---	
pH	---	---	6.5-8.5	---	

Constituent	(pCi/L)	(pCi/L)	(pCi/L)	(pCi/L)	(pCi/L)
²²⁶ Ra+ ²²⁸ Ra	5.0	5.0	---	5.0	---
Natural U	10.0	---	---	---	2 × 10 ⁴
²³⁸ U	---	---	---	---	4 × 10 ⁴
²³⁰ Th	---	---	---	---	2000
²²⁶ Ra	---	---	---	---	30
²¹⁰ Pb	---	---	---	---	100

(a) Environmental Protection Agency, "Proposed Standards for Inactive Uranium Processing Sites," 40 CFR Part 192 in FR Vol. 46, No. 6 (Jan 9, 1981) pp. 2556-2563.

(b) Environmental Protection Agency, "National Interim Primary Drinking Water Regulations," 40 CFR Part 141 in FR Vol. 45 (Aug. 27, 1980).

(c) Environmental Protection Agency, "National Secondary Drinking Water Regulation," 40 CFR Part 143 in FR Vol. 44 (July 19, 1979), pp. 42198.

(d) Environmental Protection Agency, "Quality Criteria for Water," EPA 440/a-76-023, July 1976.

(e) U.S. Nuclear Regulatory Commission, "Standards for Protection Against Radiation," Title 10-Chapter 1, Code of Federal Regulations, Part 20.

(f) Depends on temperature of water.

(g) EPA could not agree upon the level at which Mo is toxic to livestock.

NEUTRALIZED TAILINGS SOLUTION CHARACTERIZATION

The results of the analyses performed on the field neutralized tailings solution are shown in Table 5. The data show a significant reduction in dissolved constituents when compared to the low pH untreated solution. In the neutralized Lucky Mc solution, the total dissolved solids content was reduced by greater than 80% (34.2 g/L to 6.4 g/L). The Exxon neutralized solution showed an overall total dissolved solids reduction of greater than 70%, (12.5 g/L to 3.7 g/L). The difference in the total dissolved solids reduction between the two neutralized tailings solutions is due to the makeup of the untreated low pH solution. For example, ions such as Al, Fe, Mn, Cl, NO_3 , and SO_4 are two to three times higher in concentration in the Lucky Mc tailings solution than in the Exxon tailings solution. Upon neutralization the resultant pH buffered tailings solutions from both mills are relatively similar in makeup with the exception of elements such as Ca, Na, K, Cl, NO_3 and SO_4 whose solubility is not strictly dependent on solution pH.

Of the original 15 constituents (including solution pH) whose concentrations or activities in the low pH Lucky Mc tailings solution exceeded the EPA recommended water quality maximum concentration limits, only two macro-ions SO_4 and NO_3 , one trace metal, Se, and one radionuclide, ^{226}Ra , exceed the designated levels after neutralization with $\text{Ca}(\text{OH})_2$. For the Exxon solution out of the original 10 constituents exceeding the limits, only one macro ion, SO_4 , one trace metal, Se, and one radionuclide, ^{226}Ra , exceed the limits after similar neutralization. The detection limit for Mn was higher than the maximum concentration limit and as a result a less than value has been reported. Mn, in fact, may be below the set limits but its concentration cannot be verified without further study.

pH OPTIMIZATION STUDIES

The amount of reagent grade $\text{Ca}(\text{OH})_2$ necessary to neutralize 400 ml of Lucky Mc and Exxon Highland Mills acidic tailings solutions to each of the four selected pHs is presented in Table 7. Also included in Table 7 are values on the calculated reagent cost per metric ton ore processed to neutralize the tailings solutions to each of the four pH values.

The analysis of batch pH optimization solutions resulting from the neutralization of Lucky Mc and Exxon Highland acidic tailings liquors to pH 5.0, 6.5, 7.2 and 8.0 using calcium hydroxide are presented in Tables 8 and 9. Included in these tables are the chemical characterization data (Table 5) for both the Lucky Mc and Exxon Highland untreated acidic tailings liquors for comparison.

The data presented in Tables 8 and 9 demonstrate that calcium hydroxide neutralization to pH $\approx$ 7.2 is efficient in reducing the solution concentration of several constituents by greater than 98% from the original tailings solution values. Average percentage removal from both the Lucky Mc and Exxon Highland solutions at pH 7.2 to 7.3 were Al, 99.9%, Fe 99.9%, Si 99%, As 99.9%, Cr 99%, and V 99%. Zinc concentrations were reduced by 99.9% and 96% in the treated Lucky Mc and Exxon Highland mill solutions, respectively. Although the

TABLE 7. pH Optimization Reagent Cost Data for Lucky Mc and Exxon Highland Mill Tailings Solutions

<u>Acidic Tailings Liquor</u>	<u>Sample Size</u>	<u>Final Solution pH</u>	<u>grams Ca(OH)₂</u>	<u>Reagent Cost^(a) \$ per MT of Ore</u>
Lucky Mc	400 mL	5.0	4.10	0.77
Lucky Mc	400 mL	6.5	4.50	0.84
Lucky Mc	400 mL	7.3	4.60	0.86
Lucky Mc	400 mL	8.0	4.85	0.91
Exxon Highland Mill	400 mL	5.0	1.35	0.25
Exxon Highland Mill	400 mL	6.5	1.50	0.28
Exxon Highland Mill	400 mL	7.3	1.60	0.30
Exxon Highland Mill	400 mL	8.0	1.65	0.31

(a) See discussions on pages 33-35 for derivation of costs

percentage reduction of Zn in the Exxon Highland mill solution was most likely closer to 99%, the high detection level for Zn prevents reporting percent removal above 96%. While Ba concentrations were below detection limits after neutralization in the Exxon Highland mill solution, its percent reduction in the treated Lucky Mc solution was 99.9% at pH = 7.3. Further neutralization to pH = 8.0 for contaminant reduction is unnecessary for these constituents. High percentage removal was also achieved for Co, Cu and Pb for the Lucky Mc treated solutions at pH = 7.3. Cobalt concentrations were reduced by 94%, Cu 98% and Pb 98%.

