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Uranium Mill Tailings Neutralization: Contaminant Complexation and Tailings Leaching Studies

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This progress report is the fifth NUREG document prepared for the project, Tailings Neutralization, Alternatives for Immobilizing Toxic Materials in Tailings (FIN B2370 Task 4). The project has three thrust areas: selection of neutralizing methods, 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 as follows:

NUREG/CR-2398, Tailings Treatment Techniques for Uranium Mill Waste: A Review of Existing Information, D. R. Sherwood and 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 and R. J. Serne, February 1983.

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

NUREG/CR-3449, Laboratory Evaluation of Limestone and Lime Neutralization of Acidic Uranium Mill Tailings Solution: Laboratory Progress Report, B. E. Opitz, M. E. Dodson and R. J. Serne, February 1984.

ABSTRACT

Laboratory experiments were performed to compare the effectiveness of limestone (CaCO_3) and hydrated lime [$\text{Ca}(\text{OH})_2$] for improving waste water quality through the neutralization of acidic uranium mill tailings liquor. The experiments were designed to also assess the effects of three proposed mechanisms--carbonate complexation, elevated pH, and colloidal particle adsorption--on the solubility of toxic contaminants found in a typical uranium mill waste solution. Of special interest were the effects each of these possible mechanisms had on the solution concentrations of trace metals such as Cd, Co, Mo, Zn, and U after neutralization.

Results indicated that the neutralization of acidic tailings to a pH of 7.3 using hydrated lime provided the highest overall waste water quality. Both the presence of a carbonate source or elevating solution pH beyond pH = 7.3 resulted in a lowering of previously achieved water quality, while adsorption of contaminants onto colloidal particles was not found to affect the solution concentration of any constituent investigated.

At solution pHs greater than pH = 6.3, carbonate complexation affects the solid phase control for uranium and perhaps zinc concentrations, while molybdenum concentrations were found to be a function of elevated solution pH. Arsenic, Cd, Cr, Pb, and V were effectively removed from solution at all solution pHs exceeding pH = 6.5, regardless of solution carbonate content. Cobalt removal is best at pH values above 7.3, and copper removal may be enhanced in carbonate-bearing solutions. Selenium removal is only 50% for either reagent at all pH values studied. Uranium solution concentrations in the presence of excess carbonate reagents were significantly higher than in solutions created by hydrated lime-only neutralization, but all solutions were below U.S. Nuclear Regulatory Commission radiation protection limits. Molybdenum was effectively removed from solution at pH = 6.3 but was present at pH = 9.0 in concentrations corresponding to those found in the unneutralized tailings liquor. Aqueous speciation calculations with the computer code MINTEQA were used to clarify these observed results.

Acidic untreated solid tailings from two mill sites and tailings neutralized with lime were leached with a simulated ground water for several pore displacement volumes. Analyses performed on the column effluents indicate that prior neutralization results in a significant reduction in the concentration of all pH-dependent constituents. In comparing the effluent data from the neutralized and untreated tailings, ions such as Al, As, Cd, Co, Cr, Cu, Fe, Si, Sr, V, and Zn displayed reduction of several orders of magnitude and, in most cases, were below detectable limits in the effluents generated from the neutralized tailings. It appears that more molybdenum leaches from the neutralized tailings column for the Lucky Mc sample than for the untreated tailings column. Ions such as Ca, Mg, Na, Cl, and SO_4 comprised the majority of the total dissolved solids content in the lime-treated tailings effluents. In contrast relatively high concentrations of several trace metals were found in effluent solution from the untreated tailings columns.

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EXECUTIVE SUMMARY

Laboratory experiments were conducted at Pacific Northwest Laboratory (PNL) that allowed a direct comparison of the effectiveness of limestone (CaCO_3) and hydrated lime [$\text{Ca}(\text{OH})_2$] in improving waste water quality through the neutralization of acidic uranium mill tailings liquor. These batch experiments were designed to additionally assess the effects of each of three proposed mechanisms--carbonate complexation, elevated solution pH, and colloidal particle adsorption--on the solubility of contaminants found in acid tailings liquor.

Acidic uranium mill liquor was neutralized to set pH points ranging from slightly acidic (pH = 6.5) to alkaline (pH = 9.0). Neutralization was accomplished by additions of solid limestone or hydrated lime. Analyses of the resulting waste water quality at each set pH point allowed for a direct comparison of the effectiveness of each reagent, investigated the effects of elevated solution pH on contaminant solubilities, and provided data on the optimum solution pH for contaminant removal. Microfiltration techniques were employed to determine to what extent colloidal particle adsorption was contributing to the observed contaminant solution concentrations.

A second set of batch experiments were conducted to study the role of carbonate complexation in maintaining contaminant concentrations in a neutralized tailings solution. Acidic tailings liquor, which had previously been neutralized to set pH points using only hydrated lime, was left in contact with the precipitates produced by neutralization and then contacted with a carbonate source (NaHCO_3). The pH of these systems were maintained at the values for the lime-only samples so pH effects and carbonate effects could be distinguished. Sodium bicarbonate was selected as the carbonate source because it caused insignificant changes in solution pH while increasing solution carbonate levels. Adjusted carbonate levels were set equal to those measured for limestone-neutralized solutions of identical pH from the initial study for samples up to pH 8.0. At higher pH systems the carbonate concentration was maintained at a level about twice as high as the pH 8.0 samples.

Results showed that, regardless of reagent type, the highest overall water quality was obtained when the pH of the original acidic tailings liquor was elevated to pH = ~7.3. Of the anions and macro cations studied, only SO_4 , Co, Mg, and Mn concentrations decreased as solution pH was raised beyond pH = 7.3. In addition, with the exception of Mn, Mo, Se, Zn, and Ra at a solution pH of 7.3, all of the trace metals and radionuclides investigated were present in solution at concentrations below in-place or proposed waste water guidelines. Of these only radium and selenium exceed current primary drinking water standards for humans. Total dissolved solids and manganese exceed the U.S. Environmental Protection Agency (EPA) secondary drinking water standard. Molybdenum and zinc exceed proposed EPA standards for solution disposal at active tailings sites; zinc also exceeds EPA livestock consumption standards. Besides failing to significantly lower contaminant levels further, increased neutralization beyond pH = 7.3 may cause the redissolution of molybdenum and radium, which are immobilized in the pH range of 6.5 to 7.3.

Molybdenum solution concentrations were found to be a function of pH. After being initially removed from all solutions studied at pHs = 6.5 and 7.3, molybdenum concentrations increased with increasing solution pH. In those solutions raised to pH = 9.0, molybdenum concentrations reached levels similar to the original unneutralized tailings liquor. When the tailings solution is neutralized beyond pH 7.8 by the addition of lime or limestone, the total Ca^{2+} activity in solution is lowered by formation of carbonate complexes and perhaps precipitation of calcite. The lowering of the Ca^{2+} activity in the neutralized systems allows powellite to become more soluble and release molybdenum to solution. MINTEQ calculations show powellite at equilibrium at pH values above 7.3, which is consistent with the hypothesis that increased solution concentrations of molybdenum are caused by powellite dissolving.

While neutralization to pH values above 7.3 may favor the continued removal of sulfate from solution, several studies indicate that the common ion effect may cause previously precipitated radium sulfate to dissolve back into solution. If sulfate concentrations are lowered far enough, radium solution activities may exceed set water quality guidelines.

Molybdenum concentrations in solution were found to be strictly a function of solution pH; uranium, copper, and zinc concentrations also displayed a dependence on neutralizing reagent type. In the presence of a carbonate source, either limestone or sodium bicarbonate, uranium activities increased with increasing carbonate levels after being almost completely removed in all solutions at pH = 6.5. In the pH range of 6.5 to 9.0, zinc solution concentrations in the presence of a carbonate source were consistently greater than for the hydrated lime-only systems. On the other hand, copper removal was enhanced in the carbonate systems.

Solution speciation calculations performed with the computer code MINTEQ show that the presence of observed carbonate concentrations at any of the pH values studied completely dominates the uranium system. The very strong complexes $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, and UO_2CO_3^0 form and keep uranium in solution compared to systems with no carbonate. Further, the first two complexes are anionic and would probably not adsorb readily onto the hydrous oxides of iron, aluminum, and manganese formed in the more alkaline solutions. On the other hand, UO_2OH^+ and $(\text{UO}_2)_3(\text{OH})_5^+$, the projected species in a carbonate-free system, might more readily adsorb on the oxides because the net negative surface charge of the hydrous oxides would attract cations at the pHs studied. The MINTEQ speciation calculations for zinc at the observed total carbonate and pH values suggest that significant differences in zinc speciation between the carbonate reagent-bearing solutions and lime-only solutions should only occur for the pH 8.5 and 9.0. At these higher pH values in the presence of the observed carbonate concentration, species such as $\text{Zn}(\text{CO}_3)_2^{2-}$ and ZnCO_3^0 predominate whereas at lower pH values the species ZnSO_4^0 , Zn^{2+} , and $\text{Zn}(\text{SO}_4)_2^{2+}$ predominate. Therefore, speciation calculations do not support the apparent significantly higher zinc concentrations found in all carbonate reagent solutions.

Speciation predictions for copper show that, at pH values above 7.3 for all the neutralized tailings solution experiments, $\text{Cu}(\text{OH})_2^0$ predominates, regardless of the presence of carbonate. The solutions are significantly

undersaturated with respect to CuCO_3 solid; thus, carbonates do not appear to affect the solution concentration of copper. The apparent higher concentrations of copper (~ 0.09 mg/L) in the hydrated lime-neutralized solutions in comparison with the solutions where carbonate reagents were present (~ 0.01 mg/L) may be caused by analytical problems such as matrix interferences in the analyses.

The element cobalt was not in the MINTEQ data base at the time of this work; therefore, it was not possible to perform cobalt speciation calculations to predict whether carbonate complexes or elevated pH might affect cobalt solution concentrations as suggested by the observed data.

Final conclusions to be drawn from these two batch studies may be summarized by the following statements. Neutralization of acidic uranium mill tailings liquor by any of the tested methods can substantially improve waste water quality. The optimum solution pH to terminate neutralization from a water quality viewpoint is $\text{pH} \approx 7.3$, regardless of neutralizing reagent. Finally, neutralizing reagents containing no carbonate will not only provide the highest water quality at a given solution pH, but the subsequent contact of a hydrated lime-neutralized solution with a carbonate source can degrade previously obtained water quality. Note that atmospheric CO_2 will eventually interact with the lime-neutralized systems and supply a source of carbonate ions for complexation. Also the efficiency of limestone as a neutralizing agent is only 60 to 70%. Therefore, excess CaCO_3 is always present in the systems neutralized with limestone. In a thermodynamic equilibrium system, there would be no difference between the final solutions formed at a fixed pH by hydrated lime or limestone provided the reagents were free of impurities and reacted with 100% efficiency. In the practical realm (versus the theoretical ideality) it appears that hydrated lime neutralization results in a solution with slightly better water quality over the short time frames studied.

Results of the colloidal particle adsorption investigation show no effect on solution chemistry because of colloidal particle removal by filtering through an 18A filter. Rather, the results show that even with prewashing the 18A filters used in this study are a source of zinc contamination.

Column leaching experiments were also performed on untreated (acidic) and laboratory-neutralized solid tailings from two mills in Wyoming. Both the treated and untreated tailings were contacted with laboratory-prepared ground water for several pore displacement volumes in order to evaluate the long-term effectiveness of neutralizing the solid fraction of uranium mill waste. Results of these column-leaching studies indicate that the column effluents from neutralized tailings contain significantly fewer hazardous constituents than effluents from untreated acidic tailings. The majority of the total dissolved solids content in the neutralized tailings columns effluents are comprised of those elements whose solubility is not strictly dependent on solution pH. For instance, cations such as Ca, Mg, and Na, and anions such as Cl and SO_4 were detected throughout the course of the neutralized tailings leaching experiment. In addition to those ions mentioned above, the elements detected in significant quantity in the untreated acidic tailings effluents

(i.e., Al, As, Cd, Co, Cr, Cu, Se, Si, Sr, V, and Zn) were substantially reduced by neutralization prior to leaching. In fact, concentrations of several of these elements in the leachate from neutralized tailings were below the detection limits of the analytical instruments. The one exception to these findings is that molybdenum release from neutralized tailings from the Lucky Mc Mill was greater than the release from the untreated tailings. A possible mechanism for increased effluent molybdenum concentrations may be that the molybdenum solution concentrations are being controlled by the mineral powellite as previously described.

INTRODUCTION

A majority of U.S. uranium producers employ a sulfuric acid leaching process for uranium extraction. Besides refining the desired uranium, two acidic waste forms are generated by the milling process: the solid fraction known as tailings and the solution fraction known as tailings liquor or solution. As processing continues, the wastes are discharged together as a slurry in tailings disposal impoundments and/or evaporation ponds.

Several general amelioration methods (i.e., specific constituent removal, solidification or fixation processes, and neutralization) have been identified as possible means of dealing with these acidic waste forms. Based on a review of these three treatment methods by scientists at Pacific Northwest Laboratory (PNL), neutralization appears to be the best suited for treating uranium mill waste than fixation processes or specific ion removal (Sherwood and Serne 1982). Further studies on various neutralization methods were pursued for the following reasons:

- Treatment costs are reasonable.
- The solution concentration of many contaminants are significantly reduced.
- The potential for surface and ground-water contamination is greatly reduced.

If U.S. mill operators were required to neutralize acid solution, the most likely reagents chosen would be lime, either hydrated [$\text{Ca}(\text{OH})_2$] or quicklime (CaO), or limestone (CaCO_3) (Sherwood and Serne 1983; Opitz, Dodson and Serne 1984). Recommendations for further research from earlier studies logically led to experiments designed to evaluate the effectiveness of these two reagents.

