
Tailings Neutralization and Other Alternatives for Immobilizing Toxic Materials in Tailings

Final Report

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

Pacific Northwest Laboratory
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PREVIOUS DOCUMENTS IN SERIES

This 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.

NUREG/CR-3906, "Uranium Mill Tailings Neutralization: Contaminant Complexation and Tailing Leaching Studies," B. E. Opitz, M. E. Dodson and R. J. Serne, March 1985.

ABSTRACT

This document, "Tailing Neutralization and Other Alternatives for Immobilizing Toxic Materials in Tailings," is the final report in a series of six. It summarizes research completed since the beginning of the project. Three subtasks are included: Subtask A - Neutralization Methods Selection; Subtask B - Laboratory Analysis; and Subtask C - Field Testing.

Subtask A reviews treatment processes from other industries to evaluate whether current waste technology from other fields is applicable to the uranium industry. This task also identifies several reagents that were tested for their effectiveness in treating acidic tailings and tailings solution in order to immobilize the contaminants associated with the acid waste.

Subtask B describes the laboratory batch and column treatment studies performed on solid waste tailings and tailings solutions over the course of the project. The evaluation of several reagents identified in Subtask A was based on three criteria: 1) treated effluent water quality, 2) neutralized sludge handling and hydraulic properties, and 3) reagent costs and acid neutralizing efficiency.

Subtask C presents a field demonstration plan that will evaluate the effectiveness, costs, and benefits of neutralizing acidic uranium mill tailings solution to reduce the potential leaching of toxic trace metals, radionuclides, and macro ions from a tailings impoundment.

Details of the related research can be found in the documents listed in the "Previous Documents in Series."

CONTENTS

PREVIOUS DOCUMENTS IN SERIES.....	
ABSTRACT.....	iii
ACKNOWLEDGMENTS.....	xiii
EXECUTIVE SUMMARY.....	xv
INTRODUCTION.....	1
SUBTASK A. NEUTRALIZATION METHODS SELECTION.....	3
NEUTRALIZATION PROCESSES.....	3
SUMMARY.....	3
FIXATION PROCESSES.....	6
SUMMARY.....	6
REMOVAL APPROACHES FOR SPECIFIC CONSTITUENTS.....	9
ORE AND TAILINGS SOLIDS TREATMENT.....	9
Summary.....	9
EFFLUENT SEEPAGE TREATMENTS.....	10
Summary.....	10
OTHER TREATMENTS.....	11
Summary.....	11
NONRADIOACTIVE SELECTIVE EXTRACTION TECHNIQUES.....	11
Summary.....	11
TREATMENT EFFECTIVENESS AND RECOMMENDATIONS.....	13
SUBTASK B. LABORATORY ANALYSIS.....	15
METHODS AND MATERIALS.....	15
SAMPLE COLLECTION.....	15
CHEMICAL REAGENTS.....	15

LABORATORY-PREPARED SYNTHETIC GROUND WATER MAKEUP.....	16
TAILINGS SOLUTION CHARACTERIZATION.....	18
MINERALOGICAL ANALYSES.....	21
BATCH CONTACT STUDIES.....	21
Reagent Neutralization Tests.....	21
pH Optimization.....	21
Limestone/Lime Neutralization Tests.....	22
Contaminant Complexation Experiments.....	22
Solid Sludge Characterization.....	23
COLUMN EXPERIMENTS.....	24
Sludge Column Leaching Experiments.....	24
Tailings Leaching Experiments.....	24
Radium Attenuation Experiments.....	25
RESULTS AND DISCUSSION.....	28
UNTREATED TAILINGS SOLUTION CHARACTERIZATION.....	28
NEUTRALIZED TAILINGS SOLUTION CHARACTERIZATION.....	31
BATCH CONTACT STUDIES.....	31
Mineralogical Analyses.....	31
pH Optimization Studies.....	37
Limestone/Lime Batch Neutralization Studies.....	42
Contaminant Complexation Experiments.....	47
Sludge Characterization.....	60
COLUMN STUDIES.....	65
Sludge Column Leaching Experiments.....	65
Tailings Leaching Studies.....	68
Radium Attenuation Experiments.....	84

Reagent Efficiency and Costs.....	86
CONCLUSIONS.....	90
SUMMARY OF NEUTRALIZATION PROCESSES.....	90
Summary of Fixation Processes.....	90
Summary of Ore and Tailing Solids Treatments.....	90
Summary of Effluent Seepage Treatments.....	91
Summary of Other Treatments.....	92
Summary of Nonradioactive Selective Extraction Techniques.....	92
Treatment Effectiveness and Recommendations.....	92
Multi-Reagent Batch Neutralization Study.....	94
pH Optimization Study.....	95
Limestone/Lime Neutralization Study.....	95
Contaminant Complexation Study.....	96
Sludge Leaching Study.....	97
Tailings Leaching Study.....	98
Radium Attenuation Study.....	99
Reagent Costs.....	99
SUBTASK C. FIELD TESTING.....	100
INTRODUCTION.....	100
FIELD DEMONSTRATION OBJECTIVES.....	101
FIELD DEMONSTRATION DESCRIPTION.....	101
Alternatives.....	102
TECHNICAL SCOPE.....	102
TECHNICAL APPROACH.....	104
Task 1: Laboratory Testing.....	105
Task 2: Field Studies.....	105

TECHNICAL PROGRESS.....	107
First Year.....	107
Second Year.....	107
Third Year.....	107
Milestone Schedule.....	108
Field Demonstration Program Budget.....	108
SAFETY.....	109
PROGRAM CONTROL.....	110
REFERENCES.....	111

FIGURES

1	Lucky Mc Mill Site and Sampling Locations.....	16
2	Exxon Highland Mill Site and Sampling Locations.....	17
3	Total Dissolved Solids Comparison Between Limestone and Hydrated Lime-Neutralized Tailings Solution.....	48
4	Comparison of Molybdenum Concentrations in Untreated and Neutralized Tailings Solution.....	54
5	Total Uranium Concentration Comparison Between Hydrated Lime, Hydrated Lime/Sodium Bicarbonate, and Limestone-Neutralized Tailings Solution.....	58
6	Lucky Mc and Exxon Highland Acidic Tailings Total Dissolved Solids Versus Adjusted Pore Volume.....	78
7	Lucky Mc Neutralized and Untreated Tailings Total Dissolved Solids Content Versus Adjusted Pore Volume.....	81
8	Exxon Highland Tailings Neutralized and Untreated Total Dissolved Solids Content Versus Adjusted Pore Volume.....	83
9	Results of Treated and Untreated Tailings Experiments.....	84

TABLES

1	Advantages and Disadvantages of Selected Neutralization Processes....	4
2	Advantages and Disadvantages of Solidification Processes.....	7
3	Constituents in Laboratory-Prepared Ground Water.....	18
4	Comparison of the Chemical Composition of Exxon Highland Mill Process Water and Laboratory-Prepared Ground Water.....	19
5	Elements/Anions Considered and Proposed Analytical Methods.....	20
6	Sludge Column Parameters.....	24
7	Tailings Column Identification and Description.....	25
8	Tailings Column Compaction Data.....	25
9	Radium Attenuation Column Identification and Description.....	26
10	Radium Attenuation Column Compaction Data.....	26
11	Local Ground-Water Chemical Composition.....	27
12	Solution Chemistry of Lucky Mc and Exxon Highland Tailings Solutions.....	29
13	Maximum Concentration Levels for Specified Water.....	30
14	Solution Chemistry of Field Neutralized Lucky Mc and Exxon Highland Mill Tailings Solutions.....	32
15	Macro Concentrations in the Neutralized Lucky Mc Tailings Solution, mg/L.....	33
16	Macro Concentrations in the Neutralized Exxon Tailings Solution, mg/L.....	34
17	Trace Metal Concentrations in the Neutralized Lucky Mc Tailings Solution, $\mu\text{g/L}$	35
18	Trace Metal Concentrations in the Neutralized Exxon Tailings Solution, $\mu\text{g/L}$	35
19	Radionuclide Concentrations in the Neutralized Lucky Mc Solution, pCi/L	36
20	Radionuclide Concentrations in the Neutralized Exxon Tailings Solution, pCi/L	36

21	pH Optimization Reagent Cost Data for Lucky Mc and Exxon Highland Tailings Solutions.....	38
22	Solution Chemistry of Calcium Hydroxide Neutralized Lucky Mc Acidic Tailings Solution.....	39
23	Solution Chemistry of Calcium Hydroxide Neutralized Exxon Highland Acidic Tailings Solution.....	40
24	Solution Chemistry of Calcium Carbonate/Calcium Hydroxide Neutralization of Lucky Mc Mill Tailings Solution.....	43
25	Solution Chemistry of Calcium Carbonate/Calcium Hydroxide Neutralization of Exxon Highland Tailings Solution.....	44
26	Comparison of $\text{Ca}(\text{OH})_2$ Neutralization with $\text{Ca}(\text{OH})_2/\text{CaCO}_3$ Two-Step Neutralization.....	46
27	Solution Chemistry: Neutralization of Lucky Mc Tailings Solution Using Hydrated Lime.....	50
28	Solution Chemistry: Neutralization of Lucky Mc Tailings Solution Using Limestone.....	51
29	Solution Chemistry: Neutralization of Lucky Mc Tailings Solution Using $[\text{Ca}(\text{OH})_2/\text{NaHCO}_3]$	53
30	Percentage of Predominate Uranium Carbonate Species at Selected pH Values.....	59
31	Solution Chemistry of Lime-Neutralized Lucky Mc Tailings Solution Before and After 18A Filtering.....	61
32	Solution Chemistry of Limestone-Neutralized Lucky Mc Tailings Solution Before and After 18A Filtering.....	62
33	Solution Chemistry of Lime/Sodium Bicarbonate-Neutralized Lucky Mc Tailings Solution Before and After 18A Filtering.....	63
34	Total Dry Weight of Sludge Per Liter of Mill Tailings Solution Treated, g/L.....	64
35	Capillary Pressure Versus Water Content Relationship for Lucky Mc Sludge Material.....	64
36	Capillary Pressure Versus Water Content Relationship for Exxon Highland Mill Sludge Material.....	64
37	Lucky Mc Sludge Column Leaching Data.....	66
38	Exxon Highland Sludge Column Leaching Data.....	67

39	Column Effluent Solution Chemistry of Untreated Lucky Mc Tailings-Extended Leaching Data.....	70
40	Column Effluent Solution Chemistry of Untreated Exxon Tailings-Extended Data Leaching.....	71
41	Column Effluent Solution Chemistry of Untreated Exxon Highland Tailings-Extended Leaching Data.....	72
42	Column Effluent Solution Chemistry of Neutralized Lucky Mc Tailings-Extended Leaching Data.....	73
43	Column Effluent Solution Chemistry of Neutralized Exxon Highland Tailngs-Extended Leaching Data.....	75
44	Solution Composition of Untreated and Amended Tailings Effluents.....	86
45	Reagent Usage and Cost Data for Several Reagents.....	87
46	Reagent Usage and Cost Data for Limestone/Lime Neutralization.....	89

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EXECUTIVE SUMMARY

Of primary concern at uranium mill sites in the United States is the potential of ground-water contamination from mill wastes that are disposed in tailings impoundments (e.g., evaporation ponds, pits, or dammed basins). Although many systems (e.g., evaporation ponds, underdrains, liners, and solution recycling) have been used to control seepage from tailings impoundments, most of these systems are limited in their ability to handle an excess of tailings solution. If the tailings solution is not contained, the high concentration of contaminants in the acidic solution may present a potential environmental problem.

In the United States, most uranium mill tailings pond solutions are acidic (pH 1.2 to 2) and contain 15,000 to 32,000 ppm total dissolved solids (TDS) including 100,000 to 300,000 pCi/L of long-lived radioactivity from ^{238}U and its daughter products. Left untreated, the liquid waste exceeds primary and secondary drinking water standards, recommendations for livestock and irrigation water limits, and radiation protection standards for release to uncontrolled areas by two to three orders of magnitude for constituents such as Fe, Mn, NH_4 , SO_4 , ^{230}Th , ^{226}Ra , ^{210}Pb , and ^{210}Po and exceeds the standards by one order of magnitude for elements such as Ca, Na, NO_3 , and Cl. However, comparing the tailings pond concentrations to the water standards does not take into account chemical attenuation by soils (e.g., precipitation and adsorption, ground-water dilution/dispersion, or the possible total containment of the waste). Clearly, some or all of these mechanisms can be counted on to provide environmental protection. As a result of these mechanisms, no U.S. mills have been forced to neutralize the acidic wastes prior to disposal.

As evidenced by experience on acid mine drainage in Canada and in the United States, neutralization can reduce the solution concentrations of many potential contaminants. In Canada, where neutralization is practiced, the neutralized uranium tailings liquids contain only 1000 to 2500 ppm TDS including about 1000 pCi/L of long-lived radioactive elements. Compared to the U.S. acid solutions, these values show a 90% reduction in TDS and a 99% reduction in radionuclides. Even with these reductions, Canadian liquid effluents exceed U.S. standards for SO_4 , NO_3 , NH_4 , and ^{226}Ra by up to one order of magnitude. Further, pyrite oxidation of neutralized tailings often occurs in Canada resulting in reacidification of the tailings liquids and remobilization of many trace metals and radionuclides. Such pyrite reacidification is not expected in typical U.S. tailings because most U.S. tailings have low pyrite contents. Also, most soils and sediments, especially those in the western United States, contain natural neutralizing agents (e.g., CaCO_3), which, on contact with the acidic tailings waters, significantly reduce the mobility of radionuclides and other dissolved solids.

The U.S. Nuclear Regulatory Commission (NRC) established the tailings neutralization task to assess the effectiveness, benefits, and costs of neutralizing tailings under a full range of site and environmental conditions. As a

first step, we conducted a literature review to evaluate tailings amelioration techniques and to assess their effectiveness in reducing contaminant mobility.