Of those constituents showing concentration reductions due to neutralization to pH = 7.3, only Cd, Mn and Sr were reduced by less than 94% in the Lucky Mc treated solution. Seventy-six percent of the Cd was removed while Mn concentrations were reduced by only 40% and Sr by 60%. Again increased neutralization to pH = 8.0 failed to further reduce the concentrations of these constituents.

Treated Exxon Highland Mill solution produced similar results for Co, Cu, Cd, Mn and Sr when neutralization was performed to pH = 7.2. Cobalt concentrations were reduced by 98%, Cu by 98%, while Pb concentrations were below detection levels in all neutralized and untreated solutions. Manganese concentrations were reduced by 85% while Sr concentrations dropped to 50% of influent values at pH = 7.2. The concentrations of Co and Cu in the Exxon Highland treated solutions show that additional neutralization beyond pH = 7.2 fails to further reduce concentration levels of these constituents. In the case of manganese and cobalt, further neutralization beyond pH = 7.2 caused observed concentration levels to climb back to influent levels.

TABLE 8. Solution Chemistry of Calcium Hydroxide Neutralized
Lucky Mc Acidic Tailings Liquor

Parameter	Liquor Ca(OH) ₂ Neutralized to pH 5.0	Ca(OH) ₂ Neutralized to pH 6.5	Ca(OH) ₂ Neutralized to pH 7.3	Ca(OH) ₂ Neutralized to pH 8.0	Lucky Mc Influent
<u>Macro Ion (mg/L)</u>					
Al	16.5	2.6	0.3	0.4	1100
Ca	502	476	477	485	600
Fe	4.0	4.0	0.2	0.2	3000
Mg	1164	1004	1102	1063	1250
Mn	154	79	97	78	160
Na	1500	1534	1498	1524	1600
Si	32	4.5	2.8	3.0	300
Sr	5.0	5.9	5.7	6.1	14
K	153	153	154	150	160
Cl	1170	1170	1230	1200	1190
NO ₃	297	297	290	297	302
SO ₄	9700	8800	9700	9100	25,000
<u>Trace Metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	<0.02	15.50
Ba	<0.05	<0.05	<0.07	<0.07	0.07
Cd	0.35	0.03	0.06	0.05	0.25
Co	3.98	0.49	0.29	0.47	4.93
Cr	<0.01	<0.01	<0.01	<0.01	2.09
Cu	0.12	0.04	<0.02	<0.02	1.45
Mo	<0.03	0.18	0.23	0.26	7.74
Pb	<0.02	<0.02	<0.02	<0.02	0.85
Se	0.72	1.43	1.25	1.45	1.10
V	<0.02	<0.02	<0.02	<0.02	19.2
Zn	9.4	0.4	<0.2	<0.3	16.0
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	<75	<75	<75	<75	12,300
²³⁸ U	1788	<75	<75	<75	15,500
²³⁰ Th	<400	<400	<400	<400	185,400
²²⁶ Ra	1682	231	259	220	4,020

TABLE 9. Solution Chemistry of Calcium Hydroxide Neutralized Exxon Highland Mill Acidic Liquor

Parameter	Ca(OH) ₂ Neutralized to pH 5.0	Ca(OH) ₂ Neutralized to pH 6.5	Ca(OH) ₂ Neutralized to pH 7.2	Ca(OH) ₂ Neutralized to pH 8.0	Exxon Highland Influent
<u>Macro Ion (mg/L)</u>					
Al	1.9	<0.1	<0.1	<0.1	440
Ca	546	488	494	502	560
Fe	0.2	0.1	<0.1	<0.1	1000
Mg	520	503	472	513	540
Mn	48	30	7.4	44	50
Na	354	346	346	349	340
Si	32	1.9	1.0	16	310
Sr	5.1	4.5	4.0	4.6	8.5
K	42	41	42	41	44
Cl	297	299	296	300	300
NO ₃	10	8	9.5	12	9
SO ₄	4080	3975	3750	4055	9300
<u>Trace Metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	<0.02	0.21
Ba	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	0.5	0.01	<0.01	0.03	0.03
Co	1.43	0.36	<0.03	1.43	1.31
Cr	<0.01	<0.01	0.02	<0.01	1.25
Cu	0.14	<0.02	<0.02	<0.02	0.97
Mo	<0.01	<0.01	<0.01	<0.01	<0.02
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Se	1.34	1.1	1.2	1.0	1.35
V	<0.02	<0.02	<0.02	<0.02	10.7
Zn	3.5	<0.2	<0.2	2.2	4.5
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	<75	<75	<75	<75	2,100
²³⁸ U	343	<75	<75	<75	2,100
²³⁰ Th	<400	<400	<400	<400	97,140
²²⁶ Ra	<75	<75	<75	<75	758

The macro-ions, trace metals, and radionuclides followed the general trend of decreasing concentration with increasing pH. This trend continued until pH = 7.2 followed by further insignificant reduction to pH = 8.0. Six exceptions to this trend may be found in Tables 8 and 9. In both solutions, Cd concentrations increased to levels above influent concentrations at pH = 5. This initial increase was followed by a percent removal of Cd of nearly 70% of its influent concentration at pH = 7.2. Molybdenum concentrations in the treated Lucky Mc tailings liquor showed an initial reduction to just at detectable levels (99.9% removal) at pH = 5.0, followed by an increase in concentration to 98%, 97%, and 96% removal respectively at pH = 6.5, 7.3 and 8.0. This trend was not seen in the treated Exxon Highland solution due to the untreated acidic solution Mo concentration being below detection limits.

