
Evaluation of Selected Neutralizing Agents for the Treatment of Uranium Tailings Leachates

Laboratory Progress Report

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ABSTRACT

Laboratory experiments were conducted to evaluate the performance of selected neutralizing agents for the treatment of uranium tailings solutions. Highly acidic tailings solutions ($\text{pH} < 2$) from the Lucky Mc Mill in Gas Hills, Wyoming and the Exxon Highlands Mill near Casper, Wyoming were neutralized to a pH of 7 or greater using seven neutralizing agents. Reagents used included:

1. Fly Ash from Boardman Coal Plant, Boardman, Oregon
2. Fly Ash from Wyodak Coal Plant, Gillette, Wyoming
3. Calcium carbonate (CaCO_3) reagent grade
4. Calcium hydroxide [$\text{Ca}(\text{OH})_2$] reagent grade
5. Magnesium oxide (MgO) reagent grade
6. Sodium carbonate (Na_2CO_3) reagent grade
7. Sodium hydroxide (NaOH) reagent grade.

Evaluation of the effectiveness for the treatment of uranium tailings solutions for the selected neutralizing agents under controlled laboratory conditions was based on three criteria. The criteria are: 1) treated effluent water quality, 2) neutralized sludge handling and hydraulic properties, and 3) reagent costs and acid neutralizing efficiency.

On the basis of these limited laboratory results calcium hydroxide or its dehydrated form CaO (lime) appears to be the most effective option for treatment of uranium tailings solutions.

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EXECUTIVE SUMMARY

Laboratory experiments were conducted to evaluate the performance of selected neutralizing agents for the treatment of uranium tailings solutions. Highly acidic tailings solutions (pH<2) from the Lucky Mc Mill in Gas Hills, Wyoming and the Exxon Highlands Mill near Casper, Wyoming were neutralized to a pH of 7 or greater using seven neutralizing agents. Reagents used included:

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Evaluation of the effectiveness for the treatment of uranium tailings solutions for the selected neutralizing agents under controlled laboratory conditions were based on three criteria. The criteria are: 1) treated effluent water quality, 2) neutralized sludge handling and hydraulic properties, and 3) reagent costs and acid neutralizing efficiency.

Treated effluent water quality suggests that removal of many dissolved constituents (e.g., Al, Fe, Si, As, Ag, Cr, Cu, Pb, V, Zn, ^{210}Pb , and ^{230}Th) is controlled by pH buffering and does not depend upon the specific neutralizing agent. However, test results for effluent concentrations of sulfate, cobalt, ^{238}U , and ^{226}Ra have shown a marked dependence on the reagent selected. Sulfate was removed from solution only by those reagents containing calcium which promotes the formation of gypsum. Cobalt, ^{238}U , and ^{226}Ra are not removed from solution as effectively with carbonate reagents as with other reagents. This effect may be due to the formation of soluble carbonate complexes of cobalt, uranium, and radium. Other constituents (e.g., K, Na, Ca, NO_3^- , Cl^- , and Se) have shown little or no change in solution concentration during neutralization regardless of reagent used. Manganese and molybdenum removal is variable and does not seem to correlate with the reagent used.

The neutralized Lucky Mc tailings solutions exceed maximum concentration levels by 10^2 to 10^3 times for Se and Mn by 10^1 to 10^2 times for Mo, SO_4 and TDS and by 10^0 to 10^1 times to NO_3^- , Cl and ^{226}Ra . The Exxon Highland Mill tailings solution after neutralization exceeds maximum concentration levels by 10^1 to 10^2 for Se, Mn and SO_4 and by 10^0 to 10^1 times for Cl, TDS and ^{226}Ra . Thus one might conclude that potentially the most problematic constituents will be Se, Mn, SO_4 and total dissolved solids. Most likely Mn would be removed further upon contact with sediments, but Se, SO_4 and TDS would require significant dilution with low ionic strength ground water or specific treatment to ensure that their concentrations are below water quality guidelines.

Selected sludge properties were also used as a means to evaluate the performance of the neutralizing agents. The total weight of sludge generated,

sludge moisture retention, and sludge mineralogical analyses were performed for each of the reagents tested. The sludge characterization results indicate that calcium-containing reagents and fly ash produce the largest weight of sludge. Reagents without calcium produce much less sludge but of a substantially higher moisture content. Crystalline mineralogy of the two fly ash samples compared to those reacted with tailings solution indicated that lime (CaO) and periclase (MgO) present in the ash were dissolved during contact. Gypsum (CaSO₄·2H₂O) was identified as the only crystalline phase detected in the calcium reagent neutralized sludges. Crystalline phases were not detected in samples neutralized with magnesium oxide, sodium carbonate, or sodium hydroxide. Undoubtedly all sludges contain noncrystalline precipitates that form rapidly during neutralization.

The amount of reagents required to neutralize the tailings solution to pH ~7 was monitored to determine the reagent efficiency and costs. Reagent usage information indicates that the quantity of reagent required to treat a given volume of solution depends on the total acidity of the solution, the equivalent weight of the reagent, and the efficiency with which that reagent reacts to neutralize solution acidity. Results of the reagent usage tests indicate that a high-quantity total-acidity tailings solution (e.g., Lucky Mc 15,000 mg/ℓ total acidity) may require as much as three times the amount of reagent required to neutralize a low-quantity total-acidity leachate (e.g., Exxon Highland Mill 4500 mg/ℓ total acidity). Neutralization efficiency results suggest that only two reagents tested had efficiencies in excess of 90% of their theoretical neutralization capacity (e.g., sodium hydroxide = 96% and calcium hydroxide = 90%). Calcium carbonate exhibited the lowest neutralizing efficiency of the reagents tested (67%). No efficiency could be calculated for the fly ash samples, since they have no known equivalent weight. Reagent costs show that calcium carbonate, calcium hydroxide, and magnesium oxide are the least expensive neutralizing agents tested. The calculated reagent costs per ton of ore processed for treatment of the Lucky Mc solutions (high acidity) with calcium carbonate, calcium hydroxide, and magnesium oxide were \$0.88, \$0.83, and \$0.77, respectively while the costs for the Exxon solution were \$0.30, \$0.26, and \$0.26, respectively. Costs for other reagents tested were at least twice as expensive. Sodium hydroxide was the most expensive reagent examined with a reagent cost of nearly ten times that of calcium carbonate, calcium hydroxide, or magnesium oxide.

On the basis of these laboratory results either calcium hydroxide or its dehydrated form CaO (lime) appears to be the most effective option for treatment of uranium tailings solutions. Further laboratory experiments are needed to determine other information required to support the use of lime as the most applicable reagent. Experiments that evaluate the chemical stability of the sludge generated by lime neutralization are needed for a better understanding of how contaminants are immobilized (e.g., precipitation, sorption, ion exchange, occlusion, coprecipitation). These types of tests will not only be applicable to this task, but should derive valuable data for understanding the reactions which may occur in alkaline, calcium-rich soils. Further testing of lime under possible process conditions is needed to verify reagent performance prior to actual field demonstration which represents the final phase of this project. These further tests will be performed during the next year prior to the submission of a field demonstration test plan.