Three general amelioration methods were identified: neutralization, fixation, and specific constituent removal. During neutralization, a reagent is added to the tailings solution to neutralize the acidity and raise the pH to reduce the solubility of various pH-sensitive contaminants. In contrast, fixation processes add materials such as lime, cement, or asphalt to the waste to produce a physically stable composition that resists leaching of hazardous constituents. Specific constituent removal encompasses varying techniques, such as alternate ore-leaching processes, effluent treatment with sorption, or ion-exchange agents or selected precipitation that reduce specific constituent concentrations in tailings solution.

Currently, neutralization processes appear to be best suited for treating uranium mill tailings because they can, at a reasonable cost, limit the solution concentration of many contaminants, thus reducing the potential for ground-water contamination. However, the effectiveness of the process depends on the reagent used as well as the waste being treated. Of the six reagents studied (lime, limestone, caustic soda, soda ash, combined limestone/lime and combined alumina/lime/soda), a combined treatment of limestone and lime seems best. This is especially true for tailings containing ferric iron because the limestone economically buffers the solution acidity, while the lime takes the pH to ~8.0, an optimum level for heavy metal removal. For those tailings containing ferrous iron, lime alone works best. In general, the costs for the lime/limestone or lime processes range from \$0.20 to \$1.00/1000 gal of treated water, excluding capital equipment costs.

The objective of the laboratory studies was to compare various neutralizing agents for treatment of acidic uranium mill tailings solution from representative U.S. sites. Each reagent was evaluated in terms of

- the quality of treated effluent (with greater detail on radionuclides, potentially toxic trace metals, and mobile anions)
- the properties of the neutralized sludge (e.g., dewatering, hydraulic conductivity, and leaching characteristics)
- the cost of the reagents for typical U.S. uranium mill tailings treatment.

For those contaminants that are only partially immobilized by neutralization, additional treatments were studied. After the initial laboratory screening studies were completed, a field demonstration test was proposed to NRC to verify the effectiveness of selected processes under field conditions.

Studies designed to determine the optimum final pH for solution neutralization were also conducted. The optimum final pH for tailings solution neutralization is defined as the pH where further addition of a neutralizing reagent no longer significantly increases the removal of contaminants from solution. Data from this study could result in significant solution treatment

savings by preventing over-neutralization of the tailings solution through the addition of excess neutralizing reagents. Results of these experiments performed on Lucky Mc and Exxon tailings solutions showed neutralization of tailings solution above pH 7.3 does not significantly increase removal of contaminants. Tailings solution constituents such as Al, As, Ba, Cr, Fe, Si, V, ^{210}Pb , ^{238}U , and ^{230}Th showed reductions in concentrations or activities in excess of 98% after neutralization to pH 7.3. Acid tailings constituents not effectively removed by $\text{Ca}(\text{OH})_2$ neutralization include the macro ions, Ca, Na, Mg, Cl, NO_3 , and SO_4 and the trace metals, Co, Mo, and Se.

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

Studies examining the feasibility of combination limestone/lime neutralization on acidic uranium mill tailings solution were initiated. Tailings solutions from the Lucky Mc and Exxon Highland mills were neutralized to pH 4.0 or 5.0 in separate tests using limestone (CaCO_3), followed by further solution neutralization with lime ($[\text{Ca}(\text{OH})_2]$) to pH 7.3.

Evaluations of the effectiveness of the combination limestone/lime treatment for neutralizing acidic uranium tailings solutions were based on two criteria: 1) treated effluent water quality and 2) reagent cost.

Treated effluent water quality data suggest that initial solution neutralization with CaCO_3 to either pH 4.0 or 5.0 followed by lime neutralization to pH 7.3 is effective in reducing contaminant concentrations in tailings solution. Total dissolved solids contents were reduced by greater than 55% for the Lucky Mc tailings solution and greater than 57% for Exxon tailings solutions. Certain macro ions (Cl, NO_3 and SO_4), trace metals (Cd and Se) and one radionuclide (^{226}Ra) still show solution concentrations above EPA's maximum contaminant levels for various types of waters. Ions such as these will require some type of additional solution treatment, such as specific ion removal techniques, to reduce their solution concentration to meet wastewater quality guidelines.

Laboratory experiments were conducted that allowed a direct comparison of the effectiveness of limestone (CaCO_3) and hydrated lime $[\text{Ca}(\text{OH})_2]$ in improving wastewater quality through the neutralization of acidic uranium mill tailings solution. 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 solution.

Final conclusions of the batch studies are as follows:

- Neutralization of acidic uranium mill tailings solution by any of the test methods can substantially improve wastewater quality.
- The optimum solution pH to terminate neutralization from a water quality viewpoint is pH = 7.3, regardless of neutralizing reagent.

To evaluate the long-term contaminant attenuation properties of the sludge material generated, column leaching studies were conducted. These sludge leaching studies indicate the sludge end product, generated as neutralization occurs, remains as a chemically stable, low-density precipitate. When leached with low-ionic-strength ground water, the sludge does not permit the dissolution and release of the pH-dependent contaminants but does release soluble salts such as Ca, Na, Mg, Se, Cl, and SO_4 .

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.

Laboratory experiments were conducted to develop alternative control measures for those contaminants that were identified as not being effectively attenuated by common neutralization methods. Of those contaminants associated with uranium mill tailings not effectively immobilized by tailings neutralization, radium imposes an important environmental concern in terms of potential ground-water contamination.

Because of the high activity of soluble radium in the acidic uranium mill tailings environment (several hundred to several thousand picocuries per liter) specific ion-removal procedures were investigated for use in attenuating radium in order to prevent future ground-water contamination. Results of these investigations led to the development of a tailings additive comprised of a mixture of hydrated lime and barium chloride, which, when added to acidic tailings, can reduce the amount of leachable radium escaping a designated tailings impoundment.

In laboratory verification tests, this radium-specific tailings treatment reduced the effluent solution activity of radium by three orders of magnitude, from >3500 to 1.7 pCi/L, in comparison with untreated acidic tailings.

A field demonstration plan is presented that will evaluate the effectiveness, costs, and benefits of neutralization of acidic uranium mill tailings solutions to reduce the potential leaching of toxic trace, radionuclides, and macro ions from a tailings impoundment.

The effectiveness of neutralization of acidic uranium mill tailings solution of a field scale will be based on the following four criteria: 1) treated effluent water quality, 2) reagent costs and acid neutralizing efficiency, 3) neutralized sludge handling and hydraulic properties, and 4) long-term contaminant immobilization.

The plan proposes three separate alternatives for carrying out the evaluations of selected neutralizing reagents or techniques on a field-site scale. The three alternatives, only one of which will be implemented, are designed to assess the contaminant immobilization properties of acid solution neutralization.

Alternatives

The field demonstration of neutralization techniques and selected neutralizing reagents will be one of the three alternatives considered below:

Alternative A - The outright purchase of the necessary equipment for neutralization of a specified volume ($\approx 10^6$ L) of tailings solution using one reagent or a combination of more than one reagent as determined by laboratory experiments as most beneficial for the selected demonstration site.

Alternative B - Use of existing equipment and facilities at a milling site that currently neutralizes the acidic solution via incorporation of our chosen reagent or a combination of more than one reagent as determined by laboratory experiments as most beneficial.

Alternative C - Analysis and evaluation of the efficiency, costs, and benefits of an existing neutralization technique and reagent(s) in use at a mill site that currently treats acid tailings solution.

The criteria involved in selecting one of these three alternatives for fulfillment of the demonstration program is based primarily on 1) sponsor concurrence, 2) mill site owner/operator concurrence, 3) time allocated and funding availability for project completion, and 4) site location and equipment availability.

INTRODUCTION

In September 1981, the U.S. Nuclear Regulatory Commission (NRC) expanded the scope of the Uranium Research and Recovery Program at Pacific Northwest Laboratory (PNL) to address many technical issues of concern in the licensing, operation, and decommissioning of uranium recovery facilities. One of the more technical issues to be investigated dealt with the treatment and/or disposal practices associated with acidic uranium mill tailings and tailings solution. Specifically, the Tailings Neutralization and Other Alternatives for Immobilizing Toxic Materials in Tailings Task was developed to investigate ways of mitigating the movement of contaminants associated with uranium mill tailings in order to prevent future potential ground-water contamination.

In the United States, most uranium mill tailings pond solutions are acidic (pH 1.2 to 2) and contain 15,000 to 32,000 ppm total dissolved solids (TDS) including 100,000 to 300,000 pCi/L of long-lived radioactivity from uranium-238 and its daughter products. Left untreated, the liquid waste exceeds primary and secondary drinking water standards, recommendations for livestock and irrigation water limits, and radiation protection standards for release to uncontrolled areas by two to three orders of magnitude for constituents such as Fe, Mn, NH_4 , SO_4 , pH, ^{230}Th , ^{226}Ra , ^{210}Pb , and ^{210}Po and exceeds the standards by one order of magnitude for elements such as Ca, Na, NO_3 , and Cl. However, comparing the tailings pond concentrations to the water standards does not take into account chemical attenuation by soils (e.g., precipitation and adsorption, ground-water dilution/dispersion, or the possible total containment of the waste). Clearly, some or all of these mechanisms can be counted on to provide environmental protection. As a result of these mechanisms, no U.S. mills have been forced to neutralize the acidic wastes prior to disposal.

As evidenced by experience on acid mine drainage in Canada and in the United States, neutralization can reduce the solution concentrations of many potential contaminants. In Canada where neutralization is practiced, the neutralized uranium tailings liquids contain only 1000 to 2500 ppm TDS including about 1000 pCi/L of long-lived radioactive elements. Compared to the U.S. acid solutions, these values show a 90% reduction in TDS and a 99% reduction in radionuclides. Even with these reductions, Canadian liquid effluents exceed U.S. standards for SO_4 , NO_3 , NH_4 , and ^{226}Ra by up to one order of magnitude. Further, pyrite oxidation of neutralized tailings often occurs in Canada resulting in reacidification of the tailings liquids and remobilization of many trace metals and radionuclides. Such pyrite reacidification is not expected in typical U.S. tailings because most U.S. tailings have low pyrite contents. Also, most soils and sediments, especially those in the western United States, contain natural neutralizing agents (e.g., CaCO_3). When the acidic tailings waters contact the natural neutralizing agents, a significant reduction in the mobility of several radionuclides and other dissolved solids normally occurs because of the solution pH change.

The NRC established this project to assess the effectiveness, benefits, and costs of neutralizing tailings and tailings solution under a full range of

site and environmental conditions. As a first step in the Project, (Subtask A - Neutralization Methods Selection) a literature review was conducted to evaluate current tailings amelioration techniques and to assess their effectiveness in reducing contaminant mobility. Based on the recommendations for future study from the literature review, several laboratory experiments were performed (Subtask B - Laboratory Analysis). The experiments were designed to evaluate several different neutralizing reagents and techniques in terms of effluent solution quality, sludge handling properties, and treatment costs for U.S. tailings. Subtask C, field demonstration, developed a demonstration plan for field verification of the most effective treatment scheme identified in the laboratory analyses. This document describes the test methods employed, experimentation, results, and conclusions of this Uranium Recovery and Research Program task.

SUBTASK A. NEUTRALIZATION METHODS SELECTION

Neutralization Methods Selection describes the three main techniques or processes used to treat solid and liquid inorganic wastes. The three techniques for treatment are as follows: solution neutralization processes, fixation processes, and specific constituent removal. A summary of these three processes follows. For a more in-depth discussion, see Sherwood and Serne (1983a).

NEUTRALIZATION PROCESSES

Although no U.S. uranium mill sites have used neutralization processes for treating uranium mill tailings solutions, several other industries (e.g., metal plating and surface coal mine disposal) add a reagent to their acidic waste solutions to neutralize the acidity and reduce the potential mobility of contaminants. This process, known as neutralization, is used extensively to reduce the potential environmental effects of acid mine drainage (AMD) on surface and ground waters and should prove useful for uranium mill wastes. In general, the effectiveness of the neutralization processes depends on the oxidation state of the iron in the acid mine waters, the desired quality of the effluent, and the reagent used. Of these variables, the reagent is probably the most important variable of the treatment process because it affects the basic components of the treatment system: the process design, the effluent and sludge characteristics, and the costs. In the following subsections, the six most commonly used reagents (limestone, lime, soda ash, caustic soda, combination limestone/lime, and combination alumina/lime/soda) will be discussed in terms of the basic components of the treatment system. However, since neutralization has not been conducted at U.S. mill sites, the following discussion is based, in part, on experience gained on AMD.

SUMMARY

Because AMD is often treated successfully via neutralization techniques to remove contaminants, its use for uranium mill wastes is a logical extension. Table 1 summarizes the advantages and disadvantages of the selected neutralization processes discussed in this section. The following recommendations are based on experience gained treating AMD rather than uranium mill tailings waste. The next phase of our work involves developing a confirmatory data base from laboratory and field studies on uranium mill tailings typical of U.S. sites.