In the treated Exxon Highland solution, manganese, cobalt and zinc displayed limited reduction in the concentration of the pH = 5.0 filtrate, followed by further reduction of effluent concentrations to a maximum at pH = 7.2, then concentrations returned to near original solution concentrations at pH = 8.0. For example, Mn and Co concentrations in the treated Exxon solution show reductions of 4.0%, 49%, 85% and 12% for Mn and 0%, 73%, 98% and 0% for Co at pH = 5.0, 6.5, 7.2, 8.0, respectively. Manganese removal from the Lucky Mc tailings solution was also low, reaching a maximum of 51% at pH = 6.5, but remained relatively stable after this initial drop showing a reduction of 50% at pH = 8. In addition Co concentrations in the treated Lucky Mc solution also failed to increase significantly in more alkaline pHs after the initial drop at pH = 6.5.

Solution quality results for the neutralization of both Lucky Mc and Exxon Highland Mill acidic tailings liquors indicate that in the case of the macro ions, Ca, Mg, Na, K, Cl, and NO_3 and the trace metal, Se, no significant reduction in concentration resulted due to neutralization throughout the four pH ranges. Se concentrations in the neutralized Lucky Mc solutions experienced a 35% reduction at pH = 5 followed by an increase in concentration to above influent levels at pH = 6.5, 7.0, and 8.0. Se concentrations in the Exxon solution showed no reduction at pH = 5 and limited reduction (19%) at the higher pHs. These results are consistent with those of Sherwood and Serne⁽⁸⁾ where the percentage removal for these constituents was found to be low regardless of reagent used and final solution pH achieved. Thus, neutralization does not appear to be an effective method for the removal of these constituents. Elevated levels of calcium are not surprising when using calcium hydroxide as a neutralizing reagent. Furthermore, Mg concentrations tend to increase as the tailings solution becomes more alkaline. Since no additional magnesium was intentionally added the hydrated lime used throughout the study must contain a significant amount of soluble Mg. As more lime is added to raise the solution pH additional Mg dissolves and remains in solution. To decrease the amount of dissolved Mg by precipitating $\text{Mg}(\text{OH})_2$ the final solution pH would have to be in the range of pH 9.5 to 12.5 as can be seen in Table 5.

Sulfate concentrations were reduced by 61% in the treated Lucky Mc solution and 56% in the treated Exxon Highland Mill solution by pH = 5.0. Continued reagent addition failed to significantly remove more sulfate after pH = 5.0 was reached. At pH = 5.0, sulfate concentrations in both solutions are still at least an order of magnitude above the maximum concentration level

(MCL) of 250 mg/L set by the EPA for secondary drinking water. Additional solution treatment, such as specific ion removal, would be required to ensure sulfate concentrations below water quality guidelines.

Radionuclide results for the neutralization of Lucky Mc and Exxon Highland tailings solutions indicate that removal of ^{210}Pb , ^{238}U , and ^{230}Th was nearly complete (>99%) by pH = 6.5. For both solutions removal of ^{226}Ra was at least 90% by pH = 6.5 with additional neutralization causing limited further reduction in ^{226}Ra activity. The total extent of the radium removal was difficult to determine in the higher pH solutions (>pH 6.5) since the decreasing radium activities were approaching the point of being below our analytical detection limits.

For those constituents where neutralization appears to be effective in reducing solution concentrations in the treated batch filtrates, the optimum pH to elevate acidic uranium mill tailings solutions is pH = 7.2. While $\text{Ca}(\text{OH})_2$ neutralization to pH = 6.5 is sufficient to remove large percentages of several constituents, further neutralization to pH = 7.2 significantly increases removal of Al, Fe, Co, Cu, Pb, and Si. In most cases maximum reduction in constituent concentration is obtained at pH 7.2. In some cases (i.e., Co, Mn, and Zn) increasing the pH beyond 7.2 may cause constituents that had been previously removed from solution to redissolve at concentrations approaching those of the original untreated acidic solution.

LIMESTONE/LIME BATCH NEUTRALIZATION STUDIES

The results of the limestone/lime two component neutralization experiments for the Lucky Mc tailings solution and the Exxon tailings solution are shown in Tables 10 and 11, respectively. Also included in Tables 10 and 11 are the data at the intermediate pH (limestone only step) during the neutralization process. At the intermediate pH the tailings solutions have been neutralized with CaCO_3 to either pH 4.0 or 5.0 depending on the test. Once at the desired intermediate pH known amounts of $\text{Ca}(\text{OH})_2$ were added to the tailings liquor until the solution has been neutralized to pH = 7.2.

The analytical results of the tailings solutions which were subsequently neutralized to pH 7.1 with $\text{Ca}(\text{OH})_2$ after initially being neutralized with CaCO_3 , show substantial further reductions in solution constituent concentrations. This is very evident in the solutions which were limestone treated to pH 4.0, then lime neutralized to pH 7.1. Many constituents which were soluble in slightly acid solutions dropped below detection limits after treatment by the two component neutralization scheme. The solutions that were initially treated with CaCO_3 to pH 5.0 then to pH 7.1 with lime showed only slight reductions in solution concentrations when compared to the intermediate pH 5.0 solution. When the intermediate neutralized solutions were compared to the untreated tailings solutions from the respective mills the overall reduction in total dissolved solids content was greater than 50% for both Lucky Mc and Exxon solutions.