Based on previous laboratory studies, a two-step neutralization treatment was proven to be the most cost-effective treatment method tested to date for acid tailings solution (Opitz, Dodson and Serne 1984). The two-step neutralization scheme described consists of initially neutralizing acidic tailings solution to pH 4.0 with limestone followed by further neutralization to pH 7.3 with hydrated lime. The same studies also indicate that after neutralization, treated uranium mill liquors may still contain the trace metals Cd, Co, Mo, Se, Zn, and the radionuclides Ra and U in solution at levels exceeding water quality guidelines. Three possible mechanisms have been postulated to explain why these contaminants remain in solution: 1) reaction with carbonate (from limestone) to form soluble carbonate complexes, 2) increased solubility for anionic species at elevated pH (pH >8.0), and 3) adsorption onto colloidal particles that remain suspended in solution.

Adverse effects on treated solution quality because of elevated solution pH and adsorption onto colloidal particles can be easily mitigated. Neutralization can be halted at pH levels below those known to result in increased contaminant mobility, resulting in higher solution quality and a reduction in

overall neutralization costs. In addition, the pH conditions necessary to cause increased contaminant solubility ($\text{pH} > 8.0$) are seldom encountered in the natural environment, making treated solutions safe from environmental impact after disposal. Colloidal particles may be removed from solution with the addition of a flocculating agent. Contaminants sorbed onto these particles are also taken out of solution.

By contrast, if trace metal and radionuclide concentrations in neutralized liquors are being maintained by carbonate complexation, amelioration efforts may be reversed by contact with any source of carbonate, including the geologic media comprising the disposal area and atmospheric CO_2 . If the highly calcareous soils and overburdens found adjacent to western U.S. uranium milling operations, or proposed liner systems employing carbonate buffering materials, are used for solution containment, some of the benefits achieved through solution neutralization may be negated.

This report details the experimental work done at PNL for the U.S. Nuclear Regulatory Commission's (NRC) Uranium Research and Recovery Program. Two studies are presented, which were performed to determine the effectiveness of neutralizing acidic tailings solution and tailings solids. Specifically, the report evaluates waste water quality; contaminant complexation; total dissolved solids content; liquid effluent pH; and macro ion, trace metal, and radionuclide removal.

In the first study, two separate batch experiments were performed to provide a direct comparison of the effectiveness of limestone and hydrated lime in improving waste water quality through the neutralization of acidic uranium mill tailings solution. These batch experiments were designed to additionally assess the effects of each of the three proposed mechanisms (i.e., carbonate complexation, elevated pH, and colloidal particle adsorption) on the solubility of selected trace contaminants found in acid tailings liquors.

As noted earlier, neutralization of acidic uranium tailings solution can significantly reduce the levels of soluble macro ions, trace metals, radionuclides, and the total dissolved solids (TDS) content present in the original solution. Furthermore, if used prior to disposal, the neutralization process can also prevent the migration of the acid front associated with draining or seepage of untreated liquors through earthen impoundments and engineered soil liners. Although at present most laboratory research has centered around treating the liquid fraction of the waste, the long-term benefits of neutralizing an existing disposal pond that is in contact with the solid tailings fraction of the waste is not known. But, neutralization may provide a useful first step in a remedial action program.

In a second study, acidic mill tailings (solids) from two acid-leach process mills were neutralized with hydrated lime to pH 7.2 then contacted with a prepared ground water in order to simulate, on a laboratory scale, long-term leaching of treated tailings. The results of the leaching experiments are compared to results gained from an identical experiment performed on untreated tailings from the same two mill sites.

After completion of laboratory experiments, a field demonstration project using the best neutralizing process(es) determined from the available literature and laboratory studies was suggested (Opitz and Serne 1983). 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

CONTAMINANT COMPLEXATION EXPERIMENTS

Two sets of static-batch neutralization studies were conducted under identical conditions using separate neutralizing reagents or combinations of reagents. In the initial study, acidic tailings liquor containing the constituents shown in Table 1 was neutralized using either hydrated lime or limestone. Separate batches were neutralized to set pH values as follows: hydrated lime (pH = 6.5, 7.3, 8.0, 8.5, and 9.0) and limestone (pH = 6.5, 7.3, and 8.0). Neutralization was accomplished through the addition of solid reagents to 200 mL of acidic tailings liquor in sealed 250 mL polyethylene bottles. Initial reagent weights were determined by measuring the total acidity of the tailings liquor and calculating the equivalent weight of reagent necessary to reach each set pH point. Mixing was facilitated by constant shaking for a period of 48 h. When the initial reagent addition and shaking period was completed, the hydrated lime samples were allowed to settle prior to being measured for hydrogen ion activity (pH). If necessary, solution pH was further adjusted by the addition of either fresh tailings liquor to lower the pH or solid reagent to raise the pH. Prior to measuring the pH of all limestone-neutralized solutions, they were allowed to equilibrate with atmospheric carbon dioxide levels for a period not less than 24 h. Solution pH was then recorded and, if necessary, further adjusted toward the desired pH level. Once neutralization to the designated pH values was complete, all samples were centrifuged; filtered through a standard 0.45-micron membrane; measured for pH, Eh, and alkalinity; and then prepared for further analyses.

To study the effects of carbonate complexation, a second set of hydrated lime-neutralized solutions were prepared following the procedure described above. Neutralization by hydrated lime was carried out to the same set pH levels of pH = 6.0, 7.3, 8.0, 8.5, and 9.0 obtained in the initial study. Without removing the neutralization reaction precipitates, these solutions were further contacted with a carbonate source. Carbonate was introduced as solid sodium bicarbonate to avoid drastically altering solution pH while increasing carbonate levels. Enough carbonate was added to equal the alkalinity levels measured for the corresponding limestone-neutralized solutions of equal pH prepared in the first set of batch studies. Because limestone-only neutralization cannot produce a pH much above 8.0, carbonate levels of the solutions having pHs of 8.5 and 9.0 were elevated. Sodium bicarbonate was added to the hydrated lime-neutralized solution to the levels measured in the limestone-neutralized solutions in the initial study (pH 8.0 samples). Following the sodium bicarbonate addition, each sample was mixed for 48 h and then allowed to equilibrate with the atmosphere for at least 24 h. Samples were then centrifuged; filtered (0.45 micron); measured for pH, Eh, and alkalinity; and then prepared for solution analyses.

Colloidal particles were removed from selected samples by centrifugal filtering through an 18-A membrane. Prior to sample filtration, membranes were soaked overnight in double-distilled water, and an aliquot of sample was passed

TABLE 1. Lucky Mc Tailings Solution Characterization Data^(a)

Parameters	Lucky Mc Tailings Solution
pH	1.7
Eh (mV)	838
Conductivity (mmho/cm)	32.3
Total Suspended Solids (mg/L)	50
Total Dissolved Solids (g/L)	35.6
Total Acidity (as mg/L CaCO ₃)	15,735
<u>Macro ions (mg/L)</u>	
Al	1,010
Ca	570
Fe	3,100
K	200
Mg	1,217
Mn	154
Na	1,630
Si	250
Sr	14
Cl	1,280
NO ₃	250
SO ₄	25,690
<u>Trace metals (mg/L)</u>	
Ag	<0.02
As	13.6
Ba	0.01
Cd	0.30
Co	3.2
Cr	2.1
Cu	1.9
Mo	4.9
Pb	0.85
Se	1.6
V	19.2
Zn	16.0
<u>Radionuclides (pCi/L)</u>	
²¹⁰ Pb	12,300
²³⁸ U	15,500
²³⁰ Th	185,400
²²⁶ Ra	4,020

(a) See Opitz, Dodson and Serne 1984.

through the filter to fill possible adsorption sites. The subsequent sample filtrate was then analyzed for chemical composition.

TAILINGS LEACHING EXPERIMENTS

Tailings leaching experiments were performed using flow-through columns. Four polyacrylic cylindrical columns were compacted with either untreated acidic uranium mill tailings or tailings that had been neutralized to at least pH 7.0 with hydrated lime as listed in Table 2. Two columns contained tailings from the Lucky Mc Mill, one containing untreated tailings and one containing neutralized tailings; and two columns contained tailings from the Exxon Highland Mill, also one untreated and one neutralized tailings column. The tailings material was uniformly compacted to a dry weight bulk density of 1.50 g/cm^3 in all four columns. Column compaction data for the four columns are listed in Table 3. The method used for compaction was in accordance with the sliding-weight tamper method (ASTM 1978). Laboratory-prepared ground water was used to leach the tailings throughout the experiments. Flow from column bottom to column top enhanced removal of entrained air pockets in order to simulate saturated flow conditions. Constant flow rates were maintained throughout the experiment with Buchler Model 426-2000 multistatic pumps.^(a)

TABLE 2. Column Identification and Description

<u>Column</u>	<u>Description</u>
1	Untreated Exxon Tailings
2	Neutralized Exxon Tailings
3	Untreated Lucky Mc Tailings
4	Neutralized Lucky Mc Tailings

TABLE 3. Column Compaction Data

<u>Column</u>	<u>Cell Diameter (cm)</u>	<u>Length (cm)</u>	<u>Volume (cm³)</u>	<u>Dry Sample wt (g)</u>	<u>Bulk Density (g/cm³)</u>	<u>Porosity</u>	<u>Pore Volume (cm³)</u>
1	8.89	8.89	552	828	1.50	0.45	248
2	8.89	17.75	1102	1653	1.50	0.45	495
3	8.89	17.75	1102	1653	1.50	0.45	495
4	8.89	17.75	1102	1653	1.50	0.45	495

(a) Products of Haake Buchler Instruments Inc., Saddle Brook, NJ, 07662.

Flow rates were monitored daily, and effluent samples were collected dependent on the column's pore displacement volume (separate aliquots were collected approximately every pore volume for each column). Effluent aliquots were measured for pH and Eh and then subsampled for anion, cation, and radionuclide determinations. All chemical analyses were performed as described in Appendix A.

RESULTS AND DISCUSSION

CONTAMINANT COMPLEXATION EXPERIMENTS

Solution Neutralization

A useful method for comparing the overall effectiveness of limestone and hydrated lime as neutralizing reagents for acidic tailings liquors is to compare the TDS content of the original liquor and the neutralized solutions at each set pH point. Total dissolved solids content as a function of solution pH and reagent type are presented in Figure 1. Total dissolved solids levels for a given solution were calculated by simply summing the measured concentrations of each constituent analyzed. Neutralization of the original liquor to pH = 6.5 resulted in an equal reduction of TDS levels, at least 56%, regardless of reagent used. As neutralization progressed to higher pH conditions, the TDS content of the hydrated lime-neutralized solutions continued to decline slightly, with a sharp drop at pH = 9.0. In contrast, the limestone-neutralized solutions maintain a relatively constant TDS level over the range of pHs studied.

FIGURE 1. Total Dissolved Solids Comparison Between Limestone (CaCO₃) and Hydrated Lime-Neutralized [Ca(OH)₂] Tailings Liquor

The large drop in TDS content, produced through tailings liquor neutralization to pH = 6.5, was confirmed in earlier studies where several neutralizing agents were screened as potential solution treatments for acidic uranium mill liquors (Sherwood and Serne 1983). The large drop in TDS at pH = 6.5 was observed for all reagents tested and is a function of elevating the original tailings liquor pH beyond pH = 4.5 where pH sensitive cations, anions, and radionuclides are removed from solution through precipitation reactions (Serne, Peterson and Gee 1983). Of the neutralizing reagents tested, limestone and hydrated lime were chosen for further study. These two reagents are able to elevate tailings liquor pH beyond neutral pH conditions, thus increasing contaminant removal; are relatively easy to handle; are cost effective; and do not introduce additional contaminants to the system. Continued investigations have focused on 1) optimizing final solution pH to obtain the highest overall waste solution quality, 2) identifying contaminants that remain in solution at the optimum pH, and 3) understanding the mechanisms that keep certain contaminants in solution.

Measured constituent concentrations in each hydrated lime and limestone-neutralized solution at each set pH point are given in Tables 4 and 5, respectively. In addition, the solution chemistry of the original tailings liquor is presented in each table. The data in Tables 4 and 5 indicate that at pH = 7.3 both reagents are capable of reducing solution concentrations of the highly pH-sensitive constituents Al, As, Fe, Cr, Cu, Pb, Si, and V by more than 99%. Removal of Cd and Se from solution was >93% for both reagents, and limestone is not as effective in lowering Co, Zn, and U concentrations. Molybdenum removal is good at pH 6.5 but diminishes at higher pH for both reagents. Although the data were not presented here, earlier studies have shown that the very pH-sensitive radionuclides ^{230}Th and ^{210}Pb are effectively removed from solution at pH = 6.5 by both reagents and remain insoluble, regardless of increased solution pH or carbonate content (Sherwood and Serne 1983; Opitz, Dodson and Serne 1984). Selenium removal in all solutions averaged about 50% regardless of pH or carbonate content. Final selenium concentrations in solution exceeded primary drinking water standards.