Other tests on the possible complexation of cobalt, uranium, and radium, with carbonate should also be performed. These tests are needed to determine the potential mobility of these constituents in high carbonate soils and/or carbonate ground waters. An alternate method for removal of Se, major cations (e.g., K, Na, Ca, Mg), major anions (NO_3^- and Cl^-) and perhaps Mo is needed because neutralization is not effective in lowering their solution concentrations to commonly used water quality guidelines.

Cost estimates for adding the neutralization step in the overall uranium production and waste disposal scheme range from about 1 to 5% increments in production costs. More sophisticated cost estimates should be performed to verify these calculations, however.

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INTRODUCTION

The acid milling process to extract and purify uranium produces two wastes for disposal: solid tailings and process wastewater. In the United States (U.S.), disposal of the wastes varies substantially from site to site. Many systems have been used to control the volume of acid seepage released from tailings impoundments. Examples include evaporation ponds, underdrains, synthetic liners, clay liners, and solution recycling. However, each system is limited in its ability to handle an excess of tailings solution. If the acidic tailings solution is not contained, the high concentration of many contaminants in the residual solution may present a potential environmental problem because of ground-water contamination. This is a potential concern at sites where wastes are disposed in tailings impoundments with high permeability or small distances to the existing water table.

In Canada, the Elliot Lake and Bancroft areas have had the water quality adversely affected as a result of poor disposal techniques (Anon. 1972 and Brown et al. 1981). In the U.S., contamination of surface and/or ground water has also occurred, e.g., Canon City, CO (Cotter), Ford, WA (Dawn Mining), Gas Hills, WY (Union Carbide). (Details may be found in Mineral Resources Waste Management Team Report 1, 1980.) Such contamination may have been minimized or totally avoided if the waste solutions had been treated prior to disposal. As a result, the U.S. Nuclear Regulatory Commission (NRC) established a project to assess the effectiveness, benefits and costs of neutralizing tailings to reduce the quantity of toxic and radioactive constituents available for migration under a full range of site and environmental conditions. As part of this project, a literature review (Sherwood and Serne 1982) was conducted to assess current tailings amelioration techniques in terms of their effectiveness in reducing the mobility of contaminants in the residual solution and from leaching of the solid uranium mill tailings.

Three general amelioration methods were identified: neutralization, fixation and specific constituent removal. During neutralization, a reagent is added to the tailings solution to neutralize the acidity and raise the pH to reduce the solubility of various pH-sensitive contaminants. In contrast, fixation processes add materials 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 they can, at a reasonable cost, limit the solution concentration of many contaminants, thus reducing the potential for surface- and ground-water contamination. However, the effectiveness of the process depends on the reagent used as well as the waste being treated. Further, the selection of tailings solution neutralization as the most viable method of treatment was based, in part, upon results obtained on 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 have used neutralization. Data for all potentially important radionuclides and toxic trace metals and macro anions were not found in the literature reviewed. Thus, controlled laboratory experiments comparing various neutralizing agents for treatment of acidic uranium mill tailings solution from representative U.S. sites were started. The results of these controlled laboratory experiments completed through September 1982 are the subject of this progress report.

After completion of laboratory experiments in 1983 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 useful in evaluating the need and potential cost/benefits for NRC regulations on uranium mill waste treatment.

Based on the literature review (Sherwood and Serne 1982) and cost and availability information taken from recent issues of the Chemical Marketing Reporter, six chemical reagents were chosen: coal fly ash, calcium carbonate [CaCO_3], hydrated lime [$\text{Ca}(\text{OH})_2$], magnesia [MgO], soda ash [Na_2CO_3], and caustic soda [NaOH]. Within the literature review, we evaluated the strengths and weaknesses of four of these reagents: limestone, lime, soda ash and caustic soda. 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 added to the list. Finally coal fly ash was chosen 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 for the treatment of uranium tailings solutions for the selected neutralizing agents under controlled laboratory conditions was based on three criteria. The criteria are: 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 needed to raise the tailings solution pH to 7 versus the theoretical amount of reagent based on its equivalent weight. Further tests and criteria may be used in future tests on the more effective reagents chosen in this preliminary study. Examples are process considerations such as ease of handling reagents, mixing characteristics of reagents and tailings and more detailed analyses of sludge hydraulic conductivity properties.

METHODS AND MATERIALS

CHEMICAL REGEANTS

Chemical reagent-grade calcium carbonate, calcium hydroxide, magnesium oxide, sodium carbonate and sodium hydroxide were obtained from a local chemical supplier. Fly ash samples were obtained from surface piles at the Boardman Coal Plant (Boardman, Oregon) and the Wyodak Coal Plant near Gillette, Wyoming. Table 1 lists the six neutralizing agents along with the chemical composition and cost per ton of each agent.

TAILINGS SOLUTIONS

In December of 1981, PNL scientists visited the Pathfinder (Lucky Mc) Gas Hills Mill near Riverton, Wyoming and the Exxon Highland Mill near Glenrock, Wyoming. The tailings solution from the Lucky Mc Mill (~32 liters) was taken from the east side of pond 2A on the opposite side of the area where tailings were being pipeline slurried. Discussions with Jack Stevenson, Mill Superintendent, indicated that the ore being processed was a mixture coming from three sources: highly oxidized mill waste (0.02 to 0.03% U_3O_8) from old stock piles, ore (0.03 to 0.05% U_3O_8) taken from open pits at the Gas Hills mine, and higher grade ore (0.1% U_3O_8) taken from an underground operation near Jeffery City, Wyoming, about 65 km (40 miles) southeast of the Lucky Mc mill. The tailings solution from Exxon Highland Mill (~40 liters) was taken from the north edge of the present evaporation pond.

TABLE 1. Selected Neutralizing Agents and Their Corresponding Prices

<u>Chemical Composition</u>	<u>Cost/ton, \$(a)</u>
Fly Ash (Variable) ^(b)	19.00
CaCO ₃	20.00
Ca(OH) ₂	32.50
MgO	55.00
Na ₂ CO ₃	92.00
NaOH	300.00

(a) Costs do not include shipping

(b) Fly ash samples from the Boardman Coal Plant in Boardman, Oregon and from the Wyodak Coal Plant near Gillette, Wyoming.

SOLUTION CHEMICAL ANALYSES

Detailed analyses of the initial tailings solutions and the treated effluents from the batch neutralization experiments were performed. Macro-cations (Al, Ca, Fe, Mg, Mn, Si, Na, and Sr) present in the tailings solutions and treated effluents were determined using a Jarrell-Ash emission spectrometer with an inductively coupled plasma source (ICP). Potassium was determined by flame atomic absorption because spectral interferences on the ICP technique limit its use. Macro-anions (SO_4 , Cl, NO_3) 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.