The results of the final (pH 7.1) neutralized tailings solution show three macro ions, Al, Fe and Si, six trace metals, As, Cr, Cu, Mo, Pb, and V and

TABLE 10. Solution Chemistry of Calcium Carbonate/Calcium Hydroxide Neutralization of Lucky Mc Mill Tailings Solution

Parameter	CaCO ₃ Neutralized to pH 4	CaCO ₃ Neutralized to pH 5	CaCO ₃ Neutralized to pH 4/Ca(OH) ₂ Neutralized to pH 7.1	CaCO ₃ Neutralized to pH 5/Ca(OH) ₂ Neutralized to pH 7.1	Untreated Solution
<u>Macro Ion (mg/L)</u>					
Al	272	5.3	<0.3	<0.3	1100
Ca	477	458	473	516	600
Fe	30	3.8	<0.1	<0.1	3000
K	147	152	145	145	160
Mg	1141	1186	1153	1149	1250
Mn	148	150	155	149	160
Na	1504	1528	1478	1478	1600
Si	30	13.3	<0.2	2.9	300
Sr	2.8	2.5	2.3	2.6	14
SO ₄	11,650	10,750	10,700	10,400	25,000
NO ₃	292	283	330	330	302
Cl	1195	1230	1300	1285	1190
<u>Trace Metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	0.06	<0.02	<0.02	<0.02	15.50
Ba	0.14	0.07	0.07	0.10	0.07
Cd	0.20	0.29	0.27	0.29	0.25
Co	4.68	4.73	3.54	3.35	4.93
Cr	0.03	<0.01	<0.01	<0.01	2.09
Cu	1.18	0.08	0.02	0.03	1.45
Mo	0.04	<0.01	<0.01	<0.01	7.74
Pb	0.03	<0.02	<0.02	<0.02	0.85
Se	0.99	0.87	0.76	0.81	1.10
V	<0.02	<0.02	<0.02	<0.02	19.2
Zn	14	11	2.7	3.5	16.0
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	779	<75	<75	<75	12,300
²³⁸ U	4195	223	<75	126	15,550
²³⁰ Th	2192	<400	<400	<400	185,400
²²⁶ Ra	8331	253	191	<75	4,020

TABLE 11. Solution Chemistry of Calcium Carbonate/Calcium Hydroxide Neutralization of Exxon Highland Mill Tailings Solution

Parameter	CaCO ₃ Neutralized to pH 4	CaCO ₃ Neutralized to pH 5	CaCO ₃ Neutralized to pH 4/Ca(OH) ₂ Neutralized to pH 7.1	CaCO ₃ to pH 5/Ca(OH) ₂ Neutralized to pH 7.1	Untreated Solution
<u>Macro Ion (mg/L)</u>					
Al	230	1.8	<0.3	<0.3	440
Ca	500	506	503	573	560
Fe	2.3	0.4	<0.1	<0.1	1000
K	44	41	40	40	44
Mg	508	500	495	540	540
Mn	49	50	44	45	50
Na	346	342	329	339	340
Si	74	28	<0.02	32	310
Sr	4.9	4.3	4.0	4.4	8.5
SO ₄	5450	4080	4090	4200	9300
NO ₃	<20	<20	<20	<20	9
Cl	302	303	325	340	300
<u>Trace Metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	0.03	<0.02	<0.02	<0.02	0.21
Ba	0.09	0.08	0.08	<0.05	<0.05
Cd	0.04	0.02	<0.01	0.02	0.03
Co	1.42	1.40	0.31	1.06	1.31
Cr	0.04	<0.01	<0.01	<0.01	1.25
Cu	1.09	0.07	<0.02	<0.02	0.97
Mo	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Se	1.20	1.35	1.02	1.02	1.35
V	<0.02	<0.02	<0.02	<0.02	10.7
Zn	4.2	2.4	0.20	0.30	4.5
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	<75	<75	<75	<75	2100
²³⁸ U	431	105	95	<75	2100
²³⁰ Th	1180	<400	<400	<400	97,140
²²⁶ Ra	1090	156	<75	<75	758

three radionuclides ^{210}Pb , ^{230}Th and ^{238}U , were reduced by greater than 97% in the treated Lucky Mc solution. Similar reductions were seen in the treated Exxon solution for Al, Fe, Si, Cr, Cu, V, and ^{230}Th . In addition, over 90% of the As, ^{210}Pb , ^{238}U and ^{226}Ra was removed. Se removal was insignificant for both treated solutions, 24% and 26% for the Exxon and Lucky Mc respectively. In both cases Se concentrations remained above EPA's maximum concentration levels. Co removal in both solutions was similar to Se. Only 19% of the Co was removed from the treated Exxon solution and 32% from the treated Lucky Mc solution. Sulfate was removed from both solutions at nearly identical percentages, 55% and 58% for the Exxon and Lucky Mc solutions respectively. Again the final solution concentrations for SO_4 exceed the water quality guidelines.

The data presented for the Lucky Mc and Exxon solutions initially neutralized to pH 4.0 or 5.0 reinforce the need for following through with the second neutralization step. This is especially true for those solutions which were initially neutralized to pH 4.0. Macro ions such as Al and Fe, trace metals including As, Cd, Co, Se and Zn, still exceed recommended water quality guidelines at pH 4 despite being reduced, in some cases, by several orders of magnitude. Furthermore, four radionuclides monitored throughout the study, ^{210}Pb , ^{238}U , ^{230}Th and ^{226}Ra were significantly higher in solution activity when neutralized only to pH 4. Upon further lime neutralization to pH 7.1 only ^{238}U exceeded our detection limit of 75 pCi/L which is still far below the MCL.