Of the pH-sensitive metals removed by adjusting the acidic tailings liquor pH to 7.3, iron removal had perhaps the greatest effect on the overall solution chemistry. Iron (present at 3100 ppm in the original liquor) was removed from solution because of the formation of ferric hydroxide $[\text{Fe}(\text{OH})_3]$ at pH = 4.5 (Serne, Peterson and Gee 1983). The structure of ferric hydroxide ranges from amorphous to crystalline, depending on the mode of formation and age. Predictions suggest that the formation of amorphous ferric hydroxide in neutralized tailings liquor precipitates because of the short reaction times involved in most tailings neutralization experiments (<27 days) (Peterson et al. 1983). Other researchers have proposed that the incorporation of silica and aluminum, both present at substantial levels in the original liquor, into precipitated iron hydroxide will also favor amorphous ferric hydroxide formation through increased crystal disorder (Schwertmann and Thalmann 1976; Fey and Dixon 1981). Iron oxides, once formed, can serve as adsorption surfaces for trace metals,

**TABLE 4. Solution Chemistry: Neutralization of Lucky Mc Tailings
Liquor Using Hydrated Lime [Ca(OH)₂]**

Parameter	Original Tailings Liquor	pH 6.5	pH 7.3	pH 8.0	pH 8.5	pH 9.0
pH	1.7	6.5	7.3	8.0	8.5	9.0
Eh (mV)	833	339	322	303	287	283
TDS (mg/L)	35,597	15,410	14,923	14,486	13,694	8,470
Carbonate (ppm carbon)	0.0	0.0	0.0	0.0	0.0	20.6
Bicarbonate (ppm carbon)	0.0	2.8	6.5	8.2	20.7	0.0
<u>Macro ions (mg/L)</u>						
Al	1,010	0.1	0.1	0.1	0.1	0.1
Ca	570	463	455	454	464	514
Fe	3,100	0.1	0.1	0.1	0.1	0.1
K	200	495	485	465	465	485
Mg	1,217	1,183	1,097	1,009	837	18.6
Mn	154	117	54.4	21	7.2	0.01
Na	1,630	1,515	1,535	1,655	1,630	1,570
Si	250	3.0	1.5	0.1	0.1	1.0
Sr	14	7.3	5.6	4.6	4.2	2.95
Cl	1,280	1,239	1,253	1,251	1,250	1,265
NO ₃	250	254	254	253	251	248
SO ₄	25,690	10,120	9,770	9,370	8,780	4,360
<u>Trace Metals (mg/L)</u>						
Ag	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
As	13.6	<0.02	<0.02	<0.02	<0.02	<0.02
Ba	0.01	0.05	0.02	0.02	0.02	0.02
Cd	0.30	0.10	0.02	0.01	0.01	0.01
Co	3.2	0.80	0.07	0.02	0.02	0.02
Cr	2.1	0.01	0.01	0.02	0.02	0.02
Cu	1.9	0.09	0.09	0.11	0.09	0.07
Mo	4.9	0.17	0.63	1.20	1.69	4.12
Pb	0.85	0.02	0.02	0.02	0.02	0.02
Se	1.6	0.87	0.79	0.79	0.88	0.80
V	20.0	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	16.00	0.75	0.32	0.05	0.65	0.05
<u>Radionuclides (mg/L)</u>						
U (total)	40.0	0.05	0.10	0.24	0.30	0.15

**TABLE 5. Solution Chemistry: Neutralization of Lucky Mc Tailings
Liquor Using Limestone (CaCO₃)**

Parameter	Original Tailings Liquor	pH 6.5	pH 7.3	pH 8.0
pH	1.7	6.5	7.3	8.0
Eh (mV)	833	326	307	345
TDS (mg/L)	35,597	15,530	15,132	15,689
Carbonate (ppm carbon)	0.0	0.0	0.0	0.0
Bicarbonate (ppm carbon)	0.00	1.8	5.0	19.2
<u>Macro ions (mg/L)</u>				
Al	1,010	0.1	0.1	0.1
Ca	570	489	461	430
Fe	3,100	0.1	0.1	0.1
K	200	200	510	140
Mg	1,217	1,190	1,186	1,060
Mn	154	117	69.1	57.5
Na	1,630	1,585	1,500	1,455
Si	250	2.0	1.0	0.7
Sr	14.0	5.6	2.7	3.4
Cl	1,280	1,306	1,265	1,200
NO ₃	250	270	254	160
SO ₄	25,690	10,360	9,872	11,150
<u>Trace metals (mg/L)</u>				
Ag	<0.02	<0.02	<0.02	<0.02
As	13.6	<0.02	<0.02	<0.02
Ba	0.01	0.01	0.01	0.01
Cd	0.30	0.01	0.01	0.01
Co	3.2	1.18	1.01	0.01
Cr	2.1	0.03	<0.03	<0.03
Cu	1.9	0.01	0.01	0.01
Mo	4.9	0.12	0.28	0.95
Pb	0.85	0.01	0.01	0.01
Se	1.6	0.83	0.85	0.80
V	20.0	<0.1	<0.1	<0.1
Zn	16.0	2.50	2.85	0.06
<u>Radionuclides (mg/L)</u>				
U (total)	40.0	0.30	2.05	3.15

thus promoting the removal of trace metals from acidic tailings liquor through precipitation as neutralization progresses (Jenne 1968).

Although the removal of trace metals from solution (by precipitation as hydroxides or through adsorption) is nearly complete at pH = 7.3, their absence from solution represents only a fraction of the overall drop in TDS. Trace metal concentrations in the original tailings liquor are insignificant compared to the concentrations of the macrocations (Al, Ca, Fe, K, Mg, Mn, and Na) and anions (Cl, NO₃, and SO₄). In fact when neutralizing tailings liquors produced by sulfuric acid leaching, SO₄ removal comprises the highest percentage of TDS reduction of all the tailings liquor constituents.

Potassium, sodium, chloride, and nitrate concentrations remain virtually unchanged, regardless of solution pH or neutralization reagent type. These constituents form very soluble salts, are unable to compete for adsorption sites in the presence of multivalent metals, and are easily replaced by ion-exchange if they are tied up in secondary minerals formation (Bohn, McNeal and O'Connor 1979, p. 184). Potassium concentrations in solution are actually being enhanced by reagent addition, especially by the hydrated lime addition, and are probably present as an impurity in the reagents.

Manganese concentrations show a reduction of more than 50% at pH = 7.3, regardless of reagent type. This initial reduction is followed by continued removal with increasing solution pH until manganese concentrations are below our detectable limits of pH = 9.0. The data indicate that manganese concentrations are a function of solution pH. Manganese concentrations in all the neutralized solutions exceed the EPA secondary drinking water standard of 0.05 mg/L.

Figure 1 indicates that strongly alkaline solution conditions (pH >8.5) are necessary for substantial SO₄ removal beyond that achieved at pH = 7.3 (Serne, Peterson and Gee 1983; Bohn, McNeal and O'Connor 1979, p. 184). At pHs below 8.0, sulfate removal is presumably the result of jarosite and gypsum formation. The decrease in SO₄ concentrations coincides with an increase in Ca concentrations. This may indicate that a solid phase, presumably calcium sulfate, is imposing a solution activity constraint on calcium and sulfate concentrations (Serne, Peterson and Gee 1983). The large drop in sulfate concentration at pH = 9.0 in Table 4 and in the lime/sodium bicarbonate data presented in Table 6 cannot be explained by a calcium sulfate solid phase, as the increase in calcium concentration is insignificant from pH = 8.5 to pH = 9.0. The data suggest that rather than calcium and sulfate interactions, magnesium and sulfate interactions dominate in extremely alkaline conditions (pH > 8.5) (Serne, Peterson and Gee 1983). Magnesium concentrations in both Tables 4 and 6 are drastically reduced at pH = 9.0, coinciding with a reduction in sulfate concentrations. Using the reagents tested, two problems occur when elevating the tailings liquor past pH = 8.5 to remove SO₄. First, substantially higher reagent costs result from increased reagent use, especially for limestone, as the efficiency of carbonate reagents decreases drastically above pH = 6.0. Secondly, the strongly alkaline conditions and lowered SO₄ concentrations can result in the dissolution of molybdenum (as shown in Tables 4, 5,

TABLE 6. Solution Chemistry: Neutralization of Lucky Mc Tailings
Liquor Using Hydrated Lime/Sodium Bicarbonate
[Ca(OH)₂/NaHCO₃]

Parameter	Liquor	Original Tailings pH 6.5	pH 7.3	pH 8.0	pH 8.5	pH 9.0
pH	1.7	6.5	7.3	8.0	8.5	9.0
Eh (mV)	833	280	284	281	283	263
TOS (mg/L)	35,597	15,142	14,735	14,454	12,989	9,994
Carbonate (ppm carbon)	0.0	0.0	0.0	0.0	8.1	46.3
Bicarbonate (ppm carbon)	0.0	4.5	10.8	41.5	32.6	0.0
<u>Macro ions (mg/L)</u>						
Al	1,010	0.1	0.1	0.1	0.1	0.1
Ca	570	476	463	473	488	512
Fe	3,100	0.1	0.1	0.1	0.1	0.1
K	200	530	495	495	510	540
Mg	1,217	1,230	1,133	1,042	653	133
Mn	154	117	62.2	20	2.5	0.1
Na	1,630	1,495	1,415	1,490	1,485	1,520
Si	250	2.0	0.5	0.5	1.0	1.0
Sr	14	7.5	5.5	4.6	4.0	3.4
Cl	1,280	1,200	1,245	1,282	1,301	1,323
NO ₃	250	243	247	248	255	254
SO ₄	25,690	9,836	9,663	9,391	8,281	5,699
<u>Trace metals (mg/L)</u>						
Ag	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
As	13.6	<0.02	<0.02	<0.02	<0.02	<0.02
Ba	0.01	0.01	0.01	0.01	0.01	0.01
Cd	0.30	0.01	0.01	0.01	0.01	0.01
Co	3.2	0.83	0.09	0.02	<0.02	<0.02
Cr	2.1	0.02	0.02	0.02	0.03	0.06
Cu	1.8	0.01	0.01	0.01	0.01	0.01
Mo	4.9	0.15	0.07	1.3	2.0	2.8
Pb	0.85	0.01	0.01	0.01	0.01	0.01
Se	1.6	1.0	0.8	1.0	1.0	0.8
V	20.0	NA ^(a)	NA	NA	NA	NA
Zn	16.0	2.65	2.9	2.5	1.75	1.9
<u>Radionuclides (mg/L)</u>						
U (total)	40.0	0.05	1.90	2.55	2.05	1.90

(a) NA = not analyzed.

and 6) and radium into solution (Levins, Ryan and Strong 1978; Shearer and Lee 1964; Lindsay 1979; Landa 1980; Shepherd and Cherry 1980; and Dodson, Gee and Serne 1984).

Molybdenum concentrations display substantial reduction (>96%) in all solutions at pH = 6.5 and >87% at pH = 7.3, followed by a gradual increase as solution pH increases to 9.0. Molybdenum removal was an average of only 27%. Solution concentrations of molybdenum are plotted versus pH in Figure 2. The line labeled untreated tailings liquor (long dashed line) in Figure 2 represents the concentration of Mo in the original acidic liquor. The other line, labeled neutralized tailings liquor (short dashed line), represents the molybdenum concentrations at each set pH after neutralization with hydrated lime (see Table 4). Molybdenum concentrations after neutralization with limestone and lime/sodium bicarbonate (see Tables 5 and 6) are not shown here, as type of reagent used had little effect on molybdenum concentrations, and the results of neutralization in the presence of a carbonate source were similar. Molybdenum concentrations in solution behave similarly, regardless of solution carbonate contents and appear to be controlled solely by the solution pH. In

FIGURE 2. Comparison of Molybdenum Concentrations in Untreated and Neutralized Tailings Liquor

neutral tailings solutions with high calcium concentrations, one possible compound responsible for controlling molybdenum solubility is powellite (CaMoO_4). Lindsay reports that the solubility of powellite in natural systems reacts in a similar pattern to increasing solution pH, showing limited solubility up to pH = 7.8 followed by steadily increasing solubility as a function of increased pH (Lindsay 1979). The total Ca^{2+} in solution is lowered by the formation of carbonate complexes and precipitation of carbonate minerals found in typical natural systems (above pH 7.8). This lowering of the Ca^{2+} activity will cause powellite to dissolve, releasing MoO_4^{2-} to the solutions.

Using the MINTEQ code (Felmy, Girvin and Jenne 1984), analytical data for the neutralized solutions were simulated. MINTEQ was used in this study to calculate saturation indices with respect to given minerals and solid phases based on the composition of a solution. The saturation index of a mineral is the log of the ratio of the activity product calculated from the solution composition to the solubility product for that mineral or solid phase. The importance of this comparison is in defining chemical processes that may limit the concentration of potential contaminants and other constituents during tailings solution neutralization. A saturation index of zero indicates that the mineral is in equilibrium with the solution. A saturation index of less than zero means that the solution is undersaturated with respect to that mineral, and an index of greater than zero indicates oversaturation. MINTEQ calculations for the neutralized solutions show powellite to be slightly undersaturated at pH values below 7.3, at equilibrium at pH values above 7.3, and thus consistent with powellite controlling the molybdenum concentration. The fact that the calculations show slight undersaturation below pH 7.3 may reflect measurement errors or indicate that the system has not established an equilibrium. Perhaps more molybdenum has been removed from solution and trapped in the sludge or adsorbed onto the hydrous iron oxides. At this time, powellite has not been identified in the sludges produced by tailings liquor neutralization. The identification of specific minerals in the precipitated sludge material, which experience suggests (literature citations) and computer modeling predicts to be present, is currently being pursued through laboratory investigations.

While radium values are not presented in this paper because of the high sample volume requirements and analytical costs required for low-activity radium analysis, it is assumed that radium is removed from solution in the form of radium sulfate precipitates or through coprecipitation with either barium or calcium sulfates (Levins, Ryan and Strong 1978; Shearer and Lee 1964). High sulfate concentrations are known to limit the mobility of radium (Shearer and Lee 1964; Landa 1980), and radium substitution for Ca in gypsum has also been proposed (Shepherd and Cherry 1980). The low solubility of radium sulfate results in limited dissolution of radium from the host rock with conventional sulfuric acid leaching. In contrast, washing and leaching of solid tailings with deionized water or leachant with a low concentration of sulfate dissolves increasing amounts of radium as the solution-solid ratio is increased and sulfate is removed from the tailings (Levins, Ryan and Strong 1978; Shearer and Lee 1964; Landa 1980). Thus, as the sulfate concentration decreases with continued neutralization and CaSO_4 precipitation, the radium activity is likely to rise in accordance with the common ion effect.

Carbonate Complexation Study

The effects on solution chemistry caused by contacting a previously hydrated lime-neutralized solution with a carbonate source, sodium bicarbonate, are given in Table 6. The contaminants of interest are those that showed dissimilar solution concentrations after neutralization using either hydrated lime or limestone, or solubility changes at solution pHs in excess of pH = 8.0. These include the macro ions Mg, Mn, and SO_4 , the trace metals Co, Mo, and Zn, and the radionuclide uranium.