Of the six reagents studied (limestone, lime, soda ash, caustic soda, combined limestone/lime and combined alumina/lime/soda), a combined treatment of limestone and lime appears best, especially for uranium mill tailings containing ferric iron. The limestone economically neutralizes the tailings acidity, while the lime increases the pH to 8.0, an optimum level for heavy metal removal. For those uranium mill tailings containing ferrous iron, lime alone

TABLE 1. Advantages and Disadvantages of Selected Neutralization Processes

Treatments	Effluent Quality		Reagents and Treatment Process		Sludge Disposal		Cost
	Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages	
Limestone (CaCO ₃)	Limits sulfate because hard treated water precipitates	Hard treated water	Safe to handle	Reagent quality critical for reactivity	Large volume of gross high density sludge	Low reagent cost	Slow reactor required
	Reduces total dissolved solids	Maximum pH around 7.0	No potential for over-treatment	Reagent settling required low reagent efficiency above pH 7.0	Low moisture content	Low reagent cost	
Lime Ca(OH) ₂	Limits sulfate because hard treated water precipitates	Hard treated water	Safe to handle	Must store reagents dry	Large quantity of sludge	Low reagent cost	High sludge disposal costs
	Reduces total dissolved solids		Very reactive	Potential for over-treatment	Low density		
	Optimum pH 8.0 can be achieved		High reagent efficiency	Must be stored	Difficult to dewater		High construction cost
Soda Ash (Na ₂ CO ₃)	Soft water after treatment	High sodium concentration	Safe to handle dissolves readily	Difficult to obtain	Easily handled	Low capital costs	High reagent cost
		High sulfate concentration	No potential for over-treatment		Very little sludge		
		Maximum pH 7.0 settling	Reactive rapid		Low moisture	Low sludge disposal cost	
Caustic Soda	Soft water after treatment	High sodium and sulfate concentrations	Very reactive	Difficult to obtain	Does not dewater readily	Low sludge disposal costs	Higher settling pond cost
	Optimum pH 8.0 can be achieved		High reagent efficiency	Highly corrosive	Low density		High reagent cost
			Potential for over-treatment	Potential for over-treatment		Slow settling properties	
Limestone-Lime		Hard treated water	Reactor under process conditions	Two-stage process	Large quantity of calcium sulfate sludge	Low reagent cost	High sludge disposal cost
	Optimum pH 8.0 can be achieved		High reagent efficiency	Potential for over-treatment	Easily handled high density sludge		High construction costs
Ammonia-Lime Soda Combination	Low sulfate and total dissolved solids			Potential for over-treatment	Sludge must be physically dewatered	Indirect water use offset	Very high reagent costs
				Sludge recycling required	High volume		High capital and construction costs
					High moisture		High sludge disposal costs

would be most economical and efficient. Neutralization with these calcium-based reagents are capable of removing acidity, trace metals and radionuclides from acid mine drainage and Canadian uranium mill tailings. Removal of radionuclides and trace metals from U.S. mill tailings has not been documented, but because of their similarity to AMD and Canadian mill tailings wastes, we expect neutralization techniques to be quite effective for most radioactive and trace metal potential contaminants.

Neutralization may not remove all potentially mobile contaminants. The available literature concentrates on its ability to remove transition metals (e.g., Fe, Cu, Zn, Cd), selected radionuclides (U, Pb, Th, Ra) and sulfate. For other constituents like alkaline earth metals, NH_4^+ and NO_3^- data are sparse. In general, the costs for the two calcium reagent-based neutralization processes should range from \$0.20 to \$1.00/1000 gal of treated wastewater, excluding capital equipment costs.

FIXATION PROCESSES

Fixation processes are those treatment processes that produce a physically stable, leach-resistant material from waste solids, sludges, or slurries. The solidified waste produced is chemically and physically bound by additives, which can reduce leaching of hazardous contaminants from the waste. Other benefits derived from fixation processes are that the final product has a higher structural stability and can be handled more easily than the untreated waste stream.

Solidification (fixation) processes can be grouped into three major categories based on predominant additives used to fix the waste material. These processes are lime-based, cement-based, and asphalt-based (thermoplastic). These fixation treatments use lime, cement, or asphalt as well as other lesser additives to produce a waste of the desired composition and characteristics. The following chart lists the processes that represent the commercially available techniques used for solidifying hazardous and/or toxic inorganic wastes.

Solidification Process		
<u>Lime-Based</u>	<u>Cement-Based</u>	<u>Asphalt-Based</u>
Pos-O-Tec Canadian Waste Technology	Chemfix Stablex	AECL Bituminization

Four of these stabilization processes--Pos-O-Tec, Canadian Waste Technology, Chemfix, and Atomic Energy of Canada Limited, Inc. (AECL) Bituminization--were tested for use on Canadian uranium mill tailings (Ritcey et al. 1982). Tests were performed (i.e., stress tests, flexural strength, compressibility, and freeze/thaw cycling) to determine the structural stability of the solidified tailings. Ground-water leaching, acid leaching, and radon emanation experiments were also performed to determine the chemical properties of the fixed tailings. The physical properties (bulk density, moisture content, and porosity) were determined for each of the treated solids. The results of these tests are discussed below. The tests were performed by researchers at CANMET, located in Ottawa, Ontario, and the Ontario Research Foundation, located in Waterloo, Ontario. In addition, Stablex, a fifth method, is briefly described.

SUMMARY

Generally, fixation processes are not readily suited for uranium mill tailings because they increase volume and weight of the waste. (Table 2 describes the advantages and disadvantages of the various processes.) For example, some of these treated solids contain as little as 40% of the original waste, which significantly increases the waste volume. An effective lime-based solidification process such as Pos-O-Tec costs between \$10 to \$17/ton of tailings. An effective cement-based solidification process has an estimated cost of \$7/ton of tailings. The asphalt-based solidification process works only on

TABLE 2. Advantages and Disadvantage of Solidification Processes^(a)

Process	Advantages	Disadvantages
Lime-based	<ol style="list-style-type: none"> 1. The additives are generally very inexpensive and widely available. 2. Equipment required for processing is simple to operate and widely available. 3. Chemistry of pozzolanic reactions is well known. 	<ol style="list-style-type: none"> 1. Lime and other additives add to weight and bulk of waste. 2. Stabilized sludges are vulnerable to acidic solutions and to curing and settling problems associated with inorganic contaminants in the waste.
Cement-based	<ol style="list-style-type: none"> 1. Additives are available at a reasonable price. 2. Cement mixing and handling techniques are well developed. 3. Processing equipment is readily available. 4. Processing is reasonably tolerant of chemical variations in sludges. 5. The strength and permeability of the end product can be varied by controlling the amount of cement added. 	<ol style="list-style-type: none"> 1. Low-strength cement-waste mixtures are often vulnerable to acidic leaching solutions. Extreme conditions can result in decomposition of the fixed material and accelerated leaching of the contaminants. 2. Pretreatment, more expensive cement types, or costly additives may be necessary for stabilizing wastes containing impurities that affect the setting and curing of cement. 3. Cement and other additives add considerably to weight and bulk of waste.
Asphalt-based	<ol style="list-style-type: none"> 1. Contaminant migration rates are generally lower than for most other techniques. 2. End product is fairly resistant to most aqueous solutions. 3. Thermoplastic materials adhere well to incorporated materials. 	<ol style="list-style-type: none"> 1. Expensive equipment and skilled labor are generally required. Reagents are relatively expensive. 2. Sludges containing contaminants that volatilize at low temperatures must be processed carefully. 3. Thermoplastic materials are flammable. 4. Wet sludges must be dried before they can be mixed with the thermoplastic material.

(a) After Ritcey (1982)

dried tailings and is exceedingly costly: \$140 to \$420/ton of tailings treated. To compare the neutralization costs discussed in the previous section with these process costs, we converted the 1000-gal-based costs to per ton costs. Neutralization using lime or limestone would cost \$0.17 to \$0.30/ton of tailings (assuming a specific gravity of slurry of 1.4) or ~1% of the solidification costs. Thus, application of fixation processes to uranium mill tailings waste treatment should be limited and, if used at all, limited to the most toxic fraction of the waste stream such as concentrated slimes. Strictly limiting the volume of tailings treated may make this technique feasible.

REMOVAL APPROACHES FOR SPECIFIC CONSTITUENTS

The neutralization process effectively removed pH-sensitive elements such as transition metals and selected radionuclides. However, certain important constituents such as the alkaline earth elements (e.g., radium and barium) and mobile anions NO_3^- , SO_4^{2-} , and Cl^- may still exist in neutralized tailings effluents at unacceptably high concentrations. Effluent streams could be further treated to selectively remove these constituents. Or, further specific removal techniques could be incorporated into the milling process itself and used on the waste stream right after uranium extraction or just prior to tailings disposal.

Selected contaminants can be removed by 1) separating the contaminant from the solid waste (tailings) such that subsequent seepage would have no source material to leach or 2) capturing or treating the liquid effluent seepage from disposed tailings as it leaves the tailings environs. In addition, experiments are under way to develop new uranium extraction schemes for producing more environmentally compatible waste streams, which would remove contaminants prior to disposal.

ORE AND TAILINGS SOLIDS TREATMENT

The general approach to treating ore and tailings is to separate the contaminants from the waste prior to disposal. Among the techniques reviewed were a preconcentration technique, nitric and hydrochloric acid extraction, and flotation.

Summary

Alternate ore milling technology or tailings leaching prior to disposal to remove potential pollutants are in their infancy. In general, the acid or salt leachants require more complex process steps, new capital equipment, and often produce waste streams with the same or greater potential hazard as the conventional sulfuric acid leach process. For tailings treatment, long-term hazards reduction via radium-226 removal will require removal of thorium-230 also because of the ingrowth of radium-226 daughters. After 1,000 years, ingrowth reaches 35%, and after 10,000 years, it reaches 100% of the existing thorium-240 activity. Radium-226 represents the largest potential radiation hazard in tailings and thus is the focus of most treatment schemes.

The most promising alternate ore-processing technique reviewed uses ore preconcentration via flotation to remove sulfide minerals and high-intensity magnetic separation to remove radionuclide-laden minerals. The two concentrates combined represent only 33% by weight of the original ore yet contain 97% of the uranium, 98.5% of the radium, 92% of the thorium, and 98.5% of the pyrite. The bulk tailings contain only 25 pCi/g ^{226}Ra and are environmentally acceptable for mine backfill or uncontrolled pit disposal. The concentrates may be uranium extracted by conventional sulfuric acid leach to yield 1/3 the typical amount of waste. The same process may be used on spent tailings to remove residual sulfide minerals and radionuclides to produce a bulk tailings,

~2/3 of which have very low hazard potential and 1/3 of which contain the concentrated radioactive waste. Removal of pyrite also reduces the risk of tailings pile re-acidification upon pyrite oxidation, which is a demonstrable problem in Canada.

EFFLUENT SEEPAGE TREATMENTS

The second general technique to remove radionuclides and other contaminants from uranium mill tailings is to treat any associated or seepage liquids that subsequently are formed after disposal. Treatment techniques discussed include adsorption, ion exchange, precipitation, biological, solvent extraction, reverse osmosis, and selective membrane mineral extraction.

Summary

The adsorptive reactions of several clays, zeolites, hydrous oxides, and soils/sediments for the radionuclides uranium, thorium, and radium, were reviewed. Because of uranium's high solubility under oxidizing conditions and strong anionic carbonate complexes, it is only moderately adsorbed. Thorium is insoluble in neutral pH environments and readily retained in soils. Radium appears to adsorb readily to clays, soils, and sediments via ion exchange-like processes.

Ion-exchange resins have been used to remove radium from low-quality municipal and drinking water sources and mine wastewaters. Common cation exchange resins are of limited use because calcium, magnesium, and other multivalent cations load the exchange sites and compete too strongly. Other specialized resins such as manganese-impregnated acrylic fiber resins or synthetic zeolites show good radium selectivity from low-TDS neutral mine waters, but column regeneration is a problem. Without good column regeneration, the cost for treatment is high. The most promising ion-exchange resin is a new cross-linked organic polymer recently studied by Boyce and Boom (1982). Using a neutral-pH mine water with ~1350 ppm TDS and up to 100 pCi/L radium-226, the resin removed >95% of the radium-226 for 7 months, while a standard strong acid cation exchanger lasted only 1 week before calcium loading decreased radium removal.

At best ion exchange appears useful for removing radium from only neutralized, low TDS waters. Direct application to acidic tailings liquids with the 15,000 to 35,000 ppm TDS appears inappropriate excepting perhaps the new cross-linked resin for which more testing is needed. No specific costs for ion exchange removal of radium for mine waters are available but for a 1000 gal/min drinking water plant using conventional strong acid cation resins, the capital costs are estimated at \$1,000,000 (1976 dollars) and 20¢/1000 gal for operating costs. The capital costs greatly exceed those for BaCl_2 treatment but the operating costs are 3.5 times less.

Currently only one constituent, radium-226, is selectively removed by precipitation techniques from uranium mill tailings waste streams. The chosen technique is BaCl_2 treatment to precipitate $(\text{Ba,Ra})\text{SO}_4$. The BaCl_2 in the presence of high sulfate concentrations causes BaSO_4 to precipitate and

scavenge (co-precipitate) $(\text{Ba,Ra})\text{SO}_4$. If the waters are initially low in sulfate, Na_2SO_4 may be added to promote precipitation. The settling of the precipitate is enhanced by the addition of FeCl_3 and organic polymers within flocculation tanks. The supernate water from flocculators is often further clarified on inclined plate clarifiers or filtered through packed beds of anthracite coal and sand. The dissolved radium-226 is readily reduced to the current Canadian concentration guide of 3 pCi/L, but reduction of the total radium concentration (dissolved plus suspended) to 10 pCi/L is not readily met. The $(\text{Ba,Ra})\text{SO}_4$ precipitate is fine-grained and not readily removed from solution without large settling basins and long residence times. The Canadian mill operators suggest that 30 pCi/L for a total radium concentration guide would be attainable. Typical operating costs for BaCl_2 treatment in Canada are \$0.68/1000 gal. Capital equipment costs include batch reactors (often just stirred ponds) and clarifiers or filters (often mixed media sand beds). Using ponds and sand filter beds, a typical Canadian mill has set up a BaCl_2 treatment plants for \$25,000 (1978 dollars).

OTHER TREATMENTS

Literature on less common removal techniques was reviewed, and brief summaries germane to radionuclides present in uranium mill tailings are given below. The processes reviewed included biological, solvent extraction, reverse osmosis, and selective membrane mineral extraction.