Radionuclide concentrations in the tailings solutions and treated effluent were determined using high-resolution gamma spectroscopy. For these analyses, a volume of solution (250 ml) was evaporated leaving the residual evaporites. These salts were 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, ^{238}U , ^{230}Th , and ^{226}Ra concentrations were determined over a counting time of 7 hr 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 ^{226}Ra activity is calculated after correction of the count rate of the 185.8 KeV peak for a contribution from ^{235}U 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, a content for ^{235}U may be calculated and this activity subtracted from the total activity in the region of 185 to yield an estimate of the ^{226}Ra content. Detector efficiencies were determined on NBS-traceable, uranium-bearing sediments pressed into pellets identical to those used for evaporite analyses.

The pH and total acidity of the tailings solutions were also measured. Solution pH was determined using a Corning Model 130 pH meter and a combination pH electrode. The Salotto method of total acidity (Salotto 1966) was used to determine the total acidity of the Lucky Mc and Exxon leachates. Briefly, the procedure is to titrate the acid solution with sodium hydroxide to a pH of 7.3. The total dissolved solids (TDS) content of the tailings solutions and treated effluents was calculated in milligrams/liter from the macrocation and anion values that were determined as described. Ammonium analyses were not determined in these preliminary studies due to the large sample volume needed to perform an analysis.

MINERALOGIC ANALYSES

Mineralogic characterization of the two fly ash samples and the sludges generated from solution neutralization were determined by X-ray diffraction. Bulk samples of these materials were slurry-mounted on glass slides for

analysis. Diffractograms were obtained using a Philips XRG 3500 X-ray diffractometer and a $\text{CuK}\alpha$ radiation generator.

BATCH CONTACT NEUTRALIZATION TESTS

Four hundred milliliters of the acid tailings solution were placed in 0.5-liter polyethylene bottles. Based on the theoretical equivalent weight of each chemical reagent and the measured total acidity of the tailings solution, enough dry reagent was added to the bottles to raise the slurry pH to ~ 7.3 . After reagent addition, the bottles were placed on a linear oscillating shaker for two days to facilitate mixing and reaction. As no theoretical equivalent weight was available for the two fly ash samples, small quantities were initially added to the acid tailings solution.

After the two-day contact period, the sample pH was measured. If the solution pH above the sludge was 7 or greater the experiment was stopped. If the pH was less than 7 an additional portion of reagent 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 a solution pH of 7 or greater was achieved. Once each sample had achieved this condition it was centrifuged and the supernate solution was filtered through a 0.45 micron membrane. The filtered solutions were then analyzed by the techniques described in the solution chemical analysis section. Residual sludge separated from the supernate during centrifugation was used to evaluate sludge properties. The batch contact tests for all seven reagents (two fly ashes and five chemicals) and the two uranium mill tailings solutions (Lucky Mc and Highland Mill) were performed in duplicate. Tables presented in the results section show the average values obtained from the duplicate tests.

SLUDGE PROPERTIES

The total dry weight of sludge formed for each batch contact experiment was determined by measuring the sludge wet weight and sludge moisture content gravimetrically by oven drying at 105°C for 24 hr (Gardner 1965). To determine the sludge moisture retention properties, the saturated sludge samples were placed in a pressure plate apparatus (Richards 1965) and drained under various applied pressures. The drained water contents were measured gravimetrically and tabulated as a function of capillary pressure, which is equal in magnitude to the applied pressure, but opposite in sign. These measurements, taken over a range of applied pressures, provide an estimate of drainage expected for similar sludge piles under field conditions. For example, a covered sludge pile, 10-m thick, draining to a water table at its base would have capillary pressure ranging from -10 m at the top to near zero at the base.

RESULTS AND DISCUSSION

TAILINGS SOLUTION COMPOSITION

Chemical composition of the uranium tailings solutions used for the batch neutralization tests is given in Table 2. Tailings solution from the Lucky Mc site had a low pH (1.2) and a high total acidity of nearly 15,000 mg/ℓ as CaCO₃. This corresponds to an acid content of nearly 300 milliequivalents per liter (meq/ℓ). The leachate from the Exxon Highland Mill site had a pH of 2.2 and a total acidity of only 4500 mg/ℓ as CaCO₃, which corresponds to an acid content of only 90 meq/ℓ. These values of 300 meq/ℓ and 90 meq/ℓ were used to estimate the quantity of neutralizing agent which would be required to raise the pH of these leachates to 7.3. Dissolved constituents present in these leachates originate as process additives or as by-products of the ore dissolution process. The process additives are sulfuric acid (H₂SO₄), sodium perchlorate (NaClO₄), ammonium nitrate (NH₄NO₃), and ferrous carbonate (FeCO₃). These reagents account for most of the observed sulfate, sodium, chloride, nitrate, iron, and the low pH. Other constituents present in the tailings solution are dissolved from the uranium ore during the leaching process. The high concentrations of trace metals and radionuclides represent a potential source of environmental contamination. The high concentrations of many of these contaminants in these acid tailings solutions enable us to evaluate the effectiveness of selected reagents for contaminant immobilization.

TREATED EFFLUENT WATER QUALITY

The water quality of the effluents from the batch neutralization experiments is found in Tables 3 through 8. The chemical composition of the treated effluents has been divided into three subsets for comparison purposes. Macro-ion, trace metal and radionuclide results for each reagent have been tabulated for each tailings solution.

Macro-ion results for the treatment of the Lucky Mc and Exxon solutions to pHs between 7.0 and 7.5 are given in Tables 3 and 4, respectively. In each case the concentrations of aluminum, iron, and silica were reduced significantly and generally independent of the reagent used. The removal of these constituents appears to be controlled mainly by the pH of the resultant solution. The average removal percentage over all seven treatments for each tailings solution was identical for Al (99.3%), Fe (>99.9%) and Si (97.2%). It appears that the MgO and fly ash treatments removed slightly less Al (88.5%) than the other treatments. The carbonate-based reagents and the Wyodak fly ash removed slightly less Si (96.2%) than the other reagents. Manganese removal was 70% for Exxon Highland Mill (HM) and 64% for Lucky Mc (LM). Hydrated lime removes manganese better than the other chemical reagents and limestone removes the least manganese.

TABLE 2. Solution Chemistry of Lucky Mc and Exxon Highland Mill Tailings Solutions^(a)

<u>Macro Ions</u>	<u>Lucky Mc Tailings (mg/l)</u>	<u>Exxon Tailings (mg/l)</u>
Al	1,030	405
Ca	600	548
Fe	2,780	950
Mg	1,220	495
Mn	163	44
Si	283	209
Na	1,630	332
Sr	14	8
K	156	40
SO ₄	26,400	7,920
NO ₃	302	7
Cl	1,090	290
<u>Trace Metals</u>		
Ag	<0.05	<0.05
As	19.00	0.42
Ba	0.09	<0.05
Cd	0.280	0.038
Co	3.40	0.90
Cr	2.40	1.41
Cu	1.50	1.10
Pb	0.87	<0.04
Mo	8.4	<0.05
Se	1.6	1.2
V	14.0	10.6
Zn	17.0	3.7
<u>Radionuclides^(b)</u>		
²¹⁰ Pb	16,000	<50
²³⁸ U	16,800	2,375
²³⁰ Th	167,000	127,000
²²⁶ Ra	4,900	940

(a) Lucky Mc tailings solutions had a pH 1.22 of 35.7 g/l of total dissolved solids and 14,800 mg/l as CaCO₃ of total acidity; the Exxon tailings solution had values of 2.24, 11.2 and 4,500, respectively.