A review of magnesium chemistry in geologic environments (Lindsay 1979; Doner and Lynn 1977) suggests that solids that may form rapidly when acidic tailings solution are neutralized should be brucite $[\text{Mg}(\text{OH})_2]$, carbonate minerals such as magnesite (MgCO_3), or magnesium-substituted calcite or dolomite $[\text{MgCa}(\text{CO}_3)_2]$. The solution data from Tables 4, 5, and 6 were speciated. The activity products of the various species were compared to the solubility products of these mineral (e.g., the ion activity product $(\text{Mg}^{2+})(\text{OH}^-)^2$ is compared against the K_{sp} of brucite). If a particular solid phase is controlling the solution concentration of a given element, then the ion activity product and K_{sp} should agree. At pH values of 7.3 and below, the calculated ion activity products are lower than the K_{sp} values of these likely magnesium-bearing precipitates. At pH values 8.0 and 8.5, the ion activity products agree closely with the K_{sp} of magnesium-substituted calcite, assuming 7% magnesium substitution at pH 8.0 and 17% magnesium substitution at pH 8.5. These values for substitution agree with the expected substitution (Thorstenson and Plummer 1977) at the calculated activities of Ca^{2+} , Mg^{2+} , and CO_3^{2-} species for the various solutions. A more general empirical equation for magnesium substitution into calcite presented for soils by Donner and Lynn (1977) suggest that 7% substitution at all pH values above 8.0 would be expected. The pH 8.0 and 8.5 solutions are slightly oversaturated with respect to magnesite, significantly oversaturated with respect to dolomite, and significantly undersaturated with respect to brucite. These calculations suggest magnesium solution concentrations are controlled by the precipitation of magnesium-substituted calcite or, less likely, by magnesite; however, dolomite does not appear to form rapidly enough to control solution magnesium concentrations at lower values. For the pH 9.0 data, the calculated ion activity products for all magnesium solids exceed the K_{sp} values, suggesting some hinderance to reaching equilibrium. Again the solid that appears to be closest to equilibrium is a magnesium-substituted calcite, although magnesite is also a possibility. As the total observed magnesium concentration of the pH 9.0 solutions is much lower than the other solutions, magnesium is apparently precipitating but perhaps not rapidly enough to have been in equilibrium with probable solids. With more contact time magnesium concentrations probably would have been reduced further.

MINTEQ speciation and ion activity product calculations for manganese were compared with the solubility products of probable solids (Lindsay 1979). The most probable solids that might form in the neutralization experiments at the measured pH and Eh values are rhodochrosite (MnCO_3), hausmannite (Mn_3O_4), and manganite ($\gamma\text{-MnOOH}$). At pH 6.5 MINTEQ calculations suggest that none of these solids are in equilibrium with the observed manganese solution. The solution

is undersaturated with respect to all three solids and, if present, one would expect manganese dissolution. The pH 6.5 solutions for all three treatments showed 117 mg/L total manganese, which is a drop from the influent value of 154 mg/L. Perhaps the reduction in manganese reflects coprecipitation with or adsorption onto hydrous iron oxides or formation of amorphous manganese compounds with higher solubilities than the noted crystalline minerals. The pH 7.3 solutions' ion activity products suggest that the solutions are in equilibrium with rhodochrosite, while the solutions at the higher values (pH 8.0 and 8.5) are somewhat oversaturated with respect to rhodochrosite. The pH 8.0, 8.5, and 9.0 appear to be in equilibrium or slightly oversaturated with respect to hausmannite. All the solutions appear to be undersaturated with respect to manganite. The pH 9.0 solution is also undersaturated with respect to rhodochrosite. The thermodynamic calculations do not provide a clear indication of what solid might be controlling manganese solution concentrations. The effluents from column experiments where acid tailings solution interacts with sediments are best predicted assuming rhodochrosite does control the manganese concentration (Peterson et al. 1984, pp. 513-535). Lindsay (1979) concludes that rhodochrosite is more likely to form in soils than hausmannite. We could speculate that the precipitation of rhodochrosite is kinetically slow compared to the contact times used in the neutralization experiments; thus, our solutions were not yet finished precipitating MnCO_3 . On the other hand, the pH 9.0 solutions show a manganese decrease below the concentration expected if rhodochrosite was in control. Until we can isolate and identify the manganese solid phases in the sludge, no one process can be given more credence than others.

The significant drop in sulfate concentrations for the pH 9.0 solutions is caused by the continued precipitation of gypsum as more calcium (in the form of hydrated lime) is added to raise the pH. The calcium added to pH 9.0 solutions is considerably greater than any of the other samples and thus makes it easy to observe a drop in the sulfate concentrations. Close inspection of Tables 4 and 6 show a small drop in sulfate for each incremental increase in pH. Around neutrality it takes very little additional hydrated lime to increase the pH; thus, the sulfate drop between pH 7.3, 8.0, and 8.5 are less dramatic. All the solutions formed during these neutralization experiments are in equilibrium with gypsum; the presence of large amounts of gypsum in the sludges have been verified by x-ray diffraction.

MINTEQA ion speciation distributions for the neutralized solutions were calculated and show that at pH values of 8 or below ZnSO_4^0 , Zn^{2+} , and $\text{Zn}(\text{SO}_4)_2^{2-}$ predominate whether lime or limestone was used as neutralizing agents. At pH values 8.5 and 9.0, distinct changes in speciation occur, with $\text{Zn}(\text{CO}_3)_2^{2-}$ and ZnCO_3^0 predominating. There is enough measured carbonate in the lime-only solutions (from absorption of atmospheric CO_2) to also cause transformation to the carbonate-based species. Therefore, one would not expect differences in zinc solution concentrations because of species differences. A review (Lindsay 1979) of possible zinc-bearing solids that might form if neutralized include smithsonite (ZnCO_3), $\text{ZnCO}_3 \cdot \text{H}_2\text{O}$, zincite (ZnO), willemite (Zn_2SiO_4), and franklinite (ZnFe_2O_4). The appropriate ion activity products were calculated for each solution in Tables 4, 5, and 6 and compared to the solubility products for these solids. All the solutions are undersaturated with respect to the carbonate minerals and greatly oversaturated with respect to franklinite. The

solutions with $\text{pH} < 8$ are also undersaturated with respect to zincite and willemite. The pH 8.5 and 9.0 solutions with NaHCO_3 added might be at equilibrium with zincite and appear oversaturated with willemite. The pH 8.5 lime-neutralized solution could be at equilibrium with either zincite or willemite; however, the pH 9.0 lime-only solution is significantly undersaturated with respect to zincite but might be at equilibrium with willemite. In summary, no solid seems to be a control for the observed zinc concentrations except perhaps the higher pH solutions 8.5 and 9.0. A more likely control for zinc is adsorption onto amorphous iron oxides (Serne, Peterson and Gee 1983). The thermodynamic calculations do not clearly explain the observed differences in water quality for zinc between the hydrated lime- and limestone-neutralized solutions. Tables 4, 5, and 6 suggest that for a set pH value carbonate-bearing reagents allow higher zinc solution concentrations.

Trace metal concentrations in Table 6 show cobalt concentrations in the carbonate-treated solution follow the trend observed in solutions produced by neutralization with hydrated lime only (i.e., 84% removal at $\text{pH} = 6.5$ and 99% removal at $\text{pH} = 7.3$ and greater). These results offer no explanation for the slightly greater solubility of cobalt observed in the $\text{pH} = 7.3$ solution initially neutralized using limestone only. Perhaps this data point is erroneous. A lower concentration is seen in the postcarbonate-treated lime-neutralized solutions at this pH . As cobalt was not in the MINTEQ data base at the time of this work, it was not possible to calculate speciation distributions or ion activity products to identify potential cobalt-bearing controlling solids.

Of all the contaminants present in the original tailings liquor, uranium is the most sensitive to the presence of carbonate in solution. The relationship of uranium solution concentration to pH and for the three types of solutions is shown in Figure 3. Solution concentrations of uranium in the carbonate-adjusted hydrated lime-neutralized solutions above pH 6.5 ranged between 1.8 and 2.4 mg/L , while levels measured in the limestone-only neutralized solutions continued to rise with pH (peak at 3.2 mg/L). For both these test conditions, the values were significantly higher than those recorded in the hydrated lime-only neutralized solutions (0.1 to 0.2 mg/L). Thus, any source of carbonate contacting a previous lime-only neutralized tailing liquor is capable of generating soluble uranium carbonates and increasing uranium activities in solution.

MINTEQ speciation distributions of the various solutions show that carbonate does have a profound effect on uranium in solution. For the solutions in contact with added carbonate reagents, the two most predominating species at the various pH values are as follows: 51% UO_2CO_3^0 and 37% $\text{UO}_2(\text{CO}_3)_2^{2-}$ at pH 6.5, 65% $\text{UO}_2(\text{CO}_3)_2^{2-}$ and 31% $\text{UO}_2(\text{CO}_3)_3^{4-}$ at pH 7.3, 89% $\text{UO}_2(\text{CO}_3)_3^{4-}$ and 11% $\text{UO}_2(\text{CO}_3)_2^{2-}$ at pH 8.0, 98% $\text{UO}_2(\text{CO}_3)_3^{4-}$ and 2% $\text{UO}_2(\text{CO}_3)_2^{2-}$ at pH 8.5, and 100% $\text{UO}_2(\text{CO}_3)_3^{4-}$ at pH 9.0. If we assume that the lime-only treated solutions reach equilibrium with atmospheric CO_2 , only the pH 6.5 and 7.3 solutions would differ from those above with higher levels of carbonate. If we assume that during the short contact time with the air prior to solution removal adequate time is not available for CO_2 to absorb into the solution to reach equilibrium, the uranium speciation distribution would be dominated by $(\text{UO}_2)_3(\text{OH})_5^+$, UO_2OH^+ , and $\text{UO}_2(\text{SO}_4)_2^{2-}$.

FIGURE 3. Total Uranium Concentration Comparison Between Hydrated Lime $[\text{Ca}(\text{OH})_2]$, Hydrated Lime/Sodium Bicarbonate $[\text{Ca}(\text{OH})_2]$, and Limestone-Neutralized (CaCO_3) Tailings Liquor

The latter species is only important at pH 6.5. The solution species distribution of uranium is thus highly dependent on equilibration with the carbonate system. The observed data suggest that in the lime-only neutralization step that CO_2 absorption from air does not occur rapidly enough to form the significant quantities of the highly soluble uranyl carbonates.

MINTEQA was also used to calculate ion activity products for possible controlling uranium solids, schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$), $\beta\text{-UO}_2(\text{OH})_2$, and rutherfordine (UO_2CO_3). For all the solutions with carbonate reagents added or the lime-only neutralized solutions in equilibrium with atmospheric CO_2 , the observed uranium concentrations are undersaturated. If we assume the solutions were separated from the neutralized slurries prior to equilibration with atmospheric CO_2 , the lime-only solutions are slightly oversaturated with respect to schoepite and

b- $\text{UO}_2(\text{OH})_2$ at pH values 8.5 and 9.0, in equilibrium with either of these two solids at pH 7.3 and 8.0, and somewhat undersaturated with both solids at pH 6.5. Because the original acidic tailings solutions contain 40 mg/L U, significant reductions are found in all the solutions. In general the ion activity products do not suggest that any one of the above minerals should be forming and lowering the concentrations throughout the experiments. Either adsorption or a mineral not considered must be controlling the solution uranium concentrations. If we assume vanadium is present in the neutralized solutions at our detection limit of 0.1 mg/L (present at 20 mg/L in the original acidic solution), then two possible minerals that may be forming are carnotite [$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$] and tyuyamunite [$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2$]. Assuming a total analytical vanadium concentration of 0.1 mg/L in all the solutions regardless of pH and using the analytical values observed for all the other constituents, ion speciation and subsequently ion activity products were calculated with MINTEQA. At pH values 6.5 and 7.3 the observed solutions are oversaturated with respect to these two minerals. At pH 8.0 the observed solution is undersaturated slightly with respect to tyuyamunite and slightly oversaturated with respect to carnotite. At pH values above 8.0, the solutions are undersaturated with respect to both solids. Thus neither solid is likely to be controlling the uranium concentration. Other solids that might be forming are alkali or alkaline-earth uranates (Brush 1980). Currently, thermodynamic data for uranates have not been added to our version of MINTEQA; therefore, we cannot evaluate whether they are probable controls.

These thermodynamic calculations do support the fact that the presence or absence of carbonates in the neutralization scheme can dominate the fate of uranium as found in the laboratory experiments.

Colloidal Particle Adsorption

The solution chemistry of five selected solutions from the three batch neutralization studies before and after filtering through an 18Å filter are given in Tables 7, 8, and 9. The selected solutions are the lime-only neutralized solutions of pH 6.5 and pH 7.3 (Table 7), the limestone-only neutralized solution of pH 6.5 and pH 7.3 (Table 8), and the lime/sodium bicarbonate solution of pH 7.3 (Table 9). Results show that, with the exception of solution zinc concentrations, no difference exists in solution chemistry because of solution filtering at 18Å. The presence of elevated zinc concentrations in all filtered solutions suggests that even after performing a washing procedure on each filter prior to use, these filters are a source of zinc contamination. It thus appears that the data presented in Tables 4, 5, and 6 do not include significant quantities of colloidal material in the size range between 18Å and 4500Å (0.45 µm).

TAILINGS LEACHING STUDIES

Acid Tailings Leaching Results

Results of the solid acidic tailings leaching experiments are shown in Tables 10, 11, and 12 for the Lucky Mc and the Exxon untreated tailings, and

TABLE 7. Solution Chemistry of Lime-Neutralized Lucky Mc Tailings Liquor Before and After 18A Filtering

Parameter(a)	pH 6.5 0.45 μ m Filtered	pH 6.5 18A Filtered	pH 7.3 0.45 μ m Filtered	pH 7.3 18A Filtered
<u>Macro Ions (mg/L)</u>				
Al	0.1	0.1	0.1	0.1
Ca	450	454	451	462
Fe	0.1	0.1	0.1	0.1
Mg	1,202	1,181	1,066	1,083
Mn	112	116	53.2	54.8
Na	1,620	1,530	1,460	1,490
Si	3	4	2	2
Sr	7.5	7.2	5.7	5.8
K	190	170	160	160
Cl	1,093	1,204	1,205	1,201
NO ₃	228	256	252	252
SO ₄	8,430	10,130	9,740	9,720
<u>Trace Metals (mg/L)</u>				
Ag	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	<0.02
Ba	0.1	0.2	<0.02	<0.02
Cd	0.01	0.01	0.01	0.01
Co	1.0	0.7	0.01	0.1
Cr	0.01	0.01	0.01	0.01
Cu	0.01	0.01	0.01	0.01
Mo	0.1	0.1	0.01	0.01
Pb	<0.1	<0.1	<0.1	<0.1
Se	1.0	1.0	1.0	1.0
Zn	1.2	2.0	0.8	1.4
<u>Radionuclides (mg/L)</u>				
U (Total)	<0.05	<0.05	<0.05	<0.05

(a) All cation, trace metal, and uranium analyses were performed using inductively coupled plasma.