Summary

Less common treatment techniques to remove radionuclide and trace metals are not well studied, but besides selective membrane mineral extraction, they appear to be of limited use for practically treating high-acid high-salt mill tailings solutions. Biological growth is probably inhibited in these solutions and reverse osmosis would probably be only 85 to 95% efficient for most constituents. More information on the proprietary selective membrane mineral extraction technique is needed to assess its usefulness.

NONRADIOACTIVE SELECTIVE EXTRACTION TECHNIQUES

An exhaustive review of specific removal techniques for individual constituents is beyond the scope of this report. Besides the radionuclides discussed above, our review and conclusions of others (e.g., Moffett 1976) suggest that the more serious potential pollutant hazards in acid leach uranium mill wastes are sulfate, nitrate (from blasting compounds and recovery and purification of yellow cake), ammonium (from recovery of yellow cake), manganese (sometimes used an oxidizing agent in ore extraction), TDS, and acidity.

Summary

Removal of most trace metals would use techniques similar to those discussed for the radionuclides. Neutralization of the acidic tailings and waste streams is probably the most cost-effective method of immobilizing trace metals that are soluble in the acid wastes. General works on pollutant removal such as Sittig (1973) and specific works on municipal water treatment such as

Gumerman et al. (1979) should be used as references to the topic of selective constituent removal techniques. No specific literature was found on the removal of selected nonradionuclide constituents from acid leach uranium mill wastes.

Techniques such as sulfate precipitation via barium chloride treatment, sulfate removal by anion exchange, nitrate removal by biological denitrification, nitrate removal by anion exchange, ammonium removal by ammonia stripping, biological nitrification, and cation exchange on clinoptilolite were discussed but no operating data or costs for such specific removal techniques are available for uranium mill effluents.

The most mobile constituents in tailings effluents will probably be the anions SO_4^{2-} and NO_3^- , both of which can exceed drinking water and irrigation/livestock concentration limits by several orders of magnitude.

TREATMENT EFFECTIVENESS AND RECOMMENDATIONS

Using neutralization processes to treat uranium mill tailings leachate appears to significantly reduce contaminant mobility based on experience with AMD and other industrial-generated acidic solutions. Because of the high concentrations of certain contaminants, it is possible that neutralization will not be as effective as it would be for AMD. Contaminants that do not appear to be effected by neutralization techniques include nitrate and ammonia. Sulfate concentrations are only reduced if calcium-based reagents are used as neutralizing agents. Manganese and iron may remain slightly soluble if they are not present in oxidized forms. The high iron concentrations present in uranium mill tailings solutions may require long residence times in the aeration vessel to ensure the total oxidation of ferrous iron. If the iron is present in the ferric oxidation state, treatment of the solution is rapid with only short residence times. Pretreatment oxidation or long storage times prior to treatment would allow the iron to oxidize as well as make the neutralization process more efficient.

At U.S. mills, five specific situations are foreseen where the neutralization processes might be beneficial:

1. to hasten the closure process at the time of mill decommissioning; excess solution present in the tailings impoundment or in an evaporation pond may be treated.
2. to avert the possibility of an uncontrolled discharge of acid leachate, as an emergency measure
3. to protect the quality of a near-surface ground-water resource
4. to reduce the volume of leachate present in a tailings impoundment thereby increasing the usable disposal capacity
5. to mitigate the effects of a release of acidic solution through surface seeps adjacent to tailings disposal areas.

Neutralizing uranium tailings leachate with calcium alkalies appears to be the preferred technique. A two-stage combination limestone-lime treatment would be the optimum process for ferric iron uranium mill tailings solution. The majority of the solution acidity would be buffered by inexpensive limestone in the first stage of the process. The second stage would take the pH to approximately 8.0 with lime, which is the optimum pH for removal of heavy metals from AMD. Another advantage of the limestone-lime process is that the sludge generated has a high percentage of solids. This makes handling and sludge disposal fairly easy.

For the treatment of ferrous-iron-rich uranium tailings solution, we recommend lime treatment. The high pH generated in the lime process speeds the oxidation of the iron, which is more rapid at elevated pH values (pH 8.0 or

higher). This process would be slightly slower than the combination process recommended for neutralizing ferric uranium tailings solution, but much quicker for ferrous tailings leachate.

The limestone-only process is not recommended for solutions containing high iron concentrations. For this reason a single-stage limestone process would be used only in emergency situations to avert spills of acidic leachate. Sodium reagents should also be used only under emergency conditions. The high quantity of sodium alkalies required to neutralize extremely acidic uranium mill tailings solution adds hazardous concentrations of sodium to the treated water.

The alumina-lime-soda process has not been studied in depth. The performance of this process in reducing trace element concentrations is unknown. This process is the most expensive of the six neutralizing techniques reviewed.

The common problem among fixation techniques reviewed for this paper was cost. Prices for solidification ranges from \$1.50 to \$420/ton of tailings. In terms of product value to solidification cost, the processes reviewed cost from 5 to 1400% of the uranium price. This calculation was based on the recovery of 1 lb of uranium at \$50/lb for each ton of tailings solidified. Using these treatment types is only feasible if the waste to be processed is highly toxic and the volume is fairly small.

Specific constituent removal processes need careful cost/benefit analyses. The cost of radium removal from lime- and/or limestone-neutralized Canadian uranium mill waste effluents using BaCl_2 treatment is similar to the cost of neutralization (\$0.68/1000 gal versus \$0.20 to \$1.00/1000 gal). In Canada, the mill sites are often located in areas with little soil, high water tables, and in proximity to surface water bodies. Thus, the natural sediment/soil radium retardation processes are not effective and man-induced immobilization is required by government agencies. For typical U.S. mill sites where natural soil/sediment neutralization processes are prevalent and ground-water supplies are usually distant from the disposal pits, no general statement on cost effectiveness is possible. We recommend additional field studies and long-term consequence modeling that uses sophisticated coupled hydrologic-chemical predictor codes to better assess the need for mill tailings waste treatment and/or new disposal schemes. To evaluate the most economical and practical treatment/disposal schemes one must consider the natural ability of soils and sediments to neutralize acid mill wastes and retard the migration of potential contaminants.

SUBTASK B. LABORATORY ANALYSIS

METHODS AND MATERIALS

SAMPLE COLLECTION

Pacific Northwest Laboratory scientists visited the Pathfinder (Lucky Mc) Gas Hills Mill outside Riverton, Wyoming, and the Exxon Highland Mill near Glenrock, Wyoming, in December 1981 and November 1982. Samples of acidic tailings solutions, solid tailings, and undisturbed overburden sediments were collected from each mill site for experiments in the tailings neutralization project and other companion projects. The Lucky Mc and Exxon Highland acidic tailings solution collected in December 1981 were used exclusively for the batch reagents experiments (see Batch Contact Studies section). All other experiments described use the acidic tailings solution collected in November 1982.

Lucky Mc tailings solutions and solid tailings were collected from Tailings No. 2A Reservoir (Figure 1). Tailings solution was sampled from the east side of Tailings No. 2A Reservoir, 100 m north of where the tailings solution/slurry was currently being discharged into the evaporation pond. Discussions with Jack Stevenson, Mill Superintendent, indicated that the ore being processed was a mixture coming from three sources: highly oxidized mill waste (0.02 to 0.03% U_3O_8) from old stock piles, ore (0.03 to 0.05% U_3O_8) taken from open pits at the Gas Hills mine, and higher grade ore (0.1% U_3O_8) taken from an underground operation near Jeffery City, Wyoming, about 65 km (40 miles) south-east of the Lucky Mc Mill.

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

Solid tailings and overburden samples were collected from both the Lucky Mc and Exxon Highland mills. The Lucky Mc tailings were collected from material near the edge of the embankment along the dam face on the west end of the tailings impoundment. Exxon Highland tailings were collected from area 2 (Figure 2). Overburden material from the Lucky Mc Mill was collected from the surface in an area just south of Tailings No. 4 Reservoir. Exxon overburden samples were collected south of the tailings pond dam outside the existing embankment and below the existing solution level of the tailings evaporation pond at area 3 in Figure 2.

CHEMICAL REAGENTS

Laboratory-grade reagents were obtained from a local supply house, except for the fly ash used in the batch experiments, which were obtained from surface piles at the Boardman Coal Plant (Boardman, Oregon) and the Wyodak coal plant

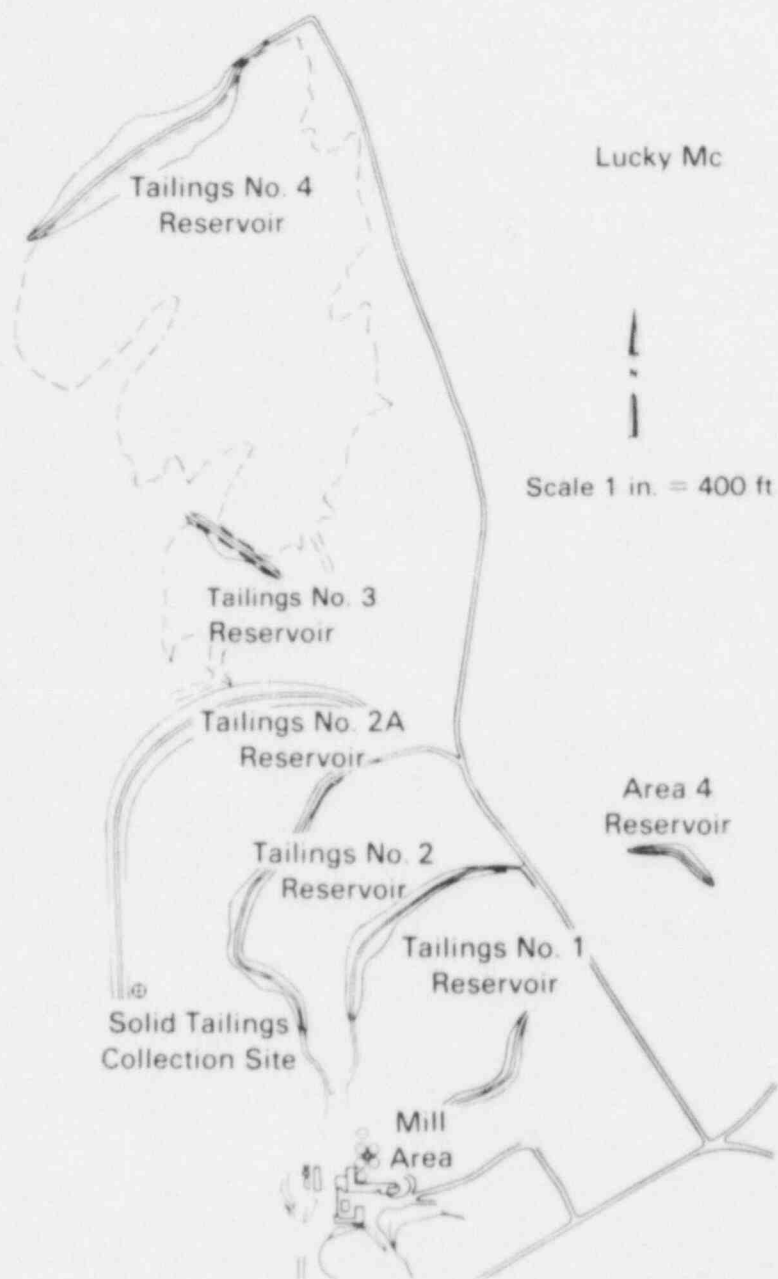


FIGURE 1. Lucky Mc Mill Site and Sampling Locations

near Gillette, Wyoming. Finely ground chemicals (<200 mesh) were used in all experiments requiring neutralizing reagents to ensure faster solution/reagent reaction rates and to facilitate mixing.

LABORATORY-PREPARED SYNTHETIC GROUND WATER MAKEUP

Laboratory-prepared ground water was produced for use in all column leaching studies except those leached with tailings solution. The procedure

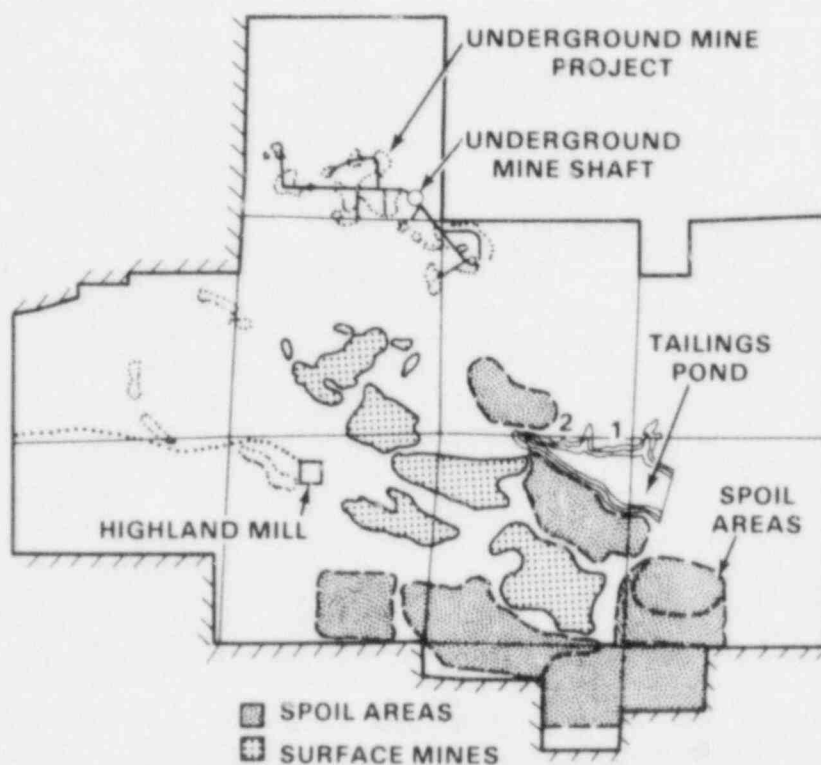


FIGURE 2. Exxon Highland Mill Site and Sampling Locations

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). The ground-water sample was collected in April 1979 from inside the Exxon Highland Mill and is used throughout Exxon's uranium extraction and purification process.