Several of the macro ions in Tables 10 and 11 remain at relatively high concentrations even at pH 7.1. Ions such as Ca, K, Mg, Mn, Na, Si, Cl, NO_3 and SO_4 seem to show little solubility dependence on final solution pH up to pH 7.1 or at the intermediate limestone pH values. Many of these ions are soluble in neutralized tailings solution regardless of the reagent used for neutralization. (7)

Comparing these limestone/lime neutralized solution analyses with the previously mentioned pH optimization results using only $\text{Ca}(\text{OH})_2$ at pH 5.0 and pH 7.1 (as shown in Table 12) show a few distinct trends for cobalt, manganese, and zinc. The combination limestone/lime neutralization data show distinctly higher cobalt and manganese concentrations for both tailings solutions and higher zinc values for the Lucky Mc solution. This suggests there may be soluble carbonate complexes forming with some trace metals during the intermediate neutralization process. Although the data are not distinct for uranium carbonate complexes, their formation may warrant additional study based on known thermodynamic stability constants.

The results of this study have lead to formulating two main conclusions concerning implementing a two component neutralization scheme: 1) Incorporation of a combination limestone/lime or lime only treatment for acidic tailings solution has greatly reduced the number of contaminants which exceed the water quality guidelines. For the case of the Lucky Mc tailings solution out of the original 17 constituents (including solution pH and TDS) that exceeded EPA maximum concentration limits only four exceed the primary drinking water standards and three exceed the secondary drinking water standards after neutralization with limestone and lime. As mentioned in the pH optimization

TABLE 12. Comparison of Ca(OH)_2 Neutralization with $\text{Ca(OH)}_2/\text{CaCO}_3$ Two Step Neutralization

Solution	pH	Element					
		Co (mg/L)		Mn (mg/L)		Zn (g/L)	
		Neutralization Method		Neutralization Method		Neutralization Method	
		Ca(OH)_2	$\text{Ca(OH)}_2/\text{CaCO}_3$	Ca(OH)_2	$\text{Ca(OH)}_2/\text{CaCO}_3$	Ca(OH)_2	$\text{Ca(OH)}_2/\text{CaCO}_3$
Lucky Mc	5.0	3.98	4.73*	154	150*	9.4	11*
Lucky Mc	7.3	0.29	3.35	97	150	<0.2	3.5
Exxon	5.0	1.43	1.40*	48	50*	3.5	2.4*
Exxon	7.2	<0.03	1.06	7.4	45	<0.2	0.3

* Only limestone used to pH 5.

discussion certain trace metals, i.e., Cd, Co and Se and the macro ions NO_3 , and SO_4 , may require additional specific ion removal techniques to bring the solution concentration below the set limits. 2) Generally speaking, initially neutralizing the acidic tailings solution to either pH 4.0 or 5.0 with limestone and subsequently to pH 7.1 with lime results in relatively identical solution quality. The formation of soluble carbonate complexes for Co, Zn and Mn and potential for uranium carbonate complexes being the only exceptions. The big advantage and very important for those in the mining and milling industry, is the relative cost of neutralizing acidic tailings solutions. The reagent cost section (see pages 33-35) goes into substantial detail on this point but briefly, the two component neutralization scheme is the least costly method of solution neutralization tested to date. Furthermore, of the two intermediate solution pH values studied, initial solution neutralization to pH 4.0 with limestone followed by lime addition to pH ~7.2 is less costly than limestone neutralization initially to pH 5.0 and then lime neutralization to pH 7.2. This is due to the inefficiency of limestone buffering above pH 4.0. For this reason limestone neutralization to pH 4.0 is preferred from a cost perspective.

COLUMN LEACHING EXPERIMENTS

Results of the column leaching experiments using field neutralized sludge material from both Lucky Mc and Exxon Highland Mills are shown in Tables 13 and 14, respectively. The data are listed with respect to the number of effluent pore displacement volumes of synthetic ground water that had passed through the sludge column.

Results of the chemical analysis of the first pore volumes of column effluent solution from both Lucky Mc and Exxon sludges show higher concentrations of some macro ions and trace metals than what was present in the influent synthetic ground water. The Lucky Mc sludge data indicate significant leaching of Ca, K, Mg, Na, Cl, and NO_3 , and SO_4 after less than 1 pore volume of ground water contact. In addition trace metals such as Mo and Se show above influent concentrations at the same pore volumes. Finally, no radionuclides were observed above the specified detection limits throughout the column leaching study.

The Exxon sludge column data show the same general trend of higher concentrations of macro ions such as Ca, Na, K, Cl and SO_4 and certain trace metals such as Cr and Se during the initial pore volumes. Again no radionuclides were detected in the effluents from the Exxon sludge columns through 6.5 pore volumes of leachate contact.