TABLE 8. Solution Chemistry of Limestone-Neutralized Lucky Mc Tailings
Liquor Before and After 18A Filtering

Parameter ^(a)	pH 6.5 0.45 μ m Filtered	pH 6.5 18A Filtered	pH 7.3 0.45 μ m Filtered	pH 7.3 18A Filtered
<u>Macro Ions (mg/L)</u>				
Al	0.1	0.1	0.1	0.1
Ca	481	477	460	462
Fe	0.1	0.1	0.1	0.1
Mg	1,195	1,186	1,146	1,123
Mn	123	122	86.1	88.0
Na	1,600	1,580	1,550	1,460
Si	3	3	2	2
Sr	4.9	4.9	3.2	3.2
K	180	180	170	160
Cl	1,204	1,216	1,210	1,219
NO ₃	258	256	256	258
SO ₄	10,170	10,210	9,980	10,040
<u>Trace Metals (mg/L)</u>				
Ag	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	<0.02
Ba	0.01	0.02	0.01	0.01
Cd	0.01	0.01	0.01	0.01
Co	1.5	1.5	1.2	1.2
Cr	<0.02	<0.02	<0.02	<0.02
Cu	0.01	0.01	0.01	0.01
Mo	<0.1	<0.1	<0.1	<0.1
Pb	<0.1	<0.1	<0.1	<0.1
Se	1	1	1	1
Zn	1.4	3.3	0.9	1.2
<u>Radionuclides (mg/L)</u>				
U (Total)	<0.05	<0.05	<0.05	<0.05

(a) All cation, trace metal, and uranium analyses were performed using inductively coupled plasma.

TABLE 9. Solution Chemistry of Lime/Sodium Bicarbonate-Neutralized Lucky Mc Tailings Liquor Before and After 18A Filtering

Parameter(a)	pH 7.3 0.45 μ m Filtered	pH 7.3 18A Filtered
<u>Macro Ions (mg/L)</u>		
Al	0.1	0.1
Ca	458	456
Fe	0.1	0.1
Mg	1,108	1,103
Mn	62.2	62.0
Na	1,560	1,550
Si	2	2
Sr	5.4	5.4
K	180	180
Cl	1,205	1,204
NO ₃	250	248
SO ₄	9,700	9,680
<u>Trace Metals (mg/L)</u>		
Ag	<0.02	<0.02
As	<0.02	<0.02
Ba	<0.02	<0.02
Cd	0.01	0.01
Co	0.01	0.01
Cr	0.01	0.01
Cu	0.01	0.01
Mo	<0.1	<0.1
Pb	<0.01	<0.01
Se	1	1
Zn	<0.05	1.2
<u>Radionuclides (mg/L)</u>		
U (Total)	0.9	1.1

(a) All cation, trace metal, and uranium analyses were performed using inductively coupled plasma.

TABLE 10. Column Effluent Solution Chemistry of Untreated Lucky Mc Tailings Leaching Data

Parameters	Effluent Sample Identification					
	1	2	3	4	5	6
pH	1.86	2.13	2.63	2.94	3.10	3.32
Eh (mV)	614	611	612	718	736	717
Pore volume	0.46	1.10	2.64	5.66	6.86	11.94
Adjusted pore volume	0.23	0.78	2.39	5.24	6.61	11.68
TDS (g/L)	74.29	39.84	4.70	3.09	2.84	2.60
<u>Macro ions (mg/L)</u>						
Al	3,900	1,900	86	19	14.4	8.2
Ca	580	540	484	554	558	576
Fe	7,700	4,000	248	130	82	17
K	0.2	0.6	0.8	1.2	1.4	1.2
Mg	2,600	1,300	112	16.2	10.6	2.4
Na	2,900	1,500	138	82	88	99
Si	122	88	46	36	37	49
Sr	7.4	5.0	1.5	1.2	1.2	1.4
Cl	2,900	1,200	75	50	48	42
NO ₃	580	310	10	<10	<10	<10
SO ₄	53,000	29,000	3,500	2,200	2,000	1,800
<u>Trace metals (mg/L)</u>						
Ag	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
As	30.2	12.6	0.15	0.35	0.24	0.15
Ba	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	0.65	0.32	0.02	<0.01	<0.01	<0.01
Co	10.68	5.37	0.44	0.04	<0.02	<0.02
Cr	6.73	3.08	0.15	0.01	0.02	<0.01
Cu	3.05	1.73	0.26	0.02	0.02	<0.02
Mo	1.31	0.55	<0.01	<0.01	<0.01	<0.01
Pb	0.09	<0.02	0.05	0.03	0.02	<0.02
Se	2.11	<0.02	<0.02	<0.02	<0.02	<0.02
V	13.75	9.53	0.06	<0.05	<0.05	<0.05
Zn	28.0	16.0	1.6	0.4	0.3	0.2
<u>Radionuclides (pCi/L)</u>						
²¹⁰ Pb	<75	<75	<75	<75	<75	<75
²³⁸ U	38,643	18,326	1,083	702	719	<75
²³⁰ Th	144,687	69,135	2,178	<400	621	<400
²²⁶ Ra	5,992	2,567	171	<75	109	<75

Note: Manganese channel of inductively coupled plasma inoperative; therefore, no values are reported.

TABLE 11. Column Effluent Solution Chemistry of Untreated Exxon Tailings Leaching Data

Parameters	Effluent Sample Identification					
	1	2	3	4	5	6
pH	3.04	3.26	3.31	3.38	3.50	3.95
Eh (mV)	749	678	704	734	764	611
Pore volume	0.90	1.87	2.88	6.04	8.73	13.54
Adjusted pore volume	0.45	1.39	2.38	5.51	8.00	12.99
TDS (g/L)	18.88	6.04	3.68	2.79	1.86	0.61
Macro ions (mg/L)						
Al	484	88	33	14	17	1.2
Ca	430	454	504	562	440	96
Fe	13.2	2.4	1.1	28.8	2.0	3.6
K	0.4	0.1	0.6	1.4	1.2	0.5
Mg	1,990	524	188	25	10.2	0.7
Na	542	150	86	82	82	98
Si	98	32	32	40	34	34
Sr	1.8	1.2	0.9	1.0	1.5	0.3
Cl	1,700	180	39	40	39	40
NO ₃	19	5.3	<1.0	<1.0	<1.0	<1.0
SO ₄	13,600	4,600	2,800	2,000	1,230	340
Trace metals (mg/L)						
Ag	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
As	0.37	0.25	<0.02	<0.02	<0.02	<0.02
Ba	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	0.08	0.02	<0.01	<0.01	<0.01	<0.01
Co	4.59	4.15	0.38	0.04	<0.02	<0.02
Cr	0.95	0.80	0.05	<0.01	<0.01	<0.01
Cu	0.49	0.54	0.04	0.02	<0.02	<0.02
Mo	<0.02	<0.02	<0.02	<0.01	<0.01	<0.01
Pb	0.10	0.03	0.10	0.03	<0.02	<0.02
Se	1.08	1.40	<0.02	<0.02	<0.02	<0.02
V	<0.05	0.06	<0.05	<0.05	<0.05	<0.05
Zn	4.4	1.3	0.5	0.5	0.3	0.1
Radionuclides (pCi/L)						
²¹⁰ Pb	<75	<75	<75	<75	<75	<75
²³⁸ U	10,766	2,153	179	103	<75	<75
²³⁰ Th	29,080	3,163	<400	<400	<400	<400
²²⁶ Ra	3,725	914	126	146	<75	<75

Note: Manganese channel of inductively coupled plasma inoperative; therefore, no values are reported.

TABLE 12. Column Effluent Solution Chemistry of Untreated Exxon Tailings-Extended Leaching Data

Parameters	Effluent Sample Identification					
	1	2	3	4	5	6
pH	2.92	3.67	3.91	4.12	4.04	4.02
Eh (mV)	678	756	694	680	486	676
Pore volume	0.87	5.47	13.49	22.43	26.99	31.15
Adjusted pore volume	0.44	4.83	10.30	21.79	26.45	30.65
TDS (g/L)	21.47	2.77	1.14	0.54	0.44	0.51
<u>Macro ions (mg/L)</u>						
Al	480	15.6	2.4	1.0	0.4	0.2
Ca	428	564	188	47	42	53
Fe	12.8	2.4	0.7	1.6	1.4	0.5
K	0.6	0.8	0.4	0.8	0.7	0.7
Mg	2,012	23.8	1.3	1.7	3.0	5.8
Na	512	86	92	94	95	103
Si	98	32	2.8	14.2	26.4	26.1
Sr	2.8	0.9	0.3	<0.1	0.2	0.2
Cl	1,900	46	45	45	38	42
NO ₃	23	2.7	2.7	<1.0	<1.0	<1.0
SO ₄	16,000	2,000	810	330	230	280
<u>Trace metals (mg/L)</u>						
Ag	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
As	0.34	<0.02	<0.02	<0.02	<0.02	<0.02
Ba	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	0.13	<0.01	<0.01	<0.01	<0.01	<0.01
Co	3.8	0.04	<0.02	<0.02	<0.02	<0.02
Cr	1.0	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	0.36	0.03	<0.02	<0.02	<0.02	<0.02
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	0.03	0.02	<0.02	<0.02	<0.02	<0.02
Se	1.24	<0.02	<0.02	<0.02	<0.02	<0.02
V	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Zn	4.4	0.4	0.2	0.1	0.1	0.2
<u>Radionuclides (pCi/L)</u>						
²¹⁰ Pb	<75	<75	<75	<75	<75	<75
²³⁸ U	10,768	196	<75	<75	<75	<75
²³⁰ Th	23,648	<400	<400	<400	<400	<400
²²⁶ Ra	2,142	184	<75	<75	<75	<75

Note: Manganese channel of inductively coupled plasma inoperative; therefore, no values are reported.

Tables 13 and 14 for the neutralized tailings. For the untreated (acidic) tailings from both mills, (Tables 10, 11, and 12), the highest concentration of dissolved constituents were leached from the solid tailings during the first few pore volumes of leachant contact. This can be seen in Figure 4 where the total TDS versus adjusted pore volume^(a) has been plotted for the column effluents from both Lucky Mc and Exxon tailings. The TDS content of a solution is an indicator of the amount of constituents present within a solution. The higher the TDS content, the higher the concentration of species that make up that solution. Figure 4 also depicts the wide variation in the total quantity of leachable constituents from two uranium mill sites both employing an acidic leach process. (Reasons for the variation in constituent content are mentioned in Appendix B).

FIGURE 4. Lucky Mc and Exxon Acidic Tailings Total Dissolved Solids Versus Adjusted Pore Volume

- (a) Results reported for any specific pore volume are actually an average concentration over that fraction of the pore volume collected. For instance, if a sample is taken at 1.0 pore volume and consists of that entire pore volume, that sample is not representative of the effluent concentration at 1.0 pore volume but is an average of the entire first pore volume. Therefore, the data collected will be plotted at 0.5 pore volume and labeled as an adjusted pore volume.

TABLE 13. Column Effluent Solution Chemistry of Neutralized Lucky Mc Tailings Leaching Data

Parameters	Effluent Sample Identification				
	1	2	3	4	5
pH	7.44	7.81	7.98	8.02	7.75
Eh (mV)	362	261	358	257	260
Pore volume	1.02	1.92	3.36	4.49	5.25
Adjusted pore volume	0.74	1.66	3.19	3.93	4.87
TDS (g/L)	14.74	7.45	4.64	3.80	3.47
<u>Macro ions (mg/L)</u>					
Al	1.0	0.7	0.7	0.5	0.7
Ca	526	475	521	534	555
Fe	<0.5	<0.5	<0.5	<0.5	<0.5
K	8.3	6.8	3.6	4.4	5.2
Mg	786	378	221	174	145
Na	2,237	779	190	135	114
Si	3.4	3.2	3.3	3.5	3.7
Sr	0.1	<0.1	<0.1	<0.1	<0.1
Cl	2,600	375	54	46	46
NO ₃	425	35	<4	<4	<4
SO ₄	8,150	5,400	3,650	2,900	2,600
<u>Trace metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	0.03	0.03	0.04	0.03	0.03
Ba	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	4.74	3.26	1.87	1.28	0.96
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Se	1.34	0.29	0.02	<0.02	<0.02
V	<0.20	<0.05	<0.05	<0.05	<0.05
Zn	<0.1	<0.1	<0.1	<0.1	<0.1
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	<75	<75	<75	<75	<75
²³⁸ U	1,486	1,279	914	1,014	1,207
²³⁰ Th	<400	<400	<400	<400	<400
²²⁶ Ra	337	223	204	231	283

NOTE: Manganese channel of inductively coupled plasma was inoperative; therefore, no values are reported.