Laboratory-prepared ground water was produced in 20-L batches by the addition of measured amounts of reagent-grade chemicals. These reagents were chosen to provide cations and anions in amounts producing concentrations matching those quoted for actual Exxon Highland Mill process water. After adding all reagents to 20 L of warm distilled water, solution pH was adjusted from pH \approx 9.0 to pH \approx 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 3.

Chemical characterization data for the laboratory-prepared ground water used in leaching studies are presented in Table 4. Also included are the characterization results from the actual (April 1979) Exxon Highland Mill process water (Gee et al. 1980).

TAILINGS SOLUTION CHARACTERIZATION

Detailed analysis of the untreated acid tailings solution and neutralized tailings solution were performed for the solutions collected from both the Lucky Mc and Exxon Highland mills. Macroanions (Al, Ca, Fe, Mg, Mn, Si, Na, and Sr) present in the tailings solution and treated effluents were determined using an inductively coupled plasma (ICP) source. Macroanions (SO_4 , NO_3 , and Cl) were determined by ion chromatograph (IC). Trace metal constituents (Ag, As, Ba, Cd, Co, Cr, Pb, Mo, Se, and V) were determined either with the ICP (Cu and Zn) or by graphite furnace atomic absorption spectroscopy (AA-GF). The various methods of analyses for the specified elements are shown in Table 5. The neutralized effluents for cation and radionuclide analyses were preserved by acidification to $\text{pH } 2.0$ with ultrapure nitric acid (APHA 1980). The neutralized effluent samples used for anion analysis were preserved by storing the samples in sealed, airtight containers.

Radionuclide concentrations in the tailings solutions and treated effluents were determined using high-resolution gamma spectroscopy. For these analyses, a volume of solution (250 mL) was evaporated leaving the residual evaporites. These salts were mixed with a cellulose binder and pressed into a pellet of fixed geometry. An intrinsic germanium diode was used to analyze the pellet for ^{238}U and three of its daughter products. Lead-210, ^{238}U , ^{230}Th , and ^{226}Ra concentrations 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 thorium-234. The radium-226 activity is calculated after correction of the count rate of the 185.8 KeV peak for a contribution from uranium-235, which also has a gamma ray (183.7 KeV) nearby. The correction factor is based on the ratio of $^{238}\text{U}/^{235}\text{U}$ activity found in natural ore deposits (~ 21.5). Thus, after calculating the ^{238}U content, an activity for ^{235}U may be calculated and subtracted from the total activity in the region of 185 KeV to yield an estimate of the radium-226 content. Detector efficiencies were determined on National Bureau of Standards traceable uranium-bearing sediments pressed into pellets identical to those used for evaporite analyses. Radium-226 activities in the radium attenuation experiments were determined by radium coprecipitation

TABLE 3. Constituents in Laboratory-Prepared Ground Water

Reagent	Grams of Reagent/20 L
MgSO_4	1.088
NaSO_4	4.091
NaCl	1.169
NaNO_3	0.075
CaCO_3	2.647

TABLE 4. Comparison of the Chemical Composition of Exxon Highland Mill Process Water and Laboratory-Prepared Ground Water

Parameter	Exxon Highland Process Water(a)	Laboratory-Prepared Ground Water
Al	<0.1	<0.1
As	<0.02	<0.02
Ca	53	69
Cr	<0.05	<0.01
Fe	<0.1	<0.1
Li	<0.05	<0.05
Mg	11.0	11.0
Mo	0.5	<0.01
Na	91	105
P	<0.01	<0.1
Pb	<0.01	<0.02
Se	<1.0	0.34 ^(b)
Si	3.5	0.54
Sr	0.9	0.03
Zn	0.05	<0.02
Cl	36	44
NO ₃	3.5	3.3
SO ₄	181	300
EC (mmhos/cm)	0.32	0.76
pH (units)	8.2	7.6

(a) Gee et al. 1980.

(b) Analysis performed by Inductively Coupled Plasma.

with barium sulfate followed by alpha scintillation counting (APHA 1980). The counters were calibrated using BaSO₄ precipitates of varying weights, each containing a known activity of radium-226.

The pH, Eh, and electrical conductivity of the tailing solutions and treated effluents were measured. Solution pH and Eh were determined using a combination pH/Eh meter and a combination pH electrode or a platinum-banded redox electrode. Electrical conductivity was measured using a portable conductivity meter.

TABLE 5. Elements/Anions Considered and Proposed Analytical Methods

Elements/Anions	ICP	IC	AA-GF	Intrinsic
<u>Macro Cations</u>				
Al	X			
B	X			
Ca	X			
Fe	X			
Mg	X			
Mn	X			
Si	X			
Na	X			
Sr	X			
<u>Trace Metals</u>				
As			X	
Ba			X	
Cd			X	
Cr			X	
Cu	X			
Pb			X	
Mo			X	
Se			X(a)	
Ag			X	
V			X	
Zn	X		X	
<u>Radionuclides</u>				
^{210}Pb				X
^{230}Th				X
^{226}Ra				X
U				X
<u>Anions</u>				
NO_3		X		
PO_4		X		
SO_4		X		
Cl		X		

(a) AA hydride

The Salotto method of total acidity (Salotto et al. 1966) was used to determine the total acidity of the Lucky Mc and Exxon tailing solutions. Briefly, the procedure requires titrating the acid solution with sodium

hydroxide to pH 7.3 and calculating the total acidity as milligrams per liter of CaCO_3 by the number of equivalents of NaOH added. The TDS content of the tailings solutions and treated effluents was calculated in milligrams per liter by summing the concentration values of the macrocations and anions that were determined by the methods described earlier.

MINERALOGICAL ANALYSES

Mineralogical characterization of the two fly ash samples were determined by x-ray diffraction. Bulk samples of these materials were slurry-mounted on glass slides for analysis. Diffractograms were obtained using an x-ray diffractometer and a $\text{CuK}\alpha$ radiation generator.

BATCH CONTACT STUDIES

Reagent Neutralization Tests

Four hundred milliliters of the acid tailings solution were placed in 0.5-L polyethylene bottles. Based on the theoretical equivalent weight of each of the five chemical reagents and the measured total acidity of the tailings solution, enough dry reagent was added to the bottles to raise the slurry to \sim pH 7.3. After reagent addition, the bottles were placed on a linear oscillating shake for 2 days to facilitate mixing and reaction. Because no theoretical equivalent weight was available for the two fly ash samples, small quantities were initially added to the acid tailings solution.

After the 2-day contact period, the sample pH was measured. If the solution pH above the sludge was 7.0 or greater, the experiment was stopped. If the pH was less than 7.0, an additional portion of reagent was weighed and added to the bottle, and the bottle was placed on the shaker for an additional 2 days.

The pH was then remeasured and the cycle continued until a solution pH of 7.0 or greater was achieved. Once each sample had achieved this condition, it was centrifuged, and the supernate solution was filtered through a 0.45- μm membrane. The filtered solutions were then analyzed by the techniques described in the tailings solution characterization section. Residual sludge separated from the supernate during centrifugation was used to evaluate sludge properties. The batch contact tests for all seven reagents (two fly ashes and five chemicals) and the two uranium mill tailings solutions (Lucky Mc and Exxon Highland) were performed in duplicate. Tables presented in the Results and Discussion section show the average values obtained from the duplicate tests.

pH Optimization

For the purpose of this study, the optimum pH for acidic uranium mill tailings solution neutralization has been defined as the solution pH where further addition of a neutralizing agent no longer significantly increases removal of contaminants. To determine the optimum pH of neutralized tailings solution, samples of both Lucky Mc and Exxon Highland acidic tailings solutions were neutralized from \sim pH 2.0 to pH values of approximately 5.0, 6.5, 7.2, and

8.0 using reagent-grade $\text{Ca}(\text{OH})_2$. After samples of each acidic tailings solution had reached the desired solution pH, they were centrifuged, filtered, and analyzed for solution quality. The neutralized solution chemical composition was then compared to solution data for the untreated solutions.

Limestone/Lime Neutralization Tests

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

After the 48-h contact period, the sample pH was measured. If the solution pH above the slurry had reached the desired pH of 4.0 or 5.0, depending on the test, the experiment was temporarily stopped. If the pH was less than desired, an additional portion of limestone was weighed and added to the bottle, and the bottle was placed on the shaker for an additional 2 days. The pH was then remeasured, and the cycle continued until the initial desired pH was attained. Once each sample had reached the desired pH, it was centrifuged, and the supernate solution filtered through a 0.45- μm membrane. The filtered solutions were subsampled, preserved (depending on the analysis to be performed), and then analyzed for anions, cations, and radionuclides by the techniques described in the tailings solution characterization section.

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

Contaminant Complexation Experiments

Two sets of static batch studies were conducted under identical conditions using separate neutralizing reagents or combinations of reagents as neutralizing techniques. In the initial study, acidic tailings solution were neutralized using either hydrated lime or limestone. Selected pH points for neutralization by hydrated lime were pH = 6.5, 7.3, 8.0, 8.5, and 9.0. Final set pH values for limestone neutralization were pH = 6.5, 7.3, and 8.0. Neutralization was accomplished through the addition of solid reagents to 200 mL of acidic tailings solution in sealed 250-mL polyethylene bottles. Initial reagent weights were determined by measuring the total acidity of the tailings solution 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 pH without agitating the sample. If necessary, solution pH was further adjusted by the addition of either fresh tailings solution 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 to atmospheric carbon dioxide levels for a period not less than 24 h. Solution pH was then recorded and, if necessary, further adjusted toward the set pH levels. Once neutralization was complete, all samples were centrifuged; filtered through a standard 0.45- μ m 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 alkalinity levels hydrated to the neutralized-lime solutions. Enough carbonate was added to equal those measured for the corresponding limestone-neutralized solutions of equal pH prepared in the first set of batch studies. The alkalinities of the hydrated-lime neutralized solutions having alkaline pHs of 8.5 and 9.0 in the second set of batch studies were elevated to the levels measured for the limestone-neutralized solutions of pH = 8.0 in the initial study. Sodium bicarbonate addition was followed by 48 h of mixing after which each sample was allowed to equilibrate to the atmosphere for at least 24 h. Samples were then centrifuged; filtered (0.45 μ m); measured for pH, Eh, and alkalinity; and then prepared for solution analyses.

Colloidal particles were removed from selected samples by centrifugal filtering through an 18Å membrane. Membranes were soaked overnight in double-distilled water, and an aliquot of sample was passed through the filter to fill possible adsorption sites prior to sample filtration.

Solid Sludge Characterization

Mineralogical characterization of the sludges generated from solution neutralization was determined by x-ray diffraction. Bulk samples of these materials were slurry-mounted on glass slides for analysis. Diffractograms were obtained using x-ray diffractometer and a CuK α radiation generator.

The total dry weight of sludge formed for each batch contact experiment was determined by measuring the sludge wet weight and sludge moisture content gravimetrically by oven drying at 105°C for 24 h (Gardner 1965). To determine the sludge moisture retention properties, the saturated sludge samples were placed in a pressure plate apparatus (Richards 1965) and drained under various applied pressures. The drained water contents were measured gravimetrically and tabulated as a function of capillary pressure, which is equal in magnitude to the applied pressure, but opposite in sign. These measurements, taken over a range of applied pressures, provide an estimate of drainage expected for

similar sludge piles under field conditions. For example, a covered sludge pile, 10-m thick, draining to a water table at its base would have capillary pressure ranging from -10 m at the top to near zero at the base.

COLUMN EXPERIMENTS

Sludge Column Leaching Experiments

Column leaching experiments were conducted on the sludge material that forms during the neutralization process. The sludge, collected as a field-neutralized solution/slurry from the Lucky Mc and Exxon Highland mill sites, had the excess solution removed by filtration through a 0.45- μ m filter. The remaining solid residue was dried in a convective oven at 105°C for 24 h. The oven-dried sludge from each mill site was placed in a ball mill, crushed, and disaggregated. Known weights of the <150 mesh sample were packed into four columns of known volume. Characteristics of the columns from each mill site are listed in Table 6. Clear acrylic tubing and end caps were used in constructing the columns for the experiments.

Laboratory-prepared ground water, with elemental composition shown in Table 4, was used as the leachate. Flow through the columns moved from the bottom to the top to enhance complete column saturation. Constant flow rates were maintained throughout the experiment with multistatic pumps adjusted to 0.11 mL/min. Flow rates were monitored daily, and samples were collected every 36 h. Sample pHs and Ehs were taken after collection, and then subsamples for anion, cation, and radionuclide determinations were prepared. Samples used for cation and radionuclide analyses were preserved by adding concentrated ultra-pure nitric acid to drop the pH to less than pH 2.0 (APHA 1980). Samples for anion analyses were not treated but were analyzed soon after collection. All chemical analyses were performed as described in the Tailings Solution Characterization section.

TABLE 6. Sludge Column Parameters

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

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 [$\text{Ca}(\text{OH})_2$] (Table 7). Two columns contained tailings from the Lucky Mc Mill, one with untreated tailings and one neutralized tailings, and two other 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 8. The method used for compaction was in accordance with the sliding-weight tamper method (ASTM 1982). Laboratory-prepared ground water was used as tailings leachate throughout the duration of the experiments. Leachate flow moved from column bottom to column top to enhance removal of entrained air pockets in order to simulate saturated flow conditions. Constant flow rates were maintained throughout the experiment with multistatic pumps. Flow rates were monitored daily, and effluent samples were collected depending on the column's pore displacement volume (approximately every one pore volume for each column). Effluent samples were measured for pH and Eh on collection, then subsampled for anion, cation, and radionuclide determinations. All chemical analyses were performed as described in the previous Tailings Solid and Solution Characterization section.