(b) In pCi/l

TABLE 3. Final Concentrations Versus Influent for Lucky Mc Solution Neutralization, mg/l

Macro Ion	Fly Ash Boardman	Fly Ash Wyodak	CaCO ₃	Ca(OH) ₂	MgO	Na ₂ CO ₃	NaOH	Lucky Mc Influent
Al	5.6	7.6	5.8	5.3	13	6.2	6.5	1,030
Ca	450	480	490	480	500	310	490	600
Fe	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2,780
Mg	1,600	2,000	1,200	810	4,900	1,200	1,000	1,220
Mn	26	120	130	14	37	11	76	163
Si	5.2	18	7.7	<0.1	8.9	9.5	5.9	283
Na	1,700	1,500	1,500	1,500	1,500	10,000	9,000	1,630
Sr	17	21	2.4	3.8	11	6.8	12	14
K	160	150	150	150	150	150	150	156
SO ₄	12,000	13,000	10,000	9,100	24,000	25,000	24,000	26,400
NO ₃	290	300	290	290	300	330	280	302
Cl	1,300	1,300	1,300	1,300	1,300	1,300	1,200	1,090
TDS ^(a)	17,500	18,900	15,100	13,700	32,800	38,300	36,200	35,700

(a) Total Dissolved Solids is a calculation based on the sum of the macro ion concentrations in each sample

The percentage of removal for the major constituents calcium, magnesium, sodium, strontium, potassium, sulfate, nitrate and chloride is not high and some of the constituents show significant dependence on the reagent used. Average removal percentages for the seven reagents for each tailings solution were: Ca, 0% for HM and 24% for LM; for Mg, 0% for both tailings solutions; for Na, 0% for both; for Sr, 0% for HM and 24% for LM; for K, 3% for HM and 14% for LM; for SO₄, 28% for HM and 37% for LM; for NO₃, 9% for HM and 2% for LM; for Cl, 0% for both. Calcium removal occurs best when sodium carbonate is used, while magnesium, silicon and sulfate removal is best when hydrated lime is used. The calcium reagents remove significantly more strontium than other reagents. The two fly ash samples appear to release magnesium and strontium to solution. Sulfate is removed only by reagents containing calcium. The two sodium reagents and the magnesium oxide release significant amounts of sodium and magnesium respectively to the effluent solution. The potassium, nitrate and chloride contents of the tailings solutions change very little no matter what reagent is used to neutralize the solution. From the calculated total dissolved solids content the two calcium-based reagents (hydrated lime and limestone) remove the most dissolved solids, 58% and 51%, respectively.

TABLE 4. Final Concentrations Versus Influent for Exxon Solution Neutralization, mg/ℓ

Macro Ion	Fly Ash Boardman	Fly Ash Wyodak	CaCO ₃	Ca(OH) ₂	MgO	Na ₂ CO ₃	NaOH	Exxon Influent
Al	5.2	5.0	<0.1	<0.1	7.6	<0.1	<0.1	405
Ca	680	590	600	540	510	440	510	548
Fe	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	950
Mg	540	430	470	340	1,700	470	360	495
Mn	7.1	1.1	330	1.8	10	24	15	44
Si	0.4	5.2	8.0	5.7	6.7	8.7	6.1	209
Na	390	380	320	310	320	2,700	2,600	332
Sr	17	14	4.3	4.0	7.6	6.3	7.7	8
K	33	28	30	27	26	27	30	40
SO ₄ ⁼	4,500	3,900	4,100	3,600	7,900	8,000	7,900	7,920
NO ₃ ⁻	6.7	6.2	6.1	6.4	6.5	6.4	6.3	7.0
Cl ⁻	300	320	310	310	290	290	290	290
TDS ^(a)	6,480	5,680	6,180	5,140	10,800	12,000	11,700	11,200

(a) Total Dissolved Solids is a calculation based on the sum of the macro ion concentrations in each sample.

Trace metal concentrations in the treated effluents for the Lucky Mc and Exxon tailings solutions appear in Tables 5 and 6. Results for silver indicate that silver had a limited solubility in these high sulfate systems independent of pH. The silver content of the acid tailings solutions is below the primary drinking water standard of 0.05 mg/ℓ. Neutralization with the seven reagents does not increase silver solubility. Arsenic, chromium, copper, lead, vanadium, and zinc results indicate that these trace contaminants were removed from solution with the change in pH independent of the reagents used. Thus, neutralization appears to be an effective method of removing these trace metals. The detection limit for zinc was quite high (2.5 mg/ℓ); therefore, complete removal can only be inferred from these experimental results. Zinc and chromium did appear in concentrations above the detection limit in one sample each. These were in leachates neutralized with Wyodak fly ash suggesting that it is a less desirable neutralizing agent.

The effluent concentrations of barium were below detection limits (0.05 mg/ℓ) except for the experiments using limestone or the fly ash as the neutralizing agents. These three reagents were not effective at removing barium. Most of the reagents remove significant amounts of cadmium. Limestone appears to be the best removal reagent and the Wyodak fly ash is least effective.

TABLE 5. Trace Metal Concentrations After Neutralization Versus Lucky Mc Tailings Solution, $\mu\text{g}/\ell$

Trace Metal	Fly Ash Boardman	Fly Ash Wyodak	CaCO_3	Ca(OH)_2	MgO	Na_2CO_3	NaOH	Lucky Mc Influent
Ag	<50	<50	<50	<50	<50	<50	<50	<50
As	<50	<50	<50	<50	<50	<50	<50	19,000
Ba	62	80	90	<50	<50	<50	<50	92
Cd	11	180	<10	20	16	31	24	280
Co	<50	2,600	1,200	<50	<50	410	<50	3,400
Cr	<40	<40	<40	<40	<40	<40	<40	2,400
Cu	<100	<100	<100	<100	<100	<100	<100	1,500
Mo	880	50	630	1,300	2,500	720	830	8,400
Pb	<50	<50	<50	<50	<50	<50	<50	870
Se	1,100	1,000	1,100	1,100	960	1,300	1,330	1,600
V	<50	<50	<50	<50	<50	<50	<50	14,000
Zn	<2,500	6,200	<2,500	<2,500	<2,500	<2,500	<2,500	17,000

TABLE 6. Trace Metal Concentrations After Neutralization Versus Exxon Tailings Solution, $\mu\text{g}/\ell$