TABLE 13. (contd)

Parameters	Effluent Sample Identification				
	6	7	8	9	10
pH	7.96	8.45	8.08	7.89	8.15
Eh (mV)	275	316	367	389	344
Pore volume	7.07	7.42	9.77	10.81	11.53
Adjusted pore volume	6.56	7.25	9.35	10.29	11.17
TDS (g/L)	3.14	3.03	2.84	2.78	2.74
<u>Macro ions (mg/L)</u>					
Al	<0.5	0.6	0.3	<0.1	<0.1
Ca	567	584	582	590	591
Fe	<0.5	<0.5	<0.5	<0.5	<0.5
K	2.3	2.3	1.2	0.2	0.3
Mg	112	97	70	61	48
Na	107	103	100	101	100
Si	3.5	3.8	3.8	3.6	4.0
Sr	<0.1	<0.1	<0.1	<0.1	<0.1
Cl	44	42	42	42	42
NO ₃	<4	<4	<4	<4	<4
SO ₄	2,300	2,200	2,040	1,980	1,950
<u>Trace metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	0.05	0.08	0.06	0.07	0.06
Ba	<0.02	<0.02	<0.02	<0.02	<0.02
Cd	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	0.64	0.54	0.42	0.30	0.21
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Se	<0.02	<0.02	<0.02	<0.02	<0.02
V	<0.05	<0.05	<0.05	<0.05	<0.05
Zn	0.3	0.4	0.4	0.6	0.4
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	<75	<75	<75	<75	<75
²³⁸ U	343	1,026	924	1,036	981
²³⁰ Th	<400	721	<400	<400	508
²²⁶ Ra	145	362	486	114	75

NOTE: Manganese channel of inductively coupled plasma was inoperative; therefore, no values are reported.

TABLE 14. Column Effluent Solution Chemistry of Neutralized Exxon Tailings Leaching Data

Parameters	Effluent Sample Identification					
	1	2	3	4	5	6
pH	7.81	7.63	7.90	7.99	8.21	8.04
Eh (mV)	250	345	255	261	333	241
Pore volume	0.91	1.83	2.70	3.53	4.28	5.16
Adjusted pore volume	0.71	1.64	2.50	3.32	4.09	4.93
TDS (g/L)	16.49	5.70	4.06	3.62	3.31	3.16
<u>Macro ions (mg/L)</u>						
Al	0.8	<0.5	1.2	0.6	0.6	<0.5
Ca	569	489	529	546	553	542
Fe	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
K	4.9	2.9	4.2	1.8	2.1	<1.0
Mg	2,327	602	334	227	161	117
Na	1,115	158	92	93	92	96
Si	0.8	3.1	3.8	3.9	3.8	3.3
Sr	0.4	0.2	0.3	0.2	0.2	0.2
Cl	3,700	65	43	43	43	43
NO ₃	170	8	5	5	5	5
SO ₄	600	4,370	3,050	2,700	2,450	2,350
<u>Trace metals (mg/L)</u>						
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	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	0.04	<0.01	<0.01	<0.01	<0.01
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	<0.02	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Se	3.14	0.09	0.04	0.05	0.04	0.05
V	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Zn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<u>Radionuclides (pCi/L)</u>						
²¹⁰ Pb	<75	<75	<75	<75	<75	<75
²³⁸ U	906	1,175	716	786	1,290	1,815
²³⁰ Th	<400	<400	<400	<400	<400	<400
²²⁶ Ra	655	701	397	493	526	442

NOTE: Manganese channel of inductively coupled plasma was inoperative; therefore, no values are reported.

TABLE 14. (contd)

Parameters	Effluent Sample Identification					
	7	8	9	10	11	12
pH	7.65	7.99	8.08	8.48	8.03	7.74
Eh (mV)	394	332	313	328	355	303
Pore volume	5.97	6.80	7.87	8.25	8.97	9.38
Adjusted pore volume	5.76	6.60	7.34	8.06	8.61	9.18
TDS (g/L)	2.98	2.95	2.82	2.83	2.76	2.69
<u>Macro ions (mg/L)</u>						
Al	<0.5	<0.5	0.6	<0.5	<0.5	<0.5
Ca	496	589	592	603	607	601
Fe	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
K	<1.0	1.3	1.8	1.8	2.9	2.1
Mg	82	65	51	39	34	27
Na	104	96	95	94	98	96
Si	2.3	4.5	4.6	4.7	4.8	4.8
Sr	0.1	0.2	0.2	0.3	0.4	0.4
Cl	43	43	43	43	43	42
NO ₃	5	5	<4	<4	<4	<4
SO ₄	2,250	2,150	2,030	2,030	1,970	1,920
<u>Trace metals (mg/L)</u>						
Ag	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	0.02	0.03	0.04
Ba	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Se	0.03	0.06	0.04	0.05	0.06	0.05
V	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Zn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<u>Radionuclides (pCi/L)</u>						
²¹⁰ Pb	<75	<75	<75	<75	<75	<75
²³⁸ U	1,754	1,197	1,002	661	739	582
²³⁰ Th	<400	<400	<400	509	<400	<400
²²⁶ Ra	251	253	406	161	<75	109

NOTE: Manganese channel of inductively coupled plasma was inoperative; therefore, no values are reported.

TABLE 14. (contd)

Parameters	Effluent Sample Identification				
	13	14	16	17	18
pH 8.08	7.73	8.11	8.19	8.02	
Eh (mV)	316	346	357	273	270
Pore volume	10.21	11.26	13.06	13.84	14.94
Adjusted pore volume	9.80	10.76	12.59	13.45	14.39
TDS (g/L)	2.61	2.65	2.59	2.55	2.56
<u>Macro ions (mg/L)</u>					
Al	<0.5	<0.5	<0.5	<0.5	<0.5
Ca	594	583	583	573	585
Fe	<0.5	<0.5	<0.5	<0.5	<0.5
K	1.1	0.4	0.2	0.2	0.1
Mg	24	20	12.6	10.2	7.2
Na	99	105	100	101	101
Si	4.8	4.7	4.8	4.8	4.8
Sr	0.5	0.6	0.7	0.7	0.8
Cl	42	42	42	42	42
NO ₃	<2	<2	<2	<2	<2
SO ₄	1,850	1,890	1,850	1,820	1,820
<u>Trace metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	0.04	0.03	0.04	0.04	0.04
Ba	<0.02	<0.02	<0.02	<0.02	<0.02
Cd	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Se	0.04	0.05	0.08	0.10	0.10
V	<0.05	<0.05	<0.05	<0.05	<0.05
Zn	0.5	1.0	0.5	0.5	0.3
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	<75	<75	<75	<75	<75
²³⁸ U	190	285	212	195	135
²³⁰ Th	<400	<400	<400	<400	566
²²⁶ Ra	157	212	160	<75	<75

NOTE: Manganese channel of inductively coupled plasma was inoperative; therefore, no values are reported.

The first effluent sample collected from the untreated Lucky Mc tailings column had a very high TDS content, nearly 75 g/L after 0.23 pore volume of leaching. This sample was comprised mainly of the macro ions SO_4 , Fe, Al, Cl, Na, Mg, NO_3 and Ca, in order of decreasing concentrations. The high TDS content is an excellent indicator of how highly soluble these constituents are in the low pH solutions associated with acidic tailings. The first effluent sample was very acidic (pH 1.86) and contained several trace metals (As, Cd, Co, Cr, Cu, Mo, Se, V, and Zn) and radionuclides (^{238}U , ^{230}Th , and ^{226}Ra) with significantly high concentrations or activities as shown in Table 10. The concentrations of Al, As, Cd, Cl, Cr, Cu, Fe, Mo, NO_3 , Se, SO_4 , and Zn, along with solution pH and TDS content, exceed the EPA's maximum permissible concentrations for various water types shown in Table 15, some by several orders of magnitude.

Note that concentrations found in the first two samples eluted from the Lucky Mc tailings (first pore volume) differ from the tailings solution composition leaving the mill (see Table 1). As the wastes leave the mill as a slurry of solution and tailings, one might expect that the tailings solution would be at equilibrium with the solids such that, on disposal, the solution would saturate the pores of the settled tailings and not react further. Apparently further reaction occurs between the tailings and interstitial solution. Also precipitation (rain and snow) and evaporation can change the interstitial solution's chemical make-up. The tailings used to pack the columns were collected from the edge of a disposal pond and were only partially saturated. They were further dried in the laboratory to a lesser moisture content to facilitate column packing. Undoubtedly the drying process left readily soluble evaporites in the tailings that could be easily flushed on contact with the synthetic ground water. There also appears to be some further dissolution of major constituents of the tailings solids after disposal such that the interstitial waters in draining tailings can exceed the concentrations observed in the solution portion of the slurry as it leaves the mill. Table 10 shows that the first two samples of eluant have larger solution concentrations of Al, Fe, Mg, Na, Cl, NO_3 , SO_4 , As, Co, Cr, Cu, Zn, and ^{238}U than the slurry leaving the mill. On the other hand the first two eluants have significantly lower concentrations of K, Si, Sr, Mo, Pb, V, ^{210}Pb , and ^{230}Th than the slurry leaving the mill. The increase in Mg, Na, Cl, NO_3 , and SO_4 suggests dissolution of evaporites in the dried tailings, but increases in Al, Fe, trace metals, and U suggest further dissolution reaction with the gangue solids.

The significant drop in K, Si, Sr, Mo, Pb, V, and Th suggests that 1) some minerals or amorphous solids also are forming during tailings consolidation, 2) some evaporites are not redissolving, or 3) adsorption reactions are occurring.

The first pore volume eluted from the acidic Exxon Highland Mills tailings column (see Tables 11 and 12) also is dissimilar to the solution in the disposal pond. The columns' eluant representing the first pore volume has larger concentrations of Al, Mg, Na, Cl, NO_3 , SO_4 , As, Cd, Co, ^{238}U , and ^{226}Ra . The eluant also has significantly lower concentrations of Fe, K, Si, Sr, Cr, Cu, V, ^{210}Pb , and ^{230}Th than solution in the disposal pond. Aside from the drop in Fe concentrations, the trends observed in the Exxon Highland Mill tailings column

eluates are quite similar to the Lucky Mc tailings column eluant data. The lowest pH observed for the Exxon Highland Mill tailings column effluent was 3, which is one pH unit higher than the tailings solution found in the disposal pond. We thus concluded that solution leaving the mill or the supernate solution in disposal ponds is not an accurate indicator of the chemical composition of the interstitial waters in disposed tailings, and that chemical reactions continue within the consolidating tailings.

The characterization results (see Table 10) for the second effluent sample (0.78 pore volume) from the untreated Lucky Mc tailings indicate that in nearly every case the concentration of each constituent was reduced to approximately half of its first effluent sample value. The exception was calcium at 540 mg/L, which is only a 40 mg/L reduction. The reduction for the remainder of the solution constituents continued through the third sample collected at 2.39 pore volume. At that time the TDS content was 4.7 g/L, and some elements (molybdenum and selenium) displayed concentrations lower than our detectable limits (see Table 10). From this point up through 11.68 pore volumes of leaching, only a slight decrease in TDS content was noted as shown by the solid line in Figure 4. The sharp drop of the TDS versus adjusted pore volume curve for the Lucky Mc tailings indicates that most of the soluble constituents will be leached from the tailings after ~2.4 pore volumes of leachant contacts the tailings. The nearly constant Ca concentration in the effluent reflects the slow removal of gypsum (CaSO_4) from the tailings column.

Similar trends were noted for the untreated Exxon tailings during the leaching experiments as shown in Figure 4 and Tables 11 and 12. High concentrations of the macro ions Al, Ca, Mg, Na, Cl, and SO_4 were detected along with the trace metals As, Co, Cr, Cu, Se, and Zn, which ranged from submilligram per liter values to ~5 mg/L. The first effluent sample collected at 0.45 pore volume had a pH of 3.04 and a TDS content of 18.88 g/L comprised mainly of the previously mentioned macro ions [see Tables 11 and 12^(a)]. The TDS content of the second collected effluent (see Table 12) was reduced to 6.04 g/L after 1.39 pore volumes of tailings leaching. The dotted line in Figure 4 shows a gradual reduction in TDS content from the third sample collected at 2.38 pore volumes, which continued until a total of 12.99 pore volumes of laboratory ground water had contacted the acidic tailings.

Sulfate comprised approximately 70% of the TDS content in the column effluents from both the Lucky Mc and Exxon mill tailings. Since both mills employ a sulfuric acid leaching process, high sulfate concentrations are not unusual. As can be seen in Tables 10, 11, and 12, the sulfate concentration in the column effluents from both mill tailings was reduced significantly as leaching continued. As tailings leaching proceeds, the sulfate source (mainly

(a) The data presented in Table 12 are similar in nature to that presented in Table 11 except that the duration of tailings leaching was extended to approximately 30 pore volumes. Therefore, data from long-term tailings leaching experiments can be presented for comparison to shorter leachant contact times.

gypsum) in the tailings column is being depleted (dissolved). For the Lucky Mc tailings eluant, gypsum appears to be still dissolving after almost 12 pore volumes of leaching. Earlier leaching tests (Gee et al. 1981, pp. 457-472) suggest gypsum is depleted after about 16 pore volumes of leaching. Tables 10 and 11 suggest that gypsum is depleted in the Exxon tailings between 8 and 12 pore volumes of leaching.

In general, a high surge of soluble constituents (Al, Ca, Cl, Fe, Mg, Na, NO_3 , and SO_4) was observed during the initial leaching experiments performed on the acidic tailings from the Lucky Mc and Exxon mills. The initial pulse of constituents seen in the early pore volumes was followed by a rapid decrease in concentration of the previously mentioned ions. This decrease was caused by the depletion of the constituent source within the tailings by redissolution of highly soluble evaporites and flushing of high ionic strength process liquors. Note that even though several pore volumes of leachant had contacted the acidic tailings, several constituents still exceed maximum permissible concentration (MPC) limits for various water types. For example, Al, As, Fe, and SO_4 all exceed certain specified water limits as shown in Table 15. In addition, Ra and Se may also exceed the maximum permissible concentration; however, the detection limits of the analytical instruments were higher than some MPCs, and definite conclusions cannot be made.

Neutralized Tailings Leaching Results

Tables 13 and 14 show the results of the neutralized tailings leaching experiments. Subsamples of the same solid tailings material from both the Lucky Mc and Exxon mills were used in this study, except the tailings were neutralized to pH 7.4 (based on saturated paste pH analyses) with hydrated lime prior to leaching. Because one option considered for treatment of acidic tailings and tailings solution is neutralization, the objective of this experiment was to illustrate the change in column effluent chemistry when laboratory ground water contacts neutral tailings rather than acidic tailings.