TABLE 7. Tailings Column Identification and Description

Column ID	Description
1	Untreated Exxon Tailings
2	Neutralized Exxon Tailings
3	Untreated Lucky Mc Tailings
4	Neutralized Lucky Mc Tailings

TABLE 8. Tailings Column Compaction Data

Column ID	Cell Diameter (cm)	Length (cm)	Volume (cm^3)	Dry Sample wt (g)	Bulk Density (g/cm^3)	Porosity	Pore Volume (cm^3)
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

Radium Attenuation Experiments

Before using the acidic tailings from the Lucky Mc Mill, they were oven dried at 105°C for 24 h to facilitate handling. The dried tailings used in the experiments were passed through a number 10 sieve and subdivided into 1000-g subsamples. One tailings subsample was amended with barium chloride and calcium hydroxide. The other subsample was left untreated, to be used as a blank or baseline value for comparison of attenuation results. The description for the amended and untreated tailings is shown in Table 9. The calcium hydroxide

TABLE 9. Radium Attenuation Column Identification and Description

Column ID	Description
1	1000 g tailings, 7.3 g Ca(OH)_2 , 151 mL BaCl_2 solution.
2	1000 g tailings, 151 mL DD H_2O

amendment was mixed into the tailings as an oven-dried solid. Barium chloride was added to the tailings in liquid form after dissolving 32.86 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 151 mL of distilled, deionized water (DD H_2O). Distilled deionized water was added to the untreated tailings not containing barium chloride.

After adding the various reagents and solutions to the acidic Lucky Mc tailings, the composite samples were thoroughly mixed and allowed to stand overnight in sealed plastic bags to ensure a uniform moisture distribution. Subsamples of each mixture were collected for moisture content determination, which was done using microwave drying (Gee and Dodson 1981).

Two polyacrylic cylindrical columns were compacted according to the sliding weight tamper method (ASTM 1982), with the composite mixture from each sample bag. Sample 1 was compacted in column 1, sample 2 in column 2. The physical compaction data for each column are listed in Table 10. Every effort was made to keep all column compaction parameters equal so a fair comparison could be made at the completion of the experiment.

TABLE 10. Radium Attenuation Column Compaction Data

Column ID	Cell Diameter (cm)	Length (cm)	Volume (cm^3)	Dry Sample wt (g)	Bulk Density (g/cm^3)	Porosity	Pore Volume (cm^3)
1	8.89	8.89	552	833	1.51	0.44	244
2	8.89	8.89	552	833	1.51	0.44	244

Once compacted, the columns containing the amended tailings mixtures and the untreated tailings were saturated with approximately one pore volume of local ground water. The method used to leach the compacted tailings columns followed the American Society for Testing and Materials (ASTM) method for measuring permeability of granular soils under constant head conditions (ASTM 1982), except that permeability values were not calculated. The chemical composition of the local ground water is shown in Table 11. Flow through the columns was from the bottom to top to enhance saturated flow conditions.

Flow rates through the columns were maintained at approximately 0.1 mL/min with multistatic constant flow pumps. Column effluent samples were collected at approximately one pore volume intervals (~250 mL) throughout the duration of the experiment. The pH and Eh of each sample was measured after collection. Subsamples were then preserved appropriately for subsequent anion, cation, and total radium determinations.

TABLE 11. Local Ground-Water Chemical Composition

<u>Parameter</u>	<u>Concentration (mg/L)</u>
Al	0.1
As	<0.02
Ba	0.03
Ca	25.1
Fe	0.04
K	0.9
Mg	4.4
Mn	<0.3
Na	2.9
Si	3.6
Sr	0.1
Zn	0.2
Cl	1.5
NO ₃	<0.5
SO ₄	19.8
pH (units)	8.2

RESULTS AND DISCUSSION

UNTREATED TAILINGS SOLUTION CHARACTERIZATION

Chemical composition of the uranium tailings solutions used for the batch neutralization tests (December 1981 solution) is given in Table 12. Tailings solution from the Lucky Mc site had a low pH (1.2) and a high total acidity of nearly 15,000 mg/L as CaCO_3 . This corresponds to an acid content of nearly 300 meq/L. The leachate from the Exxon Highland site had a pH of 2.2 and a total acidity of only 4,500 mg/L as CaCO_3 , which corresponds to an acid content of only 90 meq/L. These values of 300 meq/L and 90 meq/L were used to estimate the quantity of neutralizing agent that would be required to raise the pH of these leachates to 7.3 in the batch reagent experiments.

The results of uranium mill tailings solution characterization from the Lucky Mc and Exxon mills collected in December 1982 are shown in Table 12. The Lucky Mc Mill tailings solution had a low pH (1.7), high TDS content (34.2 g/L), and high total acidity (15,700 mg/L as CaCO_3). The total acidity content of 15,700 mg/L corresponds to a total acid content also greater than 300 meq/L similar to the solution collected in 1981. In comparison, the Exxon uranium mill tailings solution had a slightly higher pH (2.0), a TDS content of 12.5 g/L, and a total acidity of 5,269 mg/L as CaCO_3 .

The composition of the Exxon tailings solution may be more 'dilute' than the Lucky Mc tailings solution because of the addition of mine dewatering solution in order to move the tailings to the pond. Additional mine drainage is pumped directly into the pond so that samples collected from the evaporation pond include acidic tailings solutions diluted with several drainage solutions. Solution properties such as these illustrate how tailings solutions from two uranium mills can vary in solution composition even though both mills employ a sulfuric acid leaching process for uranium extraction.

The dissolved constituents shown in Table 12 originate from one of two sources: 1) process additives and 2) by-products of the ore dissolution process. Process additives used in uranium milling include sulfuric acid (H_2SO_4), sodium perchlorate (NaClO_4), ammonium nitrate (NH_4NO_3), and ferrous carbonate (FeCO_3). These additives account for most of the high solution content of sulfate, chloride, nitrate, iron, and the low pH. Other constituents in the tailings solution result from dissolution of the ore-grade rocks and sediments during the leaching process or impurities contained in industrial-grade chemical additives.

The following Lucky Mc tailings solution constituents (from Table 12) exceed the set limits of the U.S. Environmental Protection Agency's (EPA) maximum concentration levels shown in Table 13: four macro-ions, Fe, Mn, NO_3 , and SO_4 ; seven trace metals, As, Cd, Cr, Cu, Pb, Se, and Zn; and three radio-nuclides, ^{210}Pb , ^{230}Th , and ^{226}Ra . Similarly for the Exxon tailings solutions,

TABLE 12. Solution Chemistry of Lucky Mc and Exxon Highland Tailings Solutions

Parameter	Lucky Mc 1981 Solution	Lucky Mc 1982 Solution	Exxon Highland 1981 Solution	Exxon Highland 1982 Solution
pH (units)	1.2	1.7	2.2	2.0
Eh (mV)		785	NA (8)	807
Conductivity ($\mu\text{mho/cm}$)	NA	32,300	NA	10,400
Total Suspended Solids (mg/L)	NA	50	NA	20
Total Dissolved Solids (g/L)	35.7	34.2	11.2	12.5
Total Acidity (as mg/L CaCO_3)	14,800	15,735	4,500	5,269
<u>Macro ions (mg/L)</u>				
Al	1.0 to 30	1,100	405	440
B	NA	1.1	NA	0.4
Ca	600	600	548	560
Fe	2,780	3,000	950	1,000
K	156	160	40	44
Mg	1,220	1,250	495	540
Mn	163	160	44	50
Na	1,630	1,600	332	340
Si	283	300	209	310
Sr	14	14	8	8.5
SO_4	6,400	25,000	7,920	9,300
Cl	2,090	1,190	290	300
NO_3	302	302	7	9
<u>Trace Metals (mg/L)</u>				
Ag	<0.05	<0.02	<0.05	<0.02
As	19.00	15.50	0.21	0.21
Ba	0.09	0.07	<0.05	<0.05
Cd	0.280	0.25	0.04	0.03
Co	3.40	4.93	0.90	1.31
Cr	2.40	2.09	1.41	1.25
Cu	1.50	1.45	1.10	0.97
Mo	8.4	7.74	<0.05	<0.02
Pb	0.87	0.85	<0.04	<0.02
Se	1.6	1.10	1.2	1.35
V	14.6	19.17	10.6	10.71
Zn	17.9	16	3.7	4.5
<u>Radionuclides (pCi/L)</u>				
^{210}Pb	16,000	12,300	<50	2,100
^{238}U	16,800	15,550	2,375	2,100
^{230}Th	167,000	185,400	127,000	97,140
^{226}Ra	4,900	4,020	940	758

(a) NA = not applicable.

TABLE 13. Maximum Concentration Levels for Specified Water

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

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

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

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

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

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

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

(f) Depends on temperature of water.

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

three macro ions, Fe, Mn, and SO_4 , four trace metals As, Cd, Cr, and Se, and three radionuclides ^{210}Pb , ^{230}Th , and ^{226}Ra , also exceed the water quality limits in Table 13.

NEUTRALIZED TAILINGS SOLUTION CHARACTERIZATION

The results of the analyses performed on the field neutralized tailings solutions are shown in Table 14. The data show a significant reduction in dissolved constituents when compared to the low pH untreated solution. In the neutralized Lucky Mc solution, the TDS content was reduced by greater than 80% (34.2 to 6.4 g/L). The Exxon-neutralized solution showed an overall TDS reduction of greater than 70% (12.5 to 3.7 g/L). The difference in the TDS reduction between the two neutralized tailings solutions is due to the makeup of the untreated low pH solution. For example, ions such as Al, Fe, Mn, Cl, NO_3 , and SO_4 are two to three times higher in concentration in the Lucky Mc tailings solution than in the Exxon tailings solution. Upon neutralization, the resultant pH-buffered tailings solutions from both mills are relatively similar in makeup, with the exception of elements such as Ca, Na, K, Cl, NO_3 , and SO_4 whose solubility is not strictly dependent on solution pH.

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

BATCH CONTACT STUDIES

Mineralogical Analyses

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

Reagent Neutralization Tests

The water quality of the effluents from the batch neutralization experiments is found in Tables 15 through 20. The chemical composition of the treated effluents has been divided into three subsets for comparison. Macro-ion, trace metal, and radionuclide results for each reagent have been tabulated for each tailings solution.

TABLE 14. Solution Chemistry of Field Neutralized Lucky Mc and Exxon Highland Tailings Solutions (1982 solution)

Parameter	Lucky Mc Untreated Solution	Lucky Mc Neutralized Solution	Exxon Untreated Solution	Exxon Neutralized Solution
pH (units)	1.7	9.4	2.0	12.5
Eh (mV)	785	231	807	162
Conductivity ($\mu\text{mho/cm}$)	52,300	11,900	10,400	4,950
Total Suspended Solids (mg/L)	50	10	20	20
Total Dissolved Solids (g/L)	34.2	6.4	12.5	3.7
Total Acidity (as mg/L CaCO_3)	15,735	NA	5,269	NA
<u>Macro ions (mg/L)</u>				
Al	1,100	0.6	440	0.6
B	1.1	0.19	0.4	0.08
Ca	600	520	560	870
Fe	3,000	<0.5	1,000	<0.5
K	160	170	44	55
Mg	1,250	6.4	540	0.7
Mn	160	<0.2	50	<0.2
Na	1,600	1,570	340	330
Si	300	10	310	1.1
Sr	14	1.6	8.5	7.8
SO_4	25,000	3,940	9,300	1,730
Cl	1,190	1,280	300	303
NO_3	302	247	9	<1
<u>Trace Metals (mg/L)</u>				
Ag	<0.02	<0.02	<0.02	<0.02
As	15.50	0.02	0.21	<0.01
Ba	0.07	<0.05	<0.05	0.11
Cd	0.25	<0.01	0.03	<0.01
Co	4.93	<0.02	1.31	<0.02
Cr	2.09	<0.01	1.25	<0.01
Cu	1.45	<0.02	0.97	<0.02
Mo	7.74	4.1	<0.02	<0.02
Pb	0.85	<0.02	<0.02	<0.02
Se	1.10	0.78	1.35	0.82
V	19.17	<0.02	10.71	<0.02
Zn	16	<0.2	4.5	<0.2
<u>Radionuclides (pCi/L)</u>				
^{210}Pb	12,300	<50	2,100	<50
^{238}U	15,550	70	2,100	<50
^{230}Th	185,400	<400	97,140	<400
^{226}Ra	4,020	55	758	81

(a) NA = not applicable.

TABLE 15. Macro Concentrations in the Neutralized Lucky Mc Tailings Solution, mg/L

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

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

Macro-ion results for the treatment of the Lucky Mc and Exxon solutions to pHs between 7.0 and 7.5 are given in Tables 15 and 16, respectively. In each case, the concentrations of aluminum, iron, and silica were reduced significantly and were generally independent of the reagent used. The removal of these constituents appears to be controlled mainly by the pH of the resultant solution. The average removal percentage over all seven treatments for each tailings solution was identical for Al (99.3%), Fe (>99.9%), and Si (97.2%). It appears that the MgO and fly ash treatments removed slightly less Al (88.5%) than the other treatments. The carbonate-based reagents and the Wyodak fly ash removed slightly less Si (96.2%) than the other reagents. Manganese removal was 70% for Exxon Highland and 64% for Lucky Mc. Hydrated lime removed manganese better than the other chemical reagents; limestone removed the least manganese.