Trace Metal	Fly Ash Boardman	Fly Ash Wyodak	CaCO_3	Ca(OH)_2	MgO	Na_2CO_3	NaOH	Exxon Influent
Ag	<50	<50	<50	<50	<50	<50	<50	<50
As	<50	<50	<50	<50	<50	<50	<50	420
Ba	110	100	74	<50	<50	<50	<50	<50
Cd	<10	<10	<10	<10	<10	14	<10	38
Co	<50	<50	340	<50	<50	175	<50	900
Cr	<40	220	<40	<40	<40	<40	<40	1,410
Cu	<100	<100	<100	<100	<100	<100	<100	1,100
Mo	54	84	<50	<50	<50	<50	<50	<50
Pb	<40	<40	<40	<40	<40	<40	<40	<40
Se	1,100	1,200	1,100	1,590	1,100	840	1,000	1,200
V	<50	<50	<50	<50	<50	<50	<50	10,600
Zn	<2,500	<2,500	<2,500	<2,500	<2,500	<2,500	<2,500	3,700

TABLE 7. Radionuclide Results of Lucky Mc Solution Neutralization, pCi/ℓ

Radionuclide	Fly Ash Boardman	Fly Ash Wyodak	CaCO ₃	Ca(OH) ₂	MgO	Na ₂ CO ₃	NaOH	Lucky Mc Influent
²¹⁰ Pb	<50	<50	<50	<50	<50	<50	<50	16,000
²³⁸ U	93	134	798	81	106	1,680	104	16,800
²³⁰ Th	<400	<400	<400	<400	<400	<400	<400	167,000
²²⁶ Ra	84	138	368	154	235	1,590	334	4,900

TABLE 8. Radionuclide Results for Exxon Highland Mill Solution Neutralization, pCi/ℓ

Radionuclide	Fly Ash Boardman	Fly Ash Wyodak	CaCO ₃	Ca(OH) ₂	MgO	Na ₂ CO ₃	NaOH	Exxon Influent
²¹⁰ Pb	<50	<50	<50	<50	<50	<50	<50	<50
²³⁸ U	<50	112	250	149	57	350	<50	2,375
²³⁰ Th	<400	<400	<400	<400	<400	<400	<400	127,000
²²⁶ Ra	<50	215	142	174	<50	206	<50	940

Cobalt removal was variable. Carbonate bearing reagents (CaCO₃ and Na₂CO₃) and fly ash appear least efficient at removing cobalt suggesting that a soluble cobalt-carbonate complex may form or that neutralizing agents with the capability of increasing beyond pH 8 are necessary for efficient cobalt removal. Molybdenum removal was also variable. For the Exxon Highland Mill solution with less than 0.05 mg/ℓ Mo originally, neutralization with fly ash actually increased the Mo solution concentration with the Wyodak fly ash again releasing the most. For the Lucky Mc tailings solution with an original Mo content of 8.5 mg/ℓ, an average of 88% is removed. The magnesium oxide and hydrated lime removed less than the other reagents. For either tailings solution neutralization is ineffective at removing selenium, on the average only 29.6% and 5.6% of the selenium in the Lucky Mc and Highland Mill tailings solutions are removed upon neutralization. This implies that other techniques may be required to remove selenium from treated or untreated tailings solutions.

Radionuclide results for the neutralization of the Lucky Mc and Exxon Highland Mill tailings solutions appear in Tables 7 and 8. Removal of ²¹⁰Pb and ²³⁰Th was nearly complete (>99.7%) for all of the reagents tested. ²³⁸U and ²²⁶Ra results show an average 96% and 85% removal, respectively. The ²³⁸U and ²²⁶Ra treated effluent contents are greatest for the sodium carbonate reagent and also high in the calcium carbonate effluents. The data suggest that soluble carbonate complexes may be forming and thus reducing the efficiency of ²³⁸U and ²²⁶Ra removal.

Evaluation of these reagents based on treated effluent water quality suggests that removal of many of the potential contaminants is not reagent dependent. For those contaminants which are reagent dependent certain less desirable properties can be identified. It appears that the use of carbonate reagents (e.g., calcium carbonate, sodium carbonate) may complex certain potential contaminants. In addition, reagents that do not contain calcium (e.g., magnesium oxide, sodium carbonate, and sodium hydroxide) do not remove sulfate from the treated leachates. Fly ash results indicate certain coal fly ash samples may contain soluble contaminants and hence add to the contaminant inventory. Calcium hydroxide has shown none of these less desirable characteristics and in fact was the most effective neutralizing agent for removal of manganese, magnesium, silicon, sulfate and total dissolved solids. In only one instance, removal of Mo, do other reagents out perform hydrated lime, Ca(OH)_2 .

No promulgated set of Federal water quality standards exists that active uranium mill operators must meet prior to disposal of tailings and process waters but each mill is required to meet guidelines determined by state and federal regulatory agencies. The expressed purpose of the guidelines is to assure that tailings disposal will not cause ground water concentrations of selected contaminants to exceed specified levels considered harmful if directly consumed by humans and other living organisms.

For comparison purposes Table 9 lists several recommended water quality maximum concentration levels for selected constituents and the observed concentrations in the neutralized and filtered tailings solution for the three most promising reagents, calcium hydroxide, calcium carbonate and magnesium oxide.

The neutralized Lucky Mc tailings solutions exceed maximum concentration levels by 10^2 to 10^3 times for Se and Mn by 10^1 to 10^2 times for Mo, SO_4 and TDS and by 10^0 to 10^1 times for NO_3 , Cl and ^{226}Ra . The Exxon Highland Mill tailings solution after neutralization exceeds maximum concentration levels by 10^1 to 10^2 for Se, Mn and SO_4 and by 10^0 to 10^1 times for Cl, TDS and ^{226}Ra . Thus one might conclude that potentially the most problematic constituents will be Se, Mn, SO_4 and total dissolved solids. Most likely Mn would be removed further upon contact with sediments but Se, SO_4 and TDS would require significant dilution with low ionic strength ground water or specific treatment to ensure that their concentrations are below water quality guidelines.