Many of the above mentioned elements in both the Lucky Mc and Exxon sludge effluents showed dramatic decreases in solution concentration as solution continued to pass through the columns. The decrease in constituent concentration gradually approached the influent concentration as would be expected with continued leaching. The high initial effluent concentration of macro ions and some trace metals indicates a high soluble salt content left in the sludge material upon drying. Moisture retention values for sludges formed due to

TABLE 13. Lucky Mc Sludge Column Leaching Data (mg/L)

						Groundwater Leachate
Pore Volume	0.65	4.0	5.37	6.1	7.4	
pH (units)	7.14	7.25	7.85	8.74	8.75	7.6
Macro Ions						
Al	<0.3 ^(a)	<0.3	<0.3	0.3	<0.3	<0.1
Ca	480	472	480	442	396	69
Fe	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mg	182	58	60	50	38	11
Mn	ND ^(b)	ND	ND	ND	ND	0.01
Na	2540	144	144	128	120	105
Si	1.4	<0.2	<0.2	0.2	<0.2	0.5
Sr	1.7	1.3	1.4	1.1	0.8	0.03
K	362	11.8	11.5	6.9	4.2	ND
Cl	2,200	150	140	100	80	44
NO ₃	480	11	9.4	6.1	3.3	3.3
SO ₄	6,000	1,600	1,590	1,590	1,290	300
Trace Metals						
Ag	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ba	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cr	0.05	0.01	0.01	<0.01	<0.01	<0.01
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	1.64	0.37	0.44	0.27	0.20	<0.01
Pb	<0.02	<0.02	<0.02	0.02	<0.02	<0.02
Se	0.52	0.11	<0.12	0.07	<0.05	<0.1 ^(c)
V	<0.1	<0.1	<0.1	<0.1	<0.1	<0.02
Zn	<0.01	<0.1	<0.1	<0.1	<0.1	<0.05
Radionuclides						
(pCi/L)						
²¹⁰ Pb	<75	<75	<75	<75	<75	<75
²²⁶ Ra	<75	<75	<75	<75	<75	<75
²³⁰ Th	<400	<400	<400	<400	<400	<400
²³⁸ U	<75	<75	<75	<75	<75	<75

(a) All less than (<) values are respective instrument detection limits.

(b) ND = Not determined.

(c) Analysis Performed by ICP.

TABLE 14. Exxon Highland Sludge Column Leaching Data (mg/L)

					Groundwater Leachate
Pore Volume	2.0	3.4	5.1	7.2	7.6
pH (units)	11.23	11.48	11.08	10.34	
Macro Ions					
Al	<0.3(a)	<0.3	<0.3	<0.3	<0.1
Ca	624	644	602	597	69
Fe	<0.1	<0.1	0.4	<0.1	<0.1
Mg	0.5	0.6	0.6	0.9	11
Mn	ND(b)	ND	ND	ND	<0.1
Na	420	103	100	103	105
Si	4.4	1.5	1.6	2.0	0.5
Sr	2.4	2.1	1.7	1.4	0.03
K	97	11	4	6	ND
Cl	520	170	66	45	44
NO ₃	1.0	1.0	1.0	<1.5	3.3
SO ₄	1800	1450	1500	1440	300
Trace Metals					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	<0.02	<0.02
Ba	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.02	<0.02	<0.02	<0.02	<0.02
Cr	0.39	0.30	0.30	0.15	<0.01
Cu	0.04	<0.02	<0.02	<0.02	<0.02
Mo	0.02	0.01	0.01	0.01	<0.01
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Se	1.78	0.78	0.50	0.36	<0.1(c)
V	<0.1	<0.1	<0.1	<0.1	<0.02
Zn	<0.1	<0.1	<0.0	<0.1	<0.05
Radionuclides					
(pCi/L)					
²¹⁰ Pb	<75	<75	<75	<75	<75
²²⁶ Ra	<75	<75	<75	<75	<75
²³⁰ Th	<400	<400	<400	<400	<75
²³⁸ U	<75	<75	<75	<75	<75

(a) All less than (<) values are respective instrument detection limits.

(b) ND = Not Determined.

(c) Analysis performed by ICP.

Ca(OH)_2 neutralization of acidic tailings solution range from ≈ 2.2 g of moisture per gram of sludge to 2.8 g/g for the Lucky Mc and Exxon sludges, respectively.⁽²⁾ The moisture retained in the sludges from both mills has the same constituent makeup as the respective neutralized tailings solution shown in Table 5. Those solutions are the filtered fraction of the solution/sludge slurry after neutralization. The data in Table 5 show similar high concentrations of macro-ions such as Ca, K, Na, Cl, SO_4 and trace metals such as Mo and Se. Prior to the column packing steps the sludge material was oven dried to ensure that the desired packing densities are met and to facilitate handling. The moisture normally retained within the sludge was driven off leaving the residual solution evaporites comprised of the above elements normally soluble in neutral tailings solutions. Upon contact with the laboratory prepared ground water used as leachate, the evaporites redissolve and pass through the column and are collected in the first effluent. Once dissolution of the evaporites or soluble salts is complete the effluent solution constituent concentrations gradually approach that of the influent synthetic ground water. The only evident exceptions to this for the Lucky Mc solution are the macro ions, Ca, and SO_4 which seem to decrease but at a slower rate than other constituents. For the Exxon sludge effluents similar trends were seen over the period of contact with the 6.5 pore volumes of leachate. Ca and SO_4 ions show the slowest decrease in solution concentration due to the dissolution of gypsum formed during addition of Ca(OH)_2 during the in-field neutralization. The excess addition of lime in the field resulted in column effluent solution pHs ranging from pH ≈ 11.1 to pH 11.6 for the Exxon sludge column. The most notable trace metals showing significant solubility is Se with a concentration of almost 1.8 mg/L and Cr at 0.36 mg/L during the second pore volume of leaching. By the time the Exxon sludge has contacted 6.5 pore volumes of groundwater the Se value had dropped to 0.36 mg/L and Cr to 0.15 mg/L. This is approximately an 80% reduction for Se and 58% for Cr in solution concentration after 6.5 pore volumes, still substantially higher than the maximum permissible concentration value of 0.01 mg/L and 0.05 mg/L for Se and Cr, respectively, in drinking water (see Table 6) and the influent concentrations of the synthetic ground water used for leaching. Several investigators^(12,13,14) have found increased solubilities of certain species of Cr and Se (particularly chromite and selenite) in highly alkaline (pH 11) solutions such as these. For elements such as Se and Cr, an additional solution treatment such as specific ion removal may be necessary to reduce the solution concentration to acceptable limits or alternatively at more realistic pH values of 7-8, perhaps Se or Cr would not be mobile as evidenced by the Lucky Mc Sludge results.