The percentage of removal for the major constituents Ca, Mg, Na, Sr, K, sulfate, nitrate, and Cl, was not high, and some of the constituents showed significant dependence on the reagent used. Calcium removal occurred best when sodium carbonate was used. Magnesium, silicon, and sulfate removal were best when hydrated lime was used. The calcium reagents removed significantly more strontium than other reagents. The two fly ash samples appeared to release

TABLE 16. Macro Concentrations in the Neutralized Exxon Tailings Solution, mg/L

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

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

magnesium and strontium to solution. Sulfate was removed only by reagents containing calcium. The two sodium reagents and the magnesium oxide released significant amounts of sodium and magnesium, respectively, to the effluent solution. The potassium, nitrate, and chloride contents of the tailings solutions change very little no matter what reagent is used to neutralize the solution. From the calculated TDS content, the two calcium-based reagents (hydrated lime and limestone) removed the most dissolved solids, 58% and 51%, respectively.

Trace metal concentrations in the treated effluents for the Lucky Mc and Exxon tailings solutions appear in Tables 17 and 18. Results for silver indicate that silver had a limited solubility in these high-sulfate systems independent of pH. The silver content of the acid tailings solutions was below the EPA primary drinking water standard of 0.05 mg/L. Neutralization with the seven reagents did not increase silver solubility. Arsenic, Cr, Cu, Pb, V, and Zn results indicate that these trace contaminants were removed from solution with the change in pH independent of the reagents used. Thus, neutralization appears to be an effective method of removing these trace metals. The detection limit for zinc was quite high (2.5 mg/L); therefore, complete removal can be inferred only from these experimental results. Zinc and chromium did appear in concentrations above the detection limit in one sample each. They were in leachates neutralized with Wyodak fly ash suggesting that it is a less desirable neutralizing agent.

The effluent concentrations of barium were below detection limits (0.05 mg/L) except for the experiments using limestone or the two fly ash

TABLE 17. Trace Metal Concentrations in the Neutralized Lucky Mc Tailings Solution, $\mu\text{g/L}$

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

TABLE 18. Trace Metal Concentrations in the Neutralized Exxon Tailings Solution, $\mu\text{g/L}$

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

TABLE 19. Radionuclide Concentrations in the Neutralized Lucky Mc Solution, pCi/L

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

TABLE 20. Radionuclide Concentrations in the Neutralized Exxon Tailings Solution, pCi/L

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

neutralizing agents. These three reagents were not effective at removing barium. Most of the reagents removed significant amounts of cadmium. Limestone appears to be the best removal reagent and Wyodak fly ash the least effective.

Cobalt removal was variable. Carbonate-bearing reagents (CaCO₃ and Na₂CO₃) and fly ash appear least efficient at removing cobalt suggesting that a soluble cobalt-carbonate complex may form or that neutralizing agents with the capability of increasing beyond pH 8.0 are necessary for efficient cobalt removal. Molybdenum removal was also variable. For the Exxon Highland Mill solution with an original molybdenum content of <0.05 mg/L, neutralization with fly ash increased the molybdenum solution concentration, while the Wyodak fly ash again released the most molybdenum into solution. For the Lucky Mc tailings solution with an original molybdenum content of 8.5 mg/L, an average of 88% was removed. The magnesium oxide and hydrated lime removed less than the other reagents. For either tailings solution, neutralization was ineffective at removing selenium. On the average, only 29.6% and 5.6% of the selenium in the Lucky Mc and Exxon Highland tailings solutions, respectively, are removed upon neutralization. This implies that other techniques may be required to remove selenium from treated or untreated tailings solutions.

Radionuclide results for the neutralization of the Lucky Mc and Exxon Highland tailings solutions appear in Tables 19 and 20. Removal of ²¹⁰Pb and

^{230}Th was nearly complete (>99.7%) for all of the reagents tested. Uranium- ^{238}U and ^{226}Ra results show an average 96% and 85% removal, respectively. The ^{238}U - and ^{226}Ra -treated effluent contents are greatest for the sodium carbonate reagent and also high in the calcium carbonate effluents. The data suggest that soluble carbonate complexes may be forming and thus reducing the efficiency of ^{238}U and ^{226}Ra removal.

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

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

pH Optimization Studies

The amount of reagent-grade $\text{Ca}(\text{OH})_2$ necessary to neutralize 400 mL of Lucky Mc and Exxon Highland mills acidic tailings solutions to each of the four selected pHs is presented in Table 21. Also included in Table 21 are values on the calculated reagent cost per metric ton of ore processed to neutralize the tailings solutions to each of the four pH values. The economics of solution neutralization are important to the mill operators, and the cost data are valuable as one of the optimizing criteria for reagent selection and final treatment effluent pH.

The analysis of batch pH optimization solutions resulting from the neutralization of Lucky Mc and Exxon Highland acidic tailings solutions to pH 5.0, 6.5, 7.2, and 8.0 using calcium hydroxide are presented in Tables 22 and 23. Included in these tables are the chemical characterization data (Table 12) for both the Lucky Mc and Exxon Highland untreated acidic tailings solutions for comparison.

TABLE 21. pH Optimization Reagent Cost Data for Lucky Mc and Exxon Highland Tailings Solutions (sample size 400 mL)

Acidic Tailings Solutions	Final Solution pH	Ca(OH) ₂ (g)	Reagent Cost ^(a) \$ per t of Ore
Lucky Mc	5.0	4.10	0.77
Lucky Mc	6.5	4.50	0.84
Lucky Mc	7.3	4.60	0.86
Lucky Mc	8.0	4.85	0.91
Exxon Highland Mill	5.0	1.35	0.25
Exxon Highland Mill	6.5	1.50	0.28
Exxon Highland Mill	7.3	1.60	0.30
Exxon Highland Mill	8.0	1.65	0.31

(a) See section on Reagent Efficiency and Costs for cost derivations.

The data presented in Tables 22 and 23 show that calcium hydroxide neutralization to pH = 7.2 is efficient in reducing the solution concentration of several constituents by greater than 98% from the original tailings solution values. Average percentage removal from both the Lucky Mc and Exxon Highland solutions at pH 7.2 to 7.3 were as follows: Al, 99.9%; Fe, 99.9%; Si, 99%; As, 99.9%; Cr, 99%; and V, 99%. Zinc concentrations were reduced by 99.9% and 96% in the treated Lucky Mc and Exxon Highland mill solutions, respectively. Although the percentage reduction of zinc in the Exxon Highland mill solution was most likely closer to 99%, the high detection level for zinc prevents reporting percent removal above 96%. While barium concentrations were below detection limits after neutralization in the Exxon Highland mill solution, its percent reduction in the treated Lucky Mc solution was 99.9% at pH = 7.3. Further neutralization to pH = 8.0 for contaminant reduction is unnecessary for these constituents. High percentage removal was also achieved for cobalt, copper, and lead for the Lucky Mc treated solutions at pH = 7.3. Cobalt concentrations were reduced by 94%, and both copper and lead by 98%.

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

Treated Exxon Highland solution produced similar results for Co, Cu, Cd, Mn, and Sr when neutralization was performed to pH = 7.2. Cobalt and copper concentrations were reduced by 98%, while lead concentrations were below detection levels in all neutralized and untreated solutions. Manganese concentrations were reduced by 35% while strontium concentrations dropped to 50% of

TABLE 22. Solution Chemistry of Calcium Hydroxide Neutralized Lucky Mc Acidic Tailings Solution

Parameter	Solution Ca(OH)_2 Neutralized to pH 5.0	Ca(OH)_2 Neutralized to pH 6.5	Ca(OH)_2 Neutralized to pH 7.3	Ca(OH)_2 Neutralized to pH 8.0	Lucky Mc Influent
<u>Macro Ion (mg/L)</u>					
Al	16.5	2.6	0.3	0.4	1,100
Ca	502	476	477	485	600
Fe	4.0	4.0	0.2	0.2	3,000
Mg	1,164	1,004	1,102	1,063	1,250
Mn	154	79	97	78	160
Na	1,500	1,534	1,498	1,524	1,600
Si	32	4.5	2.8	3.0	300
Sr	5.0	5.9	5.7	6.1	14
K	153	153	154	150	160
Cl	1,170	1,170	1,230	1,200	1,190
NO_3^-	297	297	290	297	302
SO_4^{2-}	9,700	8,800	9,700	9,100	25,000
<u>Trace Metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	<0.02	15.50
Ba	<0.05	<0.05	<0.07	<0.07	0.07
Cd	0.35	0.03	0.06	0.05	0.25
Co	3.98	0.49	0.29	0.47	4.93
Cr	<0.01	<0.01	<0.01	<0.01	2.09
Cu	0.12	0.04	<0.02	<0.02	1.45
Mn	<0.03	0.18	0.23	0.26	7.74
Pb	<0.02	<0.02	<0.02	<0.02	0.85
Se	0.72	1.43	1.25	1.45	1.10
V	<0.02	<0.02	<0.02	<0.02	19.2
Zn	9.4	0.4	<0.2	<0.3	16.0
<u>Radionuclides (pCi/L)</u>					
^{210}Pb	<75	<75	<75	<75	12,300
^{238}U	1,788	<75	<75	<75	15,500
^{230}Th	<400	<400	<400	<400	185,400
^{226}Ra	1,682	231	259	220	4,020

TABLE 23. Solution Chemistry of Calcium Hydroxide Neutralized Exxon Highland Mill Acidic Tailings Solution

Parameter	Ca(OH) ₂ Neutralized to pH 5.0	Ca(OH) ₂ Neutralized to pH 6.5	Ca(OH) ₂ Neutralized to pH 7.2	Ca(OH) ₂ Neutralized to pH 8.0	Exxon Highland Influent
<u>Macro ion (mg/L)</u>					
Al	1.9	<0.1	<0.1	<0.1	440
Ca	546	488	494	502	560
Fe	0.2	0.1	<0.1	<0.1	1,000
Mg	520	503	472	513	540
Mn	48	30	7.4	44	50
Na	354	346	346	349	340
Si	32	1.9	1.0	16	310
Sr	5.1	4.5	4.0	4.6	8.5
K	42	41	42	41	44
Cl	297	299	296	300	300
NO ₃	10	8	9.5	12	9
SO ₄	4080	3975	3750	4055	9,300
<u>Trace Metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	<0.02	0.21
Ba	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	0.5	0.01	<0.01	0.03	0.03
Co	1.43	0.36	<0.03	1.43	1.31
Cr	<0.01	<0.01	0.02	<0.01	1.25
Cu	0.14	<0.02	<0.02	<0.02	0.97
Mo	<0.01	<0.01	<0.01	<0.01	<0.02
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Se	1.34	1.1	1.2	1.0	1.35
V	<0.02	<0.02	<0.02	<0.02	10.7
Zn	3.5	<0.2	<0.2	2.2	4.5
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	<75	<75	<75	<75	2,100
²³⁸ U	343	<75	<75	<75	2,100
²³⁰ Th	<400	<400	<400	<400	97,140
²²⁶ Ra	<75	<75	<75	<75	758

influent values at pH = 7.2. The concentrations of cobalt and copper in the Exxon Highland treated solutions show that additional neutralization beyond pH = 7.2 fails to further reduce concentration levels of these constituents. In the case of manganese and cobalt, further neutralization beyond pH = 7.2 caused observed concentration levels to climb back to influent levels.

The macro ions, trace metals, and radionuclides followed the general trend of decreasing concentration with increasing pH. This trend continued until pH = 7.2 followed by further insignificant reduction to pH = 8.0. Six exceptions to this trend may be seen in Tables 22 and 23. In both solutions, cadmium concentrations increased to levels above influent concentrations at pH = 5. This initial increase was followed by a percent removal of cadmium of nearly 70% of its influent concentration at pH = 7.2. Molybdenum concentrations in the treated Lucky Mc tailings solution showed an initial reduction to just at detectable levels (99.9% removal) at pH = 5.0, followed by an increase in concentration to 98%, 97%, and 96% removal, respectively, at pH = 6.5, 7.3 and 8.0. This trend was not seen in the treated Exxon Highland solution because of the untreated acidic solution Mo concentration being below detection limits.

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

Solution quality results for the neutralization of both Lucky Mc and Exxon Highland acidic tailings solutions indicate that in the case of the macro ions, Ca, Mg, Na, K, Cl, and NO_3 and the trace metal, Se, no significant reduction in concentration resulted because of neutralization throughout the four pH ranges. Selenium concentrations in the neutralized Lucky Mc solutions experienced a 35% reduction at pH = 5 followed by an increase in concentration to above influent levels at pH = 6.5, 7.0, and 8.0. Selenium concentrations in the Exxon solution showed no reduction at pH = 5 and limited reduction (19%) at the higher pHs. These results are consistent with those of Sherwood and Serne (1983a) where the percentage removal for these constituents was found to be low regardless of reagent used and final solution pH achieved. Thus, neutralization does not appear to be an effective method for the removal of these constituents. Elevated levels of calcium can be expected when using calcium hydroxide as a neutralizing reagent. Furthermore, manganese concentrations tend to increase as the tailings solution becomes more alkaline. Because no additional magnesium was intentionally added, the hydrated lime used throughout the study must contain a significant amount of soluble manganese. As more lime is added to raise the solution pH, additional manganese dissolves and remains in solution.

To decrease the amount of dissolved manganese by precipitating $\text{Mg}(\text{OH})_2$, the final solution pH would have to be in the range of pH 9.5 to 12.5. (See Table 14).

Sulfate concentrations were reduced by 61% in the treated Lucky Mc solution and 56% in the treated Exxon Highland Mill solution by pH = 5.0. Continued reagent addition failed to significantly remove more sulfate after pH = 5.0 was reached. At pH = 5.0, sulfate concentrations in both solutions are still at least an order of magnitude above EPA's maximum permissible concentration (MPC) of 250 mg/L for secondary drinking water. Additional solution treatment, such as specific ion removal, would be required to ensure sulfate concentrations below water quality guidelines.

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

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

Limestone/Lime Batch Neutralization Studies

The results of the limestone/lime two-component neutralization experiments for the Lucky Mc tailings solution and the Exxon tailings solution are shown in Tables 24 and 25, respectively. Also included in Tables 24 and 25 are the data at the intermediate pH (limestone-only step) during the neutralization process. At the intermediate pH, the tailings solutions have been neutralized with CaCO_3 to either pH 4.0 or 5.0 depending on the test. Once at the desired intermediate pH, known amounts of $\text{Ca}(\text{OH})_2$ were added to the tailings solution until it reached pH = 7.2.