SLUDGE PROPERTIES

Characterization of the sludges generated from neutralization of acidic tailings solution provides data needed to determine potential sludge disposal problems. Of major importance are the weight of sludge generated, its residual moisture content and its leachability. The weight of sludge is directly proportional to the handling and disposal costs. Sludge moisture retention properties are a measure of the adhesive and cohesive (capillary) forces which

TABLE 9. Observed Concentrations Versus MCLs

Constituent	Standard EPA-Inactive Tailings ⁽¹⁾	EPA-Interim Primary Drinking Water ⁽²⁾	EPA-Secondary Drinking Water ⁽³⁾	EPA Livestock Consumption ⁽⁴⁾	Radiation Protection ⁽⁵⁾	Neutralized Lucky Mc Tailings Solution			Neutralized Exxon Tailings Solution		
	mg/l	mg/l	mg/l	mg/l	pCi/l	Ca(OH) ₂ mg/l	CaCO ₃ mg/l	MgO mg/l	Ca(OH) ₂ mg/l	CaCO ₃ mg/l	MgO mg/l
Al	---	---	---	5	---	5.3	5.8	13	<0.1	<0.1	7.6
As	0.05	0.05	---	0.2	---	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Ba	1.0	1.00	---	---	---	<0.05	0.09	<0.05	<0.05	0.074	<0.05
Cd	0.01	0.01	---	0.05	---	0.02	<0.01	0.016	<0.01	<0.01	<0.01
Cr	0.05	0.05	---	1.00	---	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Pb	0.05	0.05	---	0.1	---	<0.05	<0.05	<0.05	<0.04	<0.04	<0.04
Hg	0.002	0.002	---	0.010	---	---	---	---	---	---	---
Mo	0.05	---	---	uncertain ^(b)	---	1.30	0.63	2.50	<0.05	<0.05	<0.05
N in NO ₃	10.0	10.0	---	23	---	66	66	68	1.5	1.4	1.5
Se	0.01	0.01	---	0.05	---	1.1	1.1	0.96	1.59	1.1	1.1
Ag	0.05	0.05	---	---	---	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
F	---	1.4-2.4 ^(a)	---	2.0	---	---	---	---	---	---	---
Cl	---	---	250	---	---	1,300	1,300	1,300	310	310	290
Cu	---	---	1.0	0.5	---	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe	---	---	0.3	No limit	---	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mn	---	---	0.05	No limit	---	14	130	37	1.8	330	10
SO ₄	---	---	250	---	---	9,100	1,000	24,000	3,600	4,100	7,900
Zn	---	---	5.0	2.5	---	<2.5	<2.5	<2.5	<2.5	<2.5	<2.5
B	---	---	---	5.0	---	---	---	---	---	---	---
V	---	---	---	0.1	---	---	---	---	---	---	---
TDS	---	---	500	---	---	13,700	15,100	32,800	5,140	6,180	10,80
pH	---	---	6.5-8.5	---	---	7	7	7	7	7	7

Constituent	(pCi/l)	(pCi/l)	(pCi/l)	(pCi/l)	pCi/l	(pCi/l)	(pCi/l)	(pCi/l)	(pCi/l)	(pCi/l)	(pCi/l)
²²⁶ Ra, ²²⁸ Ra	5.0	5.0	---	5.0	---	---	---	---	---	---	---
Natural U	10.0	---	---	---	2x10 ⁴	---	---	---	---	---	---
²³⁸ U	---	---	---	---	4x10 ⁴	81	798	106	149	250	57
²³⁰ Th	---	---	---	---	2000	<400	<400	<400	<400	<400	<400
²²⁶ Ra	---	---	---	---	30	154	368	235	174	142	<50
²¹⁰ Pb	---	---	---	---	100	<50	<50	<50	<50	<50	<50

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

(2) Environmental Protection Agency, "National Interim Primary Drinking Water Regulations," 40CFR Part 141 in FR Vol. 45 (Aug. 27, 1980), pp. 57342.

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

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

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

(a) Depends on temperature of water.

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

bind water in the sludge. Sludge residual moisture content is related to the ease of handling, with high moisture content sludges being much harder to handle. Sludge leachability determines the release of slightly soluble salts and potentially toxic trace metals and radionuclides. Mineralogic characterization was performed to give further information on chemical reactivity or leachability.

Results on the amount of sludge generated during neutralization appear in Table 10. Sodium hydroxide, sodium carbonate, and magnesium oxide generated the lowest quantities of sludge. These reagents produced 4 to 7 g of dry sludge for each liter of tailings solution neutralized for the Exxon Highland Mill tailings solution and 11.8 to 14.6 g/l for the Lucky Mc tailings solution. All of the other neutralizing agents produced at least twice as much sludge on a dry weight basis. The other neutralizing agents contain reactive calcium and thus remove some sulfate from the acid tailings solution (see Tables 3 and 4) which increases the quantity of sludge. Further, samples neutralized with fly ash appear to have unreacted solids present as part of the sludge. The fly ash reagents produced 27 to 32 g of dry sludge per liter of Exxon Highland Mill tailings solution and about 60 g/l for the Lucky Mc tailings solution.

Measurements of sludge moisture retention versus capillary pressure are shown in Tables 11 and 12. Sludges formed by neutralization with magnesium oxide, sodium carbonate, and sodium hydroxide contained substantially higher residual moisture contents over the entire pressure range. Values as high as twelve grams of water per gram of solids were measured for these sludges. Fly ash sludges retain the least water of any of the samples tested (0.3 to 1.5 gram of water per gram of solids over the pressure range studied). The undissolved solids remaining from the original ash contains little moisture and hence reduces the total moisture content of the fly ash sludges. Calcium carbonate and calcium hydroxide exhibit intermediate moisture contents of 1 to 3 grams water per gram of dry solids. The higher the moisture content at any capillary pressure range the more difficult the sludge will be to handle. Wet sludges also do not settle and consolidate well. The Exxon Highland Mill sludges for a majority of the treatments retain more moisture than the Lucky Mc Mill sludges at pressures >-10.2 m. For capillary pressures below (more negative than) -30.6 m the two sludge's moisture retention are quite dependent upon the neutralizing agent and show no distinct trends. The trend of these results show sodium reagents with the highest residual water content followed by magnesium oxide, calcium hydroxide, calcium carbonate, and the fly ash sludges with the lowest moisture content.

Together the total dry weight (see Table 10) and residual moisture content (see Tables 11 and 12) characteristics can be used qualitatively to project possible sludge handling and disposal problems. The non-calcium containing reagents (MgO , Na_2CO_3 , and $NaOH$) produced much less sludge, but they may contain up to 10 times the residual moisture content of the calcium containing reagents. The problems involved in handling and storage of these sludges may be much more difficult than those of the low moisture content sludges. Of the

TABLE 10. Total Dry Weight of Sludge Per Liter of Mill Tailings Solution Treated, g

	Fly Ash Boardman	Fly Ash Wyodak	CaCO ₃	Ca(OH) ₂	MgO	Na ₂ CO ₃	NaOH
Lucky Mc Tailings Solution	59.48	59.60	34.25	33.45	14.30	11.78	14.63
Exxon Highland Mill Tailings Solution	27.35	31.58	12.18	10.20	7.23	5.00	4.15

TABLE 11. Capillary Pressure Versus Water Content Relationship for Lucky Mc Sludge Material

Capillary Pressure (-m)	Sample Water Content [Dry Weight Basis (g/g)]						
	Fly Ash Boardman	Fly Ash Wyodak	CaCO ₃	Ca(OH) ₂	MgO	Na ₂ CO ₃	NaOH
0.10	1.519	1.141	1.833	2.251	5.320	7.071	7.171
0.50	1.500	1.141	1.787	2.194	5.180	6.889	7.042
1.02	1.284	1.063	1.470	1.958	3.928	5.474	6.950
3.06	1.091	0.923	1.311	1.648	3.362	4.214	4.548
10.20	1.030	0.809	1.154	1.479	3.092	3.764	4.048
30.60	0.537	0.428	0.707	0.716	2.302	2.453	2.718
51.00	0.465	0.352	0.560	0.595	2.012	2.429	1.132