The leaching studies will continue over several more pore displacement volumes to evaluate the long-term attenuation of contaminants. Results to date indicate the sludge material acts as a relatively stable neutralization end-product allowing only those readily soluble contaminants such as Ca, Na, K, Cl, and SO_4 normally present at high concentrations in tailings solution to be leached. The majority of the radionuclides and trace metals with the exceptions of Mo and Se and perhaps Cr, remain immobile within the sludge.

REAGENT COST

The total weight of each reagent added to the 400 milliliter batch contact limestone/lime neutralization experiments were used in calculating the cost of neutralizing acidic tailings solutions. The calculations are based on CaCO_3 and Ca(OH)_2 reagent costs of \$22.05/MT and \$35.83/MT, respectively, from 1982 issues of the Chemical Marketing Reporter. These costs do not include shipping charges since this would vary from site to site. In addition, the costs are strictly reagent usage costs and do not include cost for capital equipment expenditures, maintenance, etc. These types of cost factors will vary depending on the site location, solution composition (i.e., total acidity), mill production rate, and solution neutralizing capacity requirements.

The reagent usage and cost data are presented in Tables 7 and 15 for the Lucky Mc and Exxon Highland Mill tailings solutions. For comparison with the limestone/lime neutralization studies, cost data generated during the pH optimization experiments using Ca(OH)_2 alone taken from Table 7. The calculations show limestone/lime neutralization of acidic uranium mill tailings to be less expensive than incorporating a lime only solution neutralization. In addition, the data indicate that CaCO_3 neutralization to an intermediate pH of 4.0 is less expensive than initial CaCO_3 neutralization to pH 5.0. This includes in both cases, the final lime neutralization to pH 7.1. The lower treatment cost is due to the lower CaCO_3 reagent efficiency at solution pHs above pH 4.0. Furthermore, Ca(OH)_2 is extremely efficient for solution neutralization up to pH 7 to 8. The higher efficiency of lime from pH 4.0 to pH 7.2 outweighs its higher cost. The additional CaCO_3 required to raise the solution from pH 4.0 to pH 5.0 costs more despite the lower unit cost of limestone.

The combination reagent treatment cost of \$0.21 per metric ton of processed ore for the Exxon Highland solution and \$0.59 for Lucky Mc solution is the least costly solution treatment tested during the course of this laboratory study and the previous work.⁽⁸⁾

For comparison of the two step treatment to the other six reagents tested in the earlier progress report, the same values for process solution neutralization, production costs, and ore cut-off grades were used.⁽²⁾ The costs listed in Table 15 are obtained by assuming that 2087 L^(a) (550 gal) of tailings solution must be neutralized for every metric ton of ore processed and that all the tailings solution is neutralized (no solution recycled). The measured quantity in grams of reagents used to neutralize the 400 milliliters in our laboratory studies is converted to kilograms of reagent/2087 L of tailings solution (1 metric ton of ore).

In 1980, the average ore grade milled in the United States was 0.12% U_3O_8 . At that time, the cut-off grade for 0.12% uranium bearing ore was

(a) 2087 L is the value used in the first laboratory progress report. So that the cost of the two component neutralization methods can be compared with the costs of the previous seven reagents, the same quantity of tailings solution will be used in the calculations.

TABLE 15. Reagent Usage and Cost Data

Leachate	Reagents		Intermediate Solution pH	Final Solution pH	Reagent Cost, \$/MT of Ore ^(a)
	CaCO ₃ (g)	Ca(OH) ₂ (g)			
Exxon Highland Mill	1.30	0.31	4.0	7.1	0.21
Lucky Mc Mill	4.50	0.38	4.0	7.1	0.59
Exxon Highland Mill	1.90	0.03	5.0	7.1	0.22
Lucky Mc Mill	5.60	0.04	5.0	7.1	0.65
Exxon Highland Mill	--	1.60(b)	--	7.2	0.30
Lucky Mc Mill	--	4.60(b)	--	7.3	0.86

(a) 1982 costs, \$/MT of ore processed

(b) Lime only solution neutralization directly to pH 7.2 or pH 7.3 for the respective solution from pH optimization data (Table 7)

\$27.30. The cut-off grade is that which one must have to make a profit in milling and recovery at a set price for uranium. At 0.12% U₃O₈ content one ton of ore would produce 2.4 pounds of processed U₃O₈. Based on the 1980 price of processed U₃O₈, for a mill to operate and make a profit the production costs would have to be less than 2.4 x \$27.30 or \$65.52. Assuming the actual processing costs excluding capital equipment, maintenance, profit, etc., for the production of 0.12% ore is approximately \$40.00/ton, then the added cost of the reagents (limestone and lime) to neutralize the tailings solution (\$0.21 to \$0.59 dependent on which site the solution originates) represents less than a 2% increase in production costs. If we assume that the capital equipment to receive, store and slake the reagents and the reaction tanks incorporated in the two step treatment triples the cost of the reagents alone, the additional increase still remains below 4% of the fully burdened uranium production costs (\$65.52/ton of ore).⁽²⁾