The results of the tailings solutions neutralized to pH 7.1 with $\text{Ca}(\text{OH})_2$ after initially being neutralized with CaCO_3 , show substantial reductions in solution constituent concentrations. This result is evident in the solutions that were limestone treated to only pH 4.0 and then lime neutralized to pH 7.1. Many constituents that were soluble in slightly acid solutions dropped below detection limits after treatment by the two-component neutralization scheme. The solutions that were initially treated with CaCO_3 to pH 5.0 then to

TABLE 24. Solution Chemistry of Calcium Carbonate/Calcium Hydroxide Neutralization of Lucky Mc Mill Tailings Solution

Parameter	CaCO ₃ Neutralized to pH 4	CaCO ₃ Neutralized to pH 5	CaCO ₃ Neutralized to pH 4/Ca(OH) ₂ Neutralized to pH 7.1	CaCO ₃ Neutralized to pH 5/Ca(OH) ₂ Neutralized to pH 7.1	Untreated Solution
<u>Macro Ion (mg/L)</u>					
Al	272	5.3	<0.3	<0.3	1,100
Ca	477	458	473	516	600
Fe	30	3.8	<0.1	<0.1	3,000
K	147	152	145	145	160
Mg	1,141	1,186	1,153	1,149	1,250
Mn	148	150	155	149	160
Na	1,504	1,528	1,478	1,478	1,600
Si	30	13.3	<0.2	2.9	300
Sr	2.8	2.5	2.3	2.6	14
SO ₄	11,650	10,750	10,700	10,400	25,000
NO ₃	292	283	330	330	302
Cl	1,195	1,230	1,300	1,285	1,190
<u>Trace Metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	0.06	<0.02	<0.02	<0.02	15.50
Ba	0.14	0.07	0.07	0.10	0.07
Cd	0.20	0.29	0.27	0.29	0.25
Co	4.68	4.73	3.54	3.35	4.93
Cr	0.03	<0.01	<0.01	<0.01	2.09
Cu	1.18	0.08	0.02	0.03	1.45
Mo	0.04	<0.01	<0.01	<0.01	7.74
Pb	0.03	<0.02	<0.02	<0.02	0.85
Se	0.99	0.87	0.76	0.81	1.10
V	<0.02	<0.02	<0.02	<0.02	19.2
Zn	14	11	2.7	3.5	16.0
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	779	<75	<75	<75	12,300
²³⁸ U	4,195	223	<75	126	15,550
²³⁰ Th	2,192	<400	<400	<400	185,400
²²⁶ Ra	8,331	253	191	<75	4,020

TABLE 25. Solution Chemistry of Calcium Carbonate/Calcium Hydroxide Neutralization of Exxon Highland Tailings Solution

Parameter	CaCO ₃ Neutralized to pH 4	CaCO ₃ Neutralized to pH 5	CaCO ₃ Neutralized to pH 4/Ca(OH) ₂ Neutralized to pH 7.1	CaCO ₃ Neutralized to pH 5/Ca(OH) ₂ Neutralized to pH 7.1	Untreated Solution
<u>Macro Ion (mg/L)</u>					
Al	230	1.8	<0.3	<0.3	440
Ca	500	506	503	573	560
Fe	2.3	0.4	<0.1	<0.1	1,000
K	44	41	40	40	44
Mg	508	500	495	540	540
Mn	49	50	44	45	50
Na	346	342	329	339	340
SI	74	28	<0.02	32	310
Sr	4.9	4.3	4.0	4.4	8.5
SO ₄	5,450	4,080	4,090	4,200	9,300
NO ₃	<20	<20	<20	<20	9
Cl	302	303	325	340	300
<u>Trace Metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	0.03	<0.02	<0.02	<0.02	0.21
Ba	0.09	0.08	0.08	<0.05	<0.05
Cd	0.04	0.02	<0.01	0.02	0.03
Co	1.42	1.40	0.31	1.06	1.31
Cr	0.04	<0.01	<0.01	<0.01	1.25
Cu	1.09	0.07	<0.02	<0.02	0.97
Mo	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Se	1.20	1.35	1.02	1.02	1.35
V	<0.02	<0.02	<0.02	<0.02	10.7
Zn	4.2	2.4	0.20	0.30	4.5
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	<75	<75	<75	<75	2,100
²³⁸ U	431	105	95	<75	2,100
²³⁰ Th	1,180	<400	<400	<400	97,140
²²⁶ Ra	1,090	156	<75	<75	758

pH 7.1 with lime showed only slight reductions in solution concentrations when compared to the intermediate pH 5.0 solution. When the intermediate-neutralized solutions were compared to the untreated tailings solutions from the respective mills, the overall reduction in TDS content was greater than 50% for both Lucky Mc and Exxon Highland solutions.

The results of the final (pH 7.1) neutralized tailings solution show that the following constituents were reduced by greater than 97% in the treated Lucky Mc solution: Al, As, Cr, Cu, Fe, Mo, Pb, Si, V, ^{210}Pb , ^{230}Th , and ^{238}U . Similar reductions were seen in the treated Exxon solution for Al, Fe, Si, Cr, Cu, V, and ^{230}Th . In addition, over 90% of the As, ^{210}Pb , ^{238}U , and ^{226}Ra was removed. Selenium removal was insignificant for both treated solutions, 24% and 26% for the Exxon and Lucky Mc, respectively. In both cases selenium concentrations remained above EPA's MPC. Cobalt removal in both solutions was similar to selenium. Only 19% of the cobalt was removed from the treated Exxon solution and 32% from the treated Lucky Mc solution. Sulfate was removed from both solutions at nearly identical percentages, 55% and 58% for the Exxon and Lucky Mc solutions respectively. Again the final solution concentrations for SO_4 exceed the water quality guidelines.

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

Several of the macro ions in Tables 24 and 25 remain at relatively high concentrations even at pH 7.1. Ions such as Ca, K, Mg, Mn, Na, Si, Cl, NO_3 , and SO_4 seem to show little solubility dependence on final solution pH up to pH 7.1 or at the intermediate limestone pH values. Many of these ions are soluble in neutralized tailings solution regardless of the reagent used for neutralization (Moffett 1976; Sherwood and Serne 1983a).

A comparison of the limestone/lime-neutralized solution analyses with the previously mentioned pH optimization results using only $\text{Ca}(\text{OH})_2$ at pH 5.0 and pH 7.1 is shown in Table 26. The combination limestone/lime neutralization data show distinctly higher cobalt and manganese concentrations for both tailings solutions and higher zinc values for the Lucky Mc solution. This suggests there may be soluble carbonate complexes forming with some trace metals during the intermediate neutralization process. Although the data are not distinct for uranium carbonate complexes, their formation may warrant additional study based on known thermodynamic stability constants.

TABLE 26. Comparison of Ca(OH)_2 Neutralization with $\text{Ca(OH)}_2/\text{CaCO}_3$ Two-Step Neutralization

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

(a) Only limestone used to pH 5.

The results of this study have led to formulating two main conclusions for implementing a two-component neutralization scheme:

- 1) Incorporation of a combination limestone/lime or lime-only treatment for acidic tailings solution has greatly reduced the number of contaminants that exceed the water quality guidelines. Of the original 17 constituents from the Lucky Mc tailings solution (including solution pH and TDS) that exceeded the EPA MPC, only four exceed the primary drinking water standards; three exceed the secondary drinking water standards after neutralization with limestone and lime. As mentioned in the pH optimization discussion, certain trace metals (i.e., Cd, Co, and Se) and the macro ions, NO_3 and SO_4 , may require additional specific-ion removal techniques to bring the solution concentration below the set limits.
- 2) In general, initially neutralizing the acidic tailings solution to either pH 4.0 or 5.0 with limestone and subsequently to pH 7.1 with lime results in relatively identical solution quality.

The only exceptions to these two conclusions are the formation of soluble carbonate complexes for Co, Zn, and Mn and possibly for uranium.

The main advantage, especially for those in the mining and milling industry, is the relative cost of neutralizing acidic tailings solutions. Briefly, the two-component neutralization scheme is the least costly method of solution neutralization tested to date. Furthermore, of the two intermediate solution pH values studied, initial solution neutralization to pH 4.0 with limestone followed by lime addition to pH ~ 7.2 is less costly than limestone neutralization initially to pH 5.0 and then lime neutralization to pH 7.2. This is due to the inefficiency of limestone buffering above pH 4.0. For this reason limestone neutralization to pH 4.0 is preferred from a cost perspective. Cost detail may be found in the reagent cost section.

Contaminant Complexation Experiments

Contaminant complexation experiments were performed on elements that showed dissimilar solution concentrations at equivalent pH values. Results from initial laboratory studies indicate that the final concentration of certain constituents (notably Co, Mg, Mn, Mo, U, and Zn) may be affected by the type of reagent used for treatment. The results of the complexation studies are described below.

Solution Neutralization

A useful method for comparing the overall effectiveness of limestone to hydrated lime as neutralizing reagents for acidic tailings solutions is to compare the TDS content of the original solution 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 3. Total dissolved solids levels for a given solution were calculated by simply summing the measured concentrations of each constituent analyzed. Neutralization of the original solution to

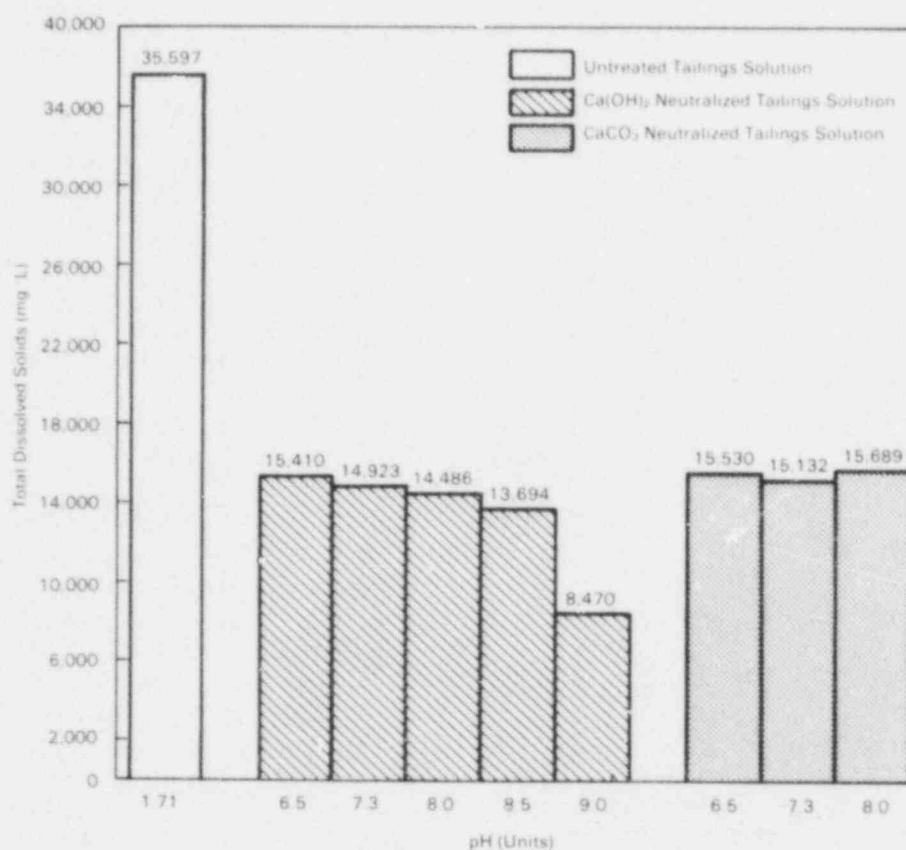


FIGURE 3. Total Dissolved Solids Comparison Between Limestone (CaCO_3) and Hydrated Lime-Neutralized [$\text{Ca}(\text{OH})_2$] Tailings Solution

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.

The large drop in TDS content, produced through tailings solution neutralization to pH = 6.5, was confirmed in earlier studies where several neutralizing agents were screened as potential solution treatments for acidic uranium mill solutions (Sherwood and Serne 1983a). The large drop in TDS at pH = 6.5 was observed for all reagents tested and is a function of elevating the original tailings solution 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 solution pH beyond neutral pH conditions, and thus increase contaminant removal; are fairly 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 27 and 28, respectively. In addition, the solution chemistry of the original tailings solution is presented in each table. The data in Tables 27 and 28 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 1983a; 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 EPA's primary drinking water standards.

Of the pH-sensitive metals removed by adjusting the acidic tailings solution pH to 7.3, iron removal had perhaps the greatest effect on the overall solution chemistry. Iron (present at 3100 ppm in the original solution) 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 solution 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 solution, 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, thus promoting the removal of trace metals from acidic tailings solution 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 solution are insignificant compared to the concentrations of the macro cations (Al, Ca, Fe, K, Mg, Mn, and Na) and anions (Cl , NO_3 , and SO_4). In fact when neutralizing tailings solutions produced by sulfuric acid leaching, SO_4 removal comprises the highest percentage of TDS reduction of all the tailings solution 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

TABLE 27. Solution Chemistry: Neutralization of Lucky Mc Tailings
Solution Using Hydrated Lime $[\text{Ca}(\text{OH})_2]$

Parameter	Original Tailings Solution	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
Macro Ions (mg/L)						
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
Trace Metals (mg/L)						
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
Radionuclides (mg/L)						
U (total)	40.0	0.05	0.10	0.24	0.30	0.15

TABLE 28. Solution Chemistry: Neutralization of Lucky Mc Tailings Solution Using Limestone (CaCO_3)

Parameter	Original Tailings Solution	