TABLE 12. Capillary Pressure Versus Water Content Relationship for Exxon Highland Mill Sludge Material

Capillary Pressure (-m)	Sample Water Content [Dry Weight Basis (g/g)]						
	Fly Ash Boardman	Fly Ash Wyodak	CaCO ₃	Ca(OH) ₂	MgO	Na ₂ CO ₃	NaOH
1.02	1.377	1.137	1.746	2.829	3.945	12.250	7.094
3.06	1.367	0.791	1.384	2.778	3.290	8.808	4.707
10.20	0.791	0.640	1.000	1.714	2.941	7.000	4.241
30.60	0.453	0.387	N.D. ^(a)	1.238	N.D.	4.500	2.452
51.00	0.436	0.356	0.511	0.990	1.607	3.950	N.D.
153.00	0.487	0.357	0.416	0.855	1.109	2.880	2.333

(a) N.D. = Not Determined

calcium-containing reagents, calcium hydroxide produced the least sludge but its sludges contained higher moisture content than the other calcium sludges. The fly ash sludges that were produced during neutralization had low moisture, but had a total dry weight of nearly 60 grams per liter of Lucky Mc tailings solution neutralized which is 75% greater mass than the other calcium-based sludges. Thus, the hydrated lime, $\text{Ca}(\text{OH})_2$, again appears to be a likely choice with its moderate sludge production and moderate moisture retention properties.

MINERALOGY

Mineralogy of the sludges and original fly ash was determined by X-ray diffraction to shed some light on the neutralization process and minerals present in the sludges. Both the untreated Boardman and Wyodak fly ashes contained α -quartz (SiO_2), lime (CaO), and periclase (MgO). Further identification of crystalline phases present in the unreacted fly ash samples was unsuccessful. Both samples contain large quantities of high temperature glasses, which could not be identified and which made identification of other minor phases more difficult.

X-ray diffraction analyses of the resultant sludges from all batch contact experiments identified only one crystalline mineral, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Gypsum was identified in all samples neutralized with calcium-containing reagents [i.e., fly ashes, CaCO_3 and $\text{Ca}(\text{OH})_2$]. Of the minerals identified in the unreacted fly ash samples, only α -quartz remained. Thus, dissolution of lime (CaO) and periclase (MgO) occurred during the neutralization process since neither was identified in the reacted samples. No identifiable crystalline phases were present in the samples neutralized with magnesium oxide, sodium carbonate, or sodium hydroxide.

As most of the sludge appears to be amorphous, the X-ray diffraction analyses provided very little insight into the potential leachability of the sludges. Actual leach experiments will be necessary in future work.

REAGENT EFFICIENCY AND COSTS

The total weight of dry reagent added to each 400 milliliter batch contact experiment was compared to the theoretical amount based on the reagent's equivalent weight needed to neutralize the measured total acidity. This ratio expressed as a percentage is called the reagent efficiency. As the fly ash has no theoretical weight an efficiency for tailings neutralization cannot be calculated. If quantitative estimates of fly ash's lime and periclase were available it would be interesting to calculate a theoretical equivalent weight solely on their composition and then to compare with the actual weight of fly ash used. The actual weight of reagent used to neutralize the 400 milliliter tailings solution, the theoretical weight needed and efficiency of the reagent

are shown in Table 13. Fly ash results suggest that large quantities of these reagents would be required to treat the acid tailings solutions tested. Most of the other reagents tested required less than half the weight necessary with fly ash treatment. Magnesium oxide and calcium hydroxide neutralization used the smallest quantity of reagent for each of tailings solutions.

Neutralization efficiency results show that sodium hydroxide and calcium hydroxide are the most efficient reagents tested. Each of these reagents had efficiencies of greater than 89% on each tailings solution with a maximum of 98% for the Lucky Mc tailings solution and sodium hydroxide. The lowest calculated efficiency was for calcium carbonate and Exxon Highland Mill solution (62%). Table 13 also lists the reagent costs to neutralize the tailings solution per ton of ore processed. This value is obtained by assuming that 500 gallons (1892.7 liters) of tailings solution is produced per ton of ore processed and that all the tailings solution requires neutralization. The measured quantity of reagents used to neutralize 400 milliliters is converted to pounds of reagent/500 gallons of tailings solution (1 ton of ore). The reagent costs per pound are found in Table 1 and thus a reagent cost per ton of ore can be calculated.

Calculated reagent costs for leachate neutralization suggest that calcium carbonate, calcium hydroxide, and magnesium oxide would be the least expensive of the neutralizing agents tested. In addition, the total acidity of the leachate (see Table 2) is directly related to the cost of the treatment. High total acidity values as in the case of the Lucky Mc tailings solution may triple the cost of treatment over that of one with low acidity such as Exxon Highland Mill tailings solution. While these tests can only be used to predict costs on a laboratory scale, it is apparent that both reagent choice and leachate acidity influence total treatment costs. Other factors such as shipping charges, capital equipment requirements, and operating expenses must also be considered when evaluating neutralizing agents. These factors are best addressed under actual field conditions at each specific mill. On the other hand generalized data contained in the neutralization literature review (Sherwood and Serne 1982) suggest that lime and limestone or a combination of the two are cost competitive at Canadian Uranium mills and acid mine drainage sites in the United States. The figures for reagent costs found in this laboratory study (\$0.26 to \$7.65/ton) are higher than the costs calculated in the literature review document (\$0.10 to \$0.50/ton of ore processed). Perhaps the total acidity of the particular tailings solutions chosen in this study exceed the average values used in the literature review calculations.

The exact costs for producing yellowcake depend upon many parameters specific to geographical, ore, mill and waste disposal such that it is difficult to present a detailed and defensible cost analysis of the impact of the additional costs that neutralization of tailings solution would generate. One simple approach to assessing the impact of adding the neutralization step is to take the reagent cost data presented in Table 13 and calculate the percentage increase over current milling costs. A more thorough approach would amortize the cost of capital equipment needed to facilitate the neutralization step and additional operating expenses incurred during neutralization.

TABLE 13. Reagent Usage and Cost Data

Reagent	Leachate	Theoretical Reagent wt (g)	Actual Reagent wt (g)	Neutralization Efficiency, %	Reagent Cost, \$ per ton of ore ^(c)
Fly Ash	Lucky Mc Mill	(a)	14.5	(b)	1.43
(Boardman)	Highland Mill	(a)	6.2	(b)	0.61
Fly Ash	Lucky Mc Mill	(a)	16.0	(b)	1.58
(Wyodak)	Highland Mill	(a)	9.0	(b)	0.89
CaCO ₃	Lucky Mc Mill	6.00	8.50	71	0.88
	Highland Mill	1.80	2.90	62	0.30
Ca(OH) ₂	Lucky Mc Mill	4.44	4.94	90	0.83
	Highland Mill	1.33	1.50	89	0.26
MgO	Lucky Mc Mill	2.42	2.70	89	0.77
	Highland Mill	0.72	0.90	81	0.26
Na ₂ CO ₃	Lucky Mc Mill	6.36	7.36	86	3.54
	Highland Mill	1.90	2.10	90	1.01
NaOH	Lucky Mc Mill	4.80	4.88	98	7.65
	Highland Mill	1.44	1.55	93	2.42

(a) No calculated reagent weight can be predicted since fly ash has no known equivalent weight.