The most significant solution parameter affected by hydrated lime addition (neutralization) is pH. Several soluble constituents within acidic uranium mill tailings liquor are dependent on the low pH (pH ~2.0) for their high solution concentrations. Macro ions such as Al and Fe, and trace metals such as As, Co, Cr, Cu, V, and Zn have high solution concentrations in the acid liquor. The macro ions contribute significantly to the TDS content of acidic tailings liquors. Upon addition of hydrated lime to the tailings and a subsequent pH increase, the solubility of the above elements is exceeded and precipitation reactions occur. At neutral pHs these precipitates remain insoluble and therefore do not elute out of the column, resulting in a greatly reduced TDS content in the neutral tailings column effluents.

A comparison of the untreated and neutralized effluent TDS contents versus adjusted pore volume for the Lucky Mc Tailings is shown in Figure 5. The solid line in Figure 5 is the same line presented in Figure 4 showing the very high TDS content during the early pore volumes of leaching (74.3 g/L at 0.23 pore volume). The dotted line shows the TDS curve for the neutralized tailings

TABLE 15. Maximum Concentration Levels for Specified Water

Constituent	Standard				
	EPA-U 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	---	---	---	5.0	---
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	uncertain (f)	---	---	uncertain (g)	---
N in NO ₃	---	10.0	---	23.0	---
Se	0.01	0.01	---	0.05	---
Ag	0.05	0.05	---	---	---
F	---	1.4-2.4 (h)	---	2.0	---
Cl	---	---	250.0	---	---
Cu	---	---	1.0	0.5	---
Fe	---	---	0.3	No limit	---
Mn	---	---	0.05	No limit	---
SO ₄	---	---	250.0	---	---
Zn	1.0	---	5.0	2.5	---
B	---	---	---	5.0	---
V	---	---	---	0.1	---
TDS	---	---	500.0	---	---
pH	6.0-9.0	---	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	---	---	---	---	2 x 10 ⁴
238 _U	---	---	---	---	4 x 10 ⁴
230 _{Th}	---	---	---	---	2000
226 _{Ra}	---	---	---	---	30
210 _{Pb}	---	---	---	---	100
Gross α (excluding U and Rn)	15.0	---	---	---	---

(a) EPA, 1982, "U.S. Environmental Protection Agency, 40 CFR 440, Ore Mining and Dressing Point Source Category Subpart C Uranium, Radium, and Vanadium Ores," 47(54609) Fed. Reg. (December 3, 1982) and EPA, 1983, "U.S. Environmental Protection Agency, 40 CFR 192, Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings," 40(602) Fed. Reg. (January 5, 1983).

(b) EPA, 1980, "U.S. Environmental Protection Agency, 40 CFR 141, National Interim Primary Drinking Water Regulations," 45 Fed. Reg. (August 27, 1980).

(c) EPA, 1979, "U.S. Environmental Protection Agency, 40 CFR 143, National Secondary Drinking Water Regulation," 44(42198) Fed. Reg. (July 19, 1979).

(d) EPA, 1976, Quality Criteria for Water, EPA 440/a-76-023, U.S. Environmental Protection Agency, Washington, D.C.

(e) NRC, 1981, "U.S. Nuclear Regulatory Commission, 10 CFR 20 Standards for Protection Against Radiation."

(f) A standard is called for but a value is not given.

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

(h) Depends on temperature of water.

FIGURE 5. Lucky Mc Neutralized and Untreated Tailings Total Dissolved Solids Content Versus Adjusted Pore Volume

effluents over the course of ~13 pore volumes of leaching. The initial sample collected after 0.74 pore volume of contact contained 14.7 g/L of TDS and consisted mainly of ions whose concentration in solution is not strictly pH dependent (i.e., Ca, Mg, Na, Cl, NO_3 , and SO_4). Ions that were either removed from solution or whose solution concentration were substantially reduced, resulting in the significant TDS reduction, include Al, As, Cd, Co, Cr, Cu, Fe, Mg, Si, V, Zn, Cl, and SO_4 . Selenium concentrations were only reduced by 36% after neutralization (2.11 mg/L to 1.34 mg/L), while molybdenum concentrations actually increased, indicating more was being leached from the neutral tailings than the untreated acidic tailings. The radioactive species, ^{238}U , ^{230}Th , and ^{226}Ra , were also dramatically reduced in the first few pore volumes; however ^{226}Ra activities were still two orders of magnitude above the present maximum permissible activity (see Table 15) of 5 pCi/L and remained above the MPC for most samples collected throughout the experiment.

As laboratory leachant continued to contact the neutral tailings for ~10 more pore volumes, the column effluent pH remained between pH 7.4 and pH 8.4. During the leachant/neutral tailings contact period, the ions soluble in neutral pH solutions continued to elute from the tailings column. For instance, SO_4 (originally present in the untreated Lucky Mc tailings effluent at 29,000 mg/L at 0.78 pore volume) was reduced initially to 8150 mg/L at 0.74 pore volume in the neutralized tailings effluent. With further leaching, the SO_4 concentrations continued to decrease until the values leveled out between

1900 mg/L and 2000 mg/L (the level controlled by gypsum dissolution). Similar values at equivalent pore volumes were observed in the untreated tailings effluent until gypsum was depleted; however, the benefit in neutralizing tailings is the significant reduction in the pH-sensitive constituents including most of the trace metals and aluminum and iron. Over time all of the sulfate originally present in the tailings would likely be redissolved by low ionic strength ground water, but the pH-sensitive elements should remain in the neutralized tailings.

In the experiments performed on the neutralized Exxon tailings, similar reductions in effluent concentrations were seen for those elements whose solubility is pH dependent. The results of the analyses performed on the effluents from the neutral tailings column are presented in Table 14. For the duration of the leaching experiment, the neutralized tailings effluent pH ranged between pH 7.6 and 8.5. At neutral pHs, elements such as As, Cd, Co, Cu, Fe, Pb, and Zn are insoluble, remain within the neutral tailings column, and exist in solution in concentrations that are below our detectable limits. Elements such as Al, Si, Sr, and SO_4 were substantially reduced but still within detectable ranges. Calcium, Mg, Na, Se, Cl, and NO_3 concentrations were high in the initial neutral effluents but dropped significantly with further leaching. In the case of NO_3 , the high value detected may be due to SO_4 interference. Anion analyses are performed by ion chromatography and rely on a particular ions retention time to quantify its concentration. Conversations with the analyst indicate that the high initial value 170 mg/L may be partially due to the high SO_4 concentration preventing sufficient peak resolution to accurately integrate the NO_3 concentration. Regardless, in the subsequent effluents with significantly lower SO_4 values, the NO_3 concentration is also significantly lower.

A plot of the total dissolved solids content versus the adjusted pore volume from both the untreated and neutralized Exxon tailings columns is shown in Figure 6. All three curves (one neutralized and two untreated lines) are basically the same, showing only about 1 g/L deviation throughout the experiment. The solid and dotted curves, showing the changes occurring for the untreated column, run for 13 pore volumes and the neutralized tailings column, respectively. These curves were practically mirror images of one another until the sixth pore volume of leaching. At that point the neutral column (dotted line) became stable with a nearly constant TDS content of between 2.5 and 3.0 g/L TDS until the experiment was stopped at 14 pore volumes. This represents the gradual dissolution of the large amount of gypsum formed during neutralization. Meanwhile, the untreated tailings column (dashed line), continued to exhibit reductions in TDS through 13 pore volumes of leaching (final TDS content of 0.6 g/L). The laboratory ground water used in the experiments contained ~0.5 g/L TDS, indicating that leaching of the rapidly dissolved salts from the solid tailings matrix was almost complete at the completion of the study. Once all the gypsum was dissolved in the neutralized column, we would expect a similar drop to ~0.5 g/L.

FIGURE 6. Exxon Neutralized and Untreated Total Dissolved Solids Content Versus Adjusted Pore Volume

In contrast to the results noted for the Lucky Mc columns, the difference in the Exxon study was not so much the total quantity of leachable constituents eluted from the tailings but, more significantly, the nature of the elements leached from the tailings. (For a brief explanation on the difference between the solutions from both mills, see Appendix B.) For instance, the initial effluents from the acidic Exxon tailings column contained Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Na, Pb, Se, Si, Zn, Cl, SO_4 , ^{226}Ra , ^{230}Th , and ^{238}U . In comparison, the neutral Exxon tailings column effluents contained only Ca, Mg, Na, Se, Cl, and SO_4 . Thorium-230 was not detected in the effluents from the neutralized columns. Radium-226 and ^{238}U were detected in the neutralized column eluants, but the total activity eluted was somewhat lower in relation to the untreated tailings eluant over the first 14 pore volumes.

In general, the Exxon tailings neutralized with hydrated lime showed a significant reduction in individual constituent concentrations, even though the TDS content was similar for both leaching conditions. The neutralized effluent TDS content was mainly comprised of macro ions (Ca, Mg, Na, Cl, and SO_4) found commonly in sediments. The naturally abundant macro ions have higher relative MPCs than several of the acid condition-dependent elements found in trace quantities in the untreated tailings solution.

CONCLUSIONS

Neutralization of acidic uranium mill liquors with either solid limestone or hydrated lime can substantially improve solution quality. At the optimum pH for neutralization ($\text{pH} = 7.3$), the TDS content of the original acidic tailings solution was reduced in excess of 50%, regardless of reagent type used in the neutralization process. Reduction in TDS at solution pHs of 6.5 and 7.3 is largely due to removal of sulfate (with the exception of Mo, Zn, and U). Trace metal and radionuclide concentrations were also reduced in excess of 99%. Trace metal and radionuclide reductions are a result of pH-induced precipitation and coprecipitation reactions caused by changes in solution pH and adsorption onto amorphous iron hydroxides.

Increasing the pH of the acidic tailings liquor beyond $\text{pH} = 8.0$ results in additional reduction of TDS contents, through sulfate and magnesium removal, but may cause the redissolution of the contaminants molybdenum and radium. Increased molybdenum solubility was found to be a function of solution pH, and increases in radium activities are suspected to be related to lowered sulfate concentrations and subsequent dissolution of radium-bearing sulfate salts.

The solubilities of uranium and perhaps zinc are a function of solution carbonate content. Increased uranium solubility because of carbonate content becomes significant in these systems at all pHs exceeding 6.5, while zinc solubility in the presence of carbonate appears to be increased at all values studied ($\text{pH} 6.5 - 9.0$). Thermodynamic calculations suggest that the carbonate should only affect zinc solution concentrations above $\text{pH} 8.5$.

Neutralization with limestone and hydrated lime proved ineffective in removing Na, K, or the anions Cl and NO_3 .

Results from this and previous laboratory studies (Opitz, Dodson and Serne 1984) indicate that if acidic uranium mill tailings are to be neutralized, optimum results will be achieved using hydrated lime. Final solution pH should be over $\text{pH} = 7.0$ but under $\text{pH} = 8.0$. After neutralization the resulting solutions should be disposed of in a manner that will minimize contact with a carbonate source to prevent redissolution of uranium and perhaps zinc. On a practical scale, isolation from atmospheric CO_2 would seem impossible, but avoidance of calcareous-rich sediments might be beneficial.

Colloidal particle removal (through 18A filtering) had no effect on the overall solution chemistry produced by any of the three acidic mill tailings liquor neutralization reagent schemes studied. Rather the experimental results indicate that, even if extreme care is taken to prewash the filters, attempting to remove colloidal particles from these systems prior to analyses may result in zinc contamination.

Results of the solid tailings leaching experiments indicate that the untreated acidic tailings from both mill sites release high quantities of macro cations, anions, trace metals, and radionuclides in the first few pore volumes of leachate. The ions comprising the high TDS content consist of Al, As, Ca,

Cd, Co, Cr, Cu, Fe, Mg, Mo, Na, Se, Si, Sr, V, Zn, Cl, SO₄, ²³⁸U, ²³⁰Th, and ²²⁶Ra. Many of these constituents exceed water quality guidelines by several orders of magnitude. As ground-water leaching of tailings continues, the quantity of readily soluble constituents within the solid tailings is reduced, resulting in a rapid decrease in the TDS content of the later column effluents. In terms of preventing surface or ground-water contamination, the period of greatest concern is during the first three pore volumes of leaching when the contaminant concentration is at its peak and the effluent pH is still very acidic (pH < 3.0).

Analyses of the effluents generated during the leaching study on the lime-neutralized tailings indicate a substantial reduction in the total number of soluble constituents over the course of the entire experiment (~30 pore volumes). During ground-water leaching, the neutralized tailings effluent solution pH remained between pH 7.4 and pH 8.5. The TDS content was comprised mainly of those elements whose solubility is not strictly dependent on solution pH and are found commonly in soil environments, namely Ca, Mg, Na, Cl, and SO₄. Although these ions were detected in higher concentrations than would be expected in soil pore waters, they too showed a gradual decrease as leaching continued and would be expected to drop to ground-water concentrations once gypsum has been depleted.

In general, the lime-neutralized tailings showed less adverse leaching effects in terms of potential surface or ground-water contamination. Effluent solution pH remained neutral, TDS content was reduced to one third of the untreated tailings value in the Lucky Mc tailings, and trace metal concentrations and radionuclide activities were significantly reduced, except the molybdenum concentrations from Lucky Mc tailings. For some constituents such as selenium and ²²⁶Ra, additional solution treatment (i.e., specific ion removal techniques) may be necessary to meet drinking water regulations. In neutralized solutions, these constituents still exceed the EPA maximum contaminant levels by ten to one hundred times. Other constituents of concern include Mo, Na, Cl, and SO₄ and should be considered on a case-by-case basis, since their concentrations in acidic tailings and tailings effluent solutions vary dramatically from site to site. These findings are in agreement with a recent report of the ground-water contamination potential from inactive tailings piles at Riverton, Wyoming, that have been draining and perhaps inundated periodically by rising ground water over the past 25 years (White et al. 1984).