CONCLUSIONS

Results of the pH optimization studies using Ca(OH)_2 as the neutralizing reagent, indicate that the optimum pH for contaminant removal is pH 7.2 for both Lucky Mc and Exxon Highland tailings solutions. These results were based strictly on effluent water quality. Several solution constituents showed steady reductions in concentrations as the acidic tailings solution (pH 1.7 to 2.0) was neutralized to pH 7.2. Several constituents, including Al, As, Ba, Cr, Fe, Si, V, ^{210}Pb , ^{238}U , ^{230}Th and ^{226}Ra , showed reductions in solution concentrations or activities in excess of 98%. Further addition of Ca(OH)_2 to increase the solution pH above pH 7.2 showed no significant further removal of contaminants. In fact, Co, Mn, and Si displayed higher solution concentrations in the neutralized Exxon tailings solutions more alkaline than pH 7.2.

Macro ions Ca, Mg, Na, K, Cl and NO_3 showed no reduction in solution concentration with Ca(OH)_2 neutralization. Although high concentrations of Ca and Mg are to be expected when using lime as a neutralizing agent, neutralization of Lucky Mc and Exxon mill tailings solutions with other reagents have shown that the concentrations of these six constituents is not pH dependent. In addition, the percent reduction of SO_4 , Mn and Se was minimal suggesting an additional solution treatment technique is necessary to reduce their concentrations to acceptable limits.

Based on the results of these laboratory experiments the two step lime-stone/lime combination neutralization appears to be the most cost effective method tested to date for treating acidic uranium mill tailings solutions. There is little difference in the end results when comparing the solution constituent concentrations of the tailings solution initially neutralized to pH 4.0 or 5.0 with limestone. As a result initial solution neutralization to pH 4.0 followed by lime addition to pH 7.2 is recommended as the best potential combination treatment scheme as it is the most cost effective. While initial neutralization to pH 5.0 was effective in reducing the contaminant concentrations in solution it was calculated to be more costly and resulted in nearly the same end product.

Two step neutralization with carbonate containing reagents may enhance the mobility of some trace metals, notably Co, Mn and Zn, and perhaps the radionuclide, ^{238}U , by formation of soluble carbonate complexes. Complexation and mobility may further be enhanced in soils rich in CaCO_3 . Ra-226 is of primary importance since the maximum contaminant level is lower than concentrations found in carbonate neutralized tailings solutions. Very little information is currently available on carbonate complexation in uranium mill tailings solutions. Future studies should evaluate whether limestone neutralization significantly decreases the potential for contaminant attenuation and whether the decrease outweighs its use as a lower cost treatment. The results of such studies may suggest the use of the more costly lime-only solution treatment which does not exhibit carbonate complexation complications.

Treated effluent quality data supports the premise that additional solution treatment (i.e., specific ion removal techniques) will be necessary for ions

such as molybdenum, selenium, sulfate and total dissolved solids content. These constituents in neutralized solution still exceed the Environmental Protection Agency maximum contaminant levels by ten to one hundred times. Other constituents of concern include Na, Cl, and Co and should be considered on a case by case basis since their concentrations in acidic tailings solutions vary dramatically from site to site.

The costs incurred in neutralizing acidic tailings solution using the combination limestone/lime treatment is predicted to be <2% of uranium (as U_3O_8) production costs. Furthermore, if we assume the costs of capital equipment expenditures and operation costs triple the cost of the reagents alone, the additional increase still remains below 4% of the fully burdened uranium production costs.

Column leaching studies performed on the field neutralized sludge material indicate that pH-independent soluble salts are flushed from the sludge material during the first few pore displacement volumes. The soluble salts, mainly calcium, magnesium, sodium, chloride and sulfate, are originally present in the pore water of the sludge material. The amount of soluble salts is very much dependent on the moisture retention properties of the sludge and the type of reagent used to neutralize the tailings solution which subsequently generates sludge. As leachate/sludge interaction continues the solution constituent concentrations approach that of the influent solution (ground water). Three trace metals, chromium, molybdenum and selenium, were detected in the effluents through 7.4 pore displacement volumes for the Lucky Mc sludge and through 6.5 pore displacement volumes for the Exxon sludge. As these were not part of the synthetic groundwater, these trace metals are redissolving as leachate continues to pass through the column. These trace metals are consistently present in neutral solutions or sludge effluents indicating that additional solution treatment may be necessary to meet water quality standards.

The tailings solution characterization data enforces the fact that neutralization studies need to be performed on a case by case basis. Both mill tailings solutions studied employed a sulfuric acid solution as the primary leachate. Despite this fact, the Lucky Mc solution contains roughly three times more mass of constituents as compared to the Exxon solution. This includes macro ions such as Al, Fe, Mg, Mn, Cl, and SO_4 , total dissolved solids content and total acidity values. The quantity of reagent required to neutralize different tailings solutions is very much dependent on the factors mentioned above.

The results presented in this progress report for the Lucky Mc and Exxon tailings solution neutralization consider a rather wide range of tailings solution constituent concentrations and solution properties. Acidic tailings solutions from many other mill sites should fall within the range of solution parameters presented here. In that sense, neutralization is an efficient and cost effective means of controlling or reducing many contaminant concentrations in acidic uranium mill tailings solutions. But for all solution parameters to meet water quality guidelines, further treatment may be necessary for those constituents not effectively removed by neutralization such as Mg, Na, Cl, SO_4 , and Se and in selected cases Mo, Co and Cd.

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