(b) No efficiency could be calculated.

(c) 1982 costs.

For the former simple case an estimate of the costs to produce yellowcake was obtained from ore cut-off grades and average ore grades milled in 1980 (see DOE 1981). In 1980 the average ore grade milled in the United States was 0.12% U₃O₈. The cut-off grade^(a) for 0.12% grade ore was \$27.30 in 1980. In other words to make it economically worthwhile to mill a uranium ore containing 0.12% U₃O₈ one must be guaranteed a sales price of \$27.30 for the processed uranium (as U₃O₈). At 0.12% U₃O₈ content one ton of ore would produce 2.4 pounds of processed U₃O₈; thus to process the ton of ore and still make a profit, the costs would be less than 2.4 x \$27.30 or \$65.50. If we assume that actual production costs excluding capital amortization, profit, etc. for the production of this average ore grade is about \$40/ton, then the added costs of just the reagent (lime) to neutralize tailings solution (\$0.26 to \$0.83 dependent upon waste acidity) represents less than a 2% increase in production

(a) the necessary ore grade that one must have to make a profit upon milling and recovery at a set price value for the uranium.

costs. If we assume that the capital equipment to receive, store and slake the lime and the reaction tanks to facilitate the neutralization and additional operating expenses triples the cost of the reagent alone, the percentage increase still remains below 4% compared with the fully burdened uranium production costs (\$65.50/ton of ore).

A separate study, Sears et al. 1975, presents much more detail on incremental costs for various radioactive waste treatment schemes for model U mills. Based on 1973 dollars and a model mill with a capacity of 2000 tons/day and an ore grade of 0.2% U_3O_8 , the incremental costs to add the lime neutralization step to conventional waste disposal practices currently used was \$0.26 per pound of U_3O_8 produced. As total production costs are not discussed, it is difficult to compare with the above computations. The \$0.26/lb increase does include amortized capital costs as well as operating costs. When compared to the 1980 cut-off price for average grade ore at 0.12%, \$27.30 per pound of U_3O_8 , the incremental costs for neutralization represents about 1% of the uranium value.

CONCLUSIONS AND RECOMMENDATIONS

Based on the results of these experiments and a past literature review (Sherwood and Serne 1982), calcium hydroxide is recommended as the best potential neutralizing agent. While other neutralizing agents were effective in reducing the concentrations of many contaminants in tailings solutions, there was no reagent as effective for all of the contaminants investigated. Furthermore, the sludge properties associated with calcium hydroxide treatment were more desirable than the other neutralizing agents tested. Reagent usage and cost results have shown that calcium hydroxide neutralizes solution acidity with an efficiency of approximately 90%, and yields reagent costs equivalent to that of the most economical reagents tested.

Results of the crystalline mineralogic analysis have provided limited information on the chemistry of the solids formed during neutralization. Crystallization of gypsum must occur rapidly under test conditions. No other crystalline substances were identified but other amorphous iron, aluminum, silica and manganese compounds are probable. Formation of such amorphous compounds are common in acidic soil systems upon neutralization.

Neutralization with carbonate reagents may enhance the mobility of Co, ^{238}U , and ^{226}Ra by formation of soluble carbonate complexes. Further, the mobility of these constituents in carbonate-rich soils and/or ground water may be enhanced. Of particular concern is ^{226}Ra which has a lower maximum control limit than concentrations found in the treated effluents especially after neutralization with carbonate reagents. Since little or no data exist on the complexation of radium with carbonates, we have not made theoretical predictions of its solution concentrations to date.

Simple incremental cost estimates for adding neutralization of tailings solution to the present milling procedures suggest an increase of 2-5% in production costs. More detailed costs estimates are necessary after larger scale demonstrations of neutralization are performed. Further cost-benefit relationships should be performed to evaluate whether neutralization is warranted as a pollutant abatement process.

Hydrated lime neutralization removed 62% and 54% of the total dissolved solids content of the Lucky Mc and Highland Mill tailings solution. For the elements Al, Fe, Si, Co, Cr, Pb, V, and ^{230}Th for both solutions the hydrated lime removed >95% from solution. Greater than 90% of the Mn, As, Cu, and ^{238}U and >80% of the Cd, Mo, Zn, and Ra were removed from the solutions upon neutralization with hydrated lime. Less than 20% of the Ca, Na, K, NO_3 , Cl, and Se present in the tailings solutions were removed upon neutralization.

Based upon water quality guidelines that to date have been used to regulate waste water disposal activities, the laboratory observations presented herein suggest that selenium, sulfate and total dissolved solids will still exceed maximum control limits by ten to a hundred times. As sediment sorption is not high for these constituents under oxidizing conditions and neutral to slightly basic pH values, substantial groundwater dilution may be required.

Other potentially problematic species on a case by case basis include Mn, Mo, Cl, ^{226}Ra and NO_3 . From the observed differences in reagent usage at the mill sites studied, contamination problems will have to be addressed on a site specific basis.

FUTURE STUDIES

Future work on immobilization of toxic constituents in tailings and tailings solutions should address:

1. More detailed neutralization process considerations prior to formulation of the field demonstration tests.
2. More complete sludge chemical identification especially the form and fate of contaminants within the neutralized sludges.
3. Investigation of carbonate complexation of ^{226}Ra , ^{238}U , and Co to determine whether carbonate complexes significantly increase contaminant mobility.

Process considerations such as ease of handling reagents, mixing characteristics of reagent and tailings, etc. need to be examined prior to the actual field demonstration of any technique. Since calcium hydroxide appears to be the preferred reagent, tests should be performed to determine optimum treatment conditions for this neutralizing agent. Among the most important process parameters which should be investigated are determination of optimum treatment pH (to remove soluble constituents in these studies), performance under continuous flow treatment, and residence time within the reaction/mixing chamber where the reagent and slurry are mixed.

Studies should also be performed which examine the chemical stability of the hydrated solids formed by neutralization. These tests should attempt to identify amorphous compounds and the contaminants associated with each compound. Leaching studies of these sludges should also be initiated to determine the parameters affecting the release of contaminants from amorphous precipitates.

Finally, detailed investigation on the effects of carbonate complexation on the mobility of radium should be undertaken. This work is necessary prior to formulation of any predictive capability on the migration of radium. Other carbonate complexation studies which should be initiated include complexation of uranium and cobalt.

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