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APPENDIX A

METHODS AND MATERIALS

APPENDIX A

METHODS AND MATERIALS

SAMPLE COLLECTION

In November 1982, Pacific Northwest Laboratory (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 and solid tailings 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 reservoir 2A at the location shown in Figure A.1. Tailings liquor was sampled from the east side of reservoir 2A, 100 m north of where tailings solution/slurry was currently being discharged into the evaporation pond.

Exxon Highland Mill's tailings liquor and solid tailings were sampled in November 1982 from the north side of the present tailings pond as shown in Figure A.2.

Solid tailings samples were collected from both the Lucky Mc and Exxon Highland mills. The Lucky Mc tailings were collected near the edge of the embankment along the dam face on the west end of the tailings impoundment. Exxon tailings were also collected from the north edge of the tailings pond as shown in Figure A.2.

Solid Tailings Characterization

Detailed characterization studies were performed on the solid tailings collected from both the Lucky Mc and Exxon Highland mill sites. Various physical properties, including saturated paste pH, Eh, and particle-size determinations, were measured for each solid material. In addition, to determine which constituents present in the acidic Lucky Mc and Exxon tailings were readily leachable, water extract analyses were conducted. Four hundred milliliters of distilled deionized water were added to 400 g of air-dry tailings and allowed to stand for 24 h. The tests were performed in duplicate. The 1:1 solid to solution mixtures were centrifuged and the solution fraction was collected and filtered through a 0.45-micron membrane filter. The filtrate was then subsampled for anion, cation, and radionuclide analyses.

Saturated paste pH and Eh analyses were performed on the tailings in a manner similar to the Bower method for Saturation Extracts with some modifications (Bower and Wilcox 1965, pp. 933-936). Briefly, while mixing with a spatula, distilled water was added to a known amount of solid tailings until a condition of saturation was reached. At saturation the solid material paste glistens and flows slightly when the container is tipped. After a brief equilibration period, the pH and Eh of the saturated paste were recorded.

FIGURE A.1. Lucky Mc Mill Site and Sampling Locations

A Corning® model 130 pH/Eh meter was used for the determinations with either a combination pH electrode or a platinum-banded redox electrode to measure pH or Eh, respectively.

The method used for the particle-size analyses was a modified version of the Day hydrometer method for particle fractionation and particle-size analysis (Day 1965, pp. 562-567). The modifications to the Day method were as follows:

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FIGURE A.2. Exxon Highland Mill Site and Sampling Locations

1) a factor was included to account for temperature fluctuations; 2) sodium hexametaphosphate was used in place of calgon as a dispersing agent; and 3) an antifoam agent was added to eliminate foam after mixing, making it easier to read the hydrometer. The antifoam agent was also added to the blank sample.

Macroelements (Al, Ca, Fe, Mg, Mn, Na, Si, and Sr) present in the extract solutions were determined using a Jarrell-Ash® emission spectrometer with an inductively coupled plasma (ICP) source. Macroanions (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 (zinc) or by graphite furnace atomic absorption (Ag, As, Ba, Cd, Co, Cr, Cu, Mo, Pb, Se, and V) using a Perkin Elmer® Model 5000 and HGA-5000 graphite furnace. Matrix interferences common to such heterogeneous samples were compensated for by sample dilution until known addition spikes showed at least 80% recovery. The analysis of selenium required a nickel-based matrix modification (Ediger 1975; Martin et al. 1975) and for Pb analyses, the L'vov platform method (Slavin and Manning 1979) was employed. Pulsed laser fluorimetry was used to follow the behavior of the total uranium concentrations throughout the studies when concentrations are reported as parts per million or milligrams per liter.

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Matrix interferences were eliminated through sample dilution until 100% spike recovery was achieved. Solutions analyzed for cation and radionuclide determinations were preserved by acidification to less than pH 2 with ultrapure nitric acid (APHA 1980, pp. 141-143). Samples analyzed for anion concentrations were preserved by storing the samples in sealed, airtight containers and were analyzed as soon as possible after collection.

Radionuclide activities in the solid acidic tailings materials and the filtrates from the 1:1 extracts were determined by using high-resolution gamma spectroscopy. For solid analyses, 15 g of dried sediment 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 ^{238}U and three of its daughter products. Lead-210, ^{238}U , ^{230}Th , and ^{226}Ra activities were determined over a counting time of 7 h 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 (185.7 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, when the ^{238}U content is calculated, 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 ^{226}Ra content. Detector efficiencies were determined on National Bureau of Standards traceable uranium-bearing sediments pressed into pellets identical to those used for sediment analyses. For solution analyses, a volume of solution (250 mL) was evaporated leaving the residual evaporites. These salts were mixed with a cellulose binder, pressed into a pellet of fixed geometry, and counted in a similar fashion as the solid sediment described earlier.

Chemical Reagents

Laboratory-grade chemical reagents were obtained from a local supply house. Finely ground (<200 mesh) reagents were used in all experiments requiring neutralizing reagents as well as in the preparation of laboratory ground water to ensure faster solution/reagent reaction rates and to facilitate mixing.

Preparation of Laboratory Ground Water

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 ground water) (Gee et al. 1980). A ground-water sample was collected in April 1979 from inside the Exxon Highland Mill from a water system used throughout Exxon's uranium extraction and purification process.

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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. When all reagents were added to 20 L of warm, distilled water, solution pH was adjusted from approximately pH = 9.0 to pH = 7.6 with the addition of small aliquots of concentrated sulfuric acid.

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

Chemical characterization data for the laboratory-prepared ground water used in the column studies are presented in Table A.2. Also included are the characterization results from the actual (April 1979) Exxon Highland Mill process water (Gee et al. 1980).

Solution Characterization

The collected acidic tailings solutions from both mill sites were characterized for anions, cations, and radionuclides by the same methods described for the analysis of the 1:1 tailings extracts described earlier in Appendix A.

Total acidity measurements on the as-collected Lucky Mc tailings liquor were determined by sodium hydroxide titration (Salotto 1966). Alkalinities of the neutralized tailings solutions in the batch experiments were measured by automated potentiometric titration with standardized 0.02 N sulfuric acid (APHA 1980, pp. 253-256).

TABLE A.1. Laboratory-Prepared Ground Water Reagents

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

TABLE A.2. Chemical Composition (mg/L) of Laboratory Ground Water

Parameter	Exxon Highland Mill Process Water ^(a)	Laboratory-Prepared Ground Water
Al	<0.1	<0.1
As	<0.02	<0.02
Ca	53.0	69.0
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	91.0	105.0
P	<0.01	<0.1
Pb	<0.01	<0.02
Se	<1.0	0.34 ^(b)
Si	3.5	0.54
Sr	0.9	0.03
Zn	0.05	<0.02
Cl	36.0	44.0
NO ₃	3.5	3.3
SO ₄	181.0	300.0
EC (mmhos/cm)	0.82	0.76
pH	8.2	7.6

(a) Gee et al. 1980.

(b) Analysis performed by inductively coupled plasma.

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APPENDIX B

RESULTS AND DISCUSSION

APPENDIX B

RESULTS AND DISCUSSION

SOLIDS CHARACTERIZATION

The results of the solids characterization studies performed on the Lucky Mc and Exxon Highland acidic tailings are shown in Table B.1.

Based on the particle-size distribution information, the Lucky Mc tailings were classified as a sandy loam and the Exxon tailings as a loamy sand. (The loamy sand sediment having a higher percentage of sand-sized particles than the sandy loam (Soil Survey Staff 1951.) The primary difference between the two tailings is the percentage of sand-sized particles present. Exxon and Lucky Mc tailings are comprised of 85% and 63%, respectively, sand-sized particles (>50 μm).

Results of the pH and Eh measurements taken on the 1:1 solution to solid tailings extracts indicate that the discharged tailings from both mills remain acidic and that most elements within the tailings would be present in their respective oxidized form as evidenced by the high Eh values.

In comparing the results of the individual tailings 1:1 extract solutions, the Lucky Mc data show that a much higher concentration of constituents were soluble in the extract solution, which was distilled deionized water (D₂O). An indicator of the relative amount of constituents dissolved in solution is the total dissolved solids (TDS) content of a particular solution sample. The TDS value for the Exxon extract solution is approximately one third that of the Lucky Mc extract. One reason for the difference is based on the pH-dependent solubility of certain elements. Previous tailings solution laboratory studies have demonstrated a pronounced effect on solution pH for selected constituent solubility (Sherwood and Serne 1983). Macro ions such as Al, Fe, Mn, and Si are soluble at low pHs and comprise a large portion of the TDS content in the Lucky Mc extract solution. As a solution approaches pH 4 (i.e., Exxon extract solution), the relatively low solubility of these species is exceeded, and they begin to precipitate out of solution. This is one reason for the reduced levels of these ions in the Exxon extract solution.

The second reason may be the amount of available surface area for constituents to adsorb onto or for precipitates to form (typically as a surface coating). The particle-size distribution data indicate a significantly larger percentage of small particles (fines) are present in the Lucky Mc tailings material as compared to the Exxon tailings. Recalling the sample collection section (in Appendix A), the tailings from both mills were collected from the edge of the existing tailings slurry disposal pond. Considering the normal cycling of the solution level in the tailings pond, the areas where the tailings used in this study were collected were covered with acidic tailings solution at some past point in time. As onsite draining reduced mill outflow

TABLE B.1. Solid Tailings and 1:1 Extract Characterization
Results for Lucky Mc and Exxon Highland Tailings

Parameter	Lucky Mc Tailings	Exxon Tailings
<u>Solids Analysis</u>		
Particle-Size Distribution		
% Clay	5	5
% Silt	32	10
% Sand	63	85
Radionuclides (pCi/g)		
²¹⁰ Pb	214	188
²³⁸ U	20	13
²³⁰ Th	283	122
²²⁶ Ra	213	17
<u>Tailings Extract</u>		
(1:1 solution:solid)		
pH	2.37	3.91
Eh (mV)	605	573
Macro ions (mg/L)		
Al	1,200	43
Ca	470	530
Fe	1,200	1.5
K	<3	4
Mg	950	890
Mn	120	31
Na	950	170
Si	81	35
Sr	3.3	1.4
Cl	530	500
NO ₃	31	<10
SO ₄	13,900	4,600
Trace Metals (mg/L)		
Ag	<0.02	<0.02
As	1.43	<0.01
Ba	<0.05	<0.05
Cd	0.38	0.02
Co	4.41	1.56
Cr	2.33	0.02
Cu	1.21	0.06
Mo	0.28	<0.02
Pb	<0.02	<0.02
Se	0.21	0.45
Zn	14	3.0
Radionuclides (pCi/L)		
²¹⁰ Pb	<75	<75
²³⁸ U	6,946	1,333
²³⁰ Th	22,459	<400
²²⁶ Ra	2,709	2,168

to the pond, and especially when water evaporation occurred, precipitated salts from the tailings solution could adsorb to or form around the solid tailings particles. The solid material with the higher percentage of 'nucleation sites' (i.e., the Lucky Mc tailings) could then contain a larger portion of tailings solution salts. On contact with a fairly ion-free solution (DD H₂O used in the 1:1 extracts), many of the precipitated salts could redissolve in a low pH solution matrix (pH 2.37).

A final reason for high extract constituent concentrations is based on the different mining strategies practiced by each mill prior to the milling process. This, in fact, may be the biggest factor explaining the difference in extract concentrations for the two mills. Lucky Mc and Exxon Highland tailings solution characterization data from earlier laboratory studies are presented in Tables 1 and B.2, respectively, for comparison (Opitz, Dodson and Serne 1984). The data presented indicate a large difference in the discharge solution composition from the respective milling circuits. The difference is due to disposal practices. The ore at the Exxon Highland site is located beneath the local water table. Mining the ore and operating the mine necessitated lowering the water level. The water drained into a sump and then was pumped to a settling pond for clarification. From there, the water was transferred to the tailings pond where significant acidic solution dilution occurred, resulting in reduced constituent concentrations as compared to the Lucky Mc solution (AEC 1973).

TABLE B.2. Exxon Tailings Solution Characterization Data^(a)

Parameters	Exxon Tailings Solution
pH	2.0
Eh (mV)	807
Conductivity (mmho/cm)	10.4
Total Suspended Solids (mg/L)	20
Total Dissolved Solids (g/L)	12.5
Total Acidity (as mg/L CaCO ₃)	5,269
<u>Macro ions (mg/L)</u>	
Al	440
B	0.4
Ca	560
Fe	1,000
K	44
Mg	540
Mn	50
Na	340
Si	310
Sr	8.5
Cl	300
NO ₃	9
SO ₄	9,300
<u>Trace metals (mg/L)</u>	
Ag	<0.02
As	0.21
Ba	<0.05
Cd	0.03
Co	1.31
Cr	1.25
Cu	0.97
Mo	<0.02
Pb	<0.02
Se	1.35
V	10.71
Zn	4.5
<u>Radionuclides (pCi/L)</u>	
²¹⁰ Pb	2,100
²³⁸ U	2,100
²³⁰ Th	97,140
²²⁶ Ra	758

(a) See Opitz, Dodson and Serne 1984.

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13 ABSTRACT (200 words or less) <p>Laboratory experiments were performed to compare the effectiveness of limestone and hydrated lime for improving waste water quality through the neutralization of acidic uranium mill tailings liquor. The experiments were designed to assess the effects of three proposed mechanisms — carbonate complexation, elevated pH and colloidal particle adsorption — on the solubility of toxic contaminants found in a typical uranium mill waste solution. Of special interest were the effects of each of these possible mechanisms on the solution concentrations of trace metals such as Cd, Co, Mo, Zn and U after neutralization.</p> <p>Acidic untreated solid tailings from two mill sites and tailings neutralized with lime were leached with a laboratory-prepared ground water for several pore displacement volumes. Analyses performed on the column effluents indicate that prior neutralization results in a significant reduction in the concentration of all pH dependent constituents in the column effluents. In contrast, relatively high concentrations of several trace metals and macro ions were found in effluent solution from the untreated tailings columns.</p>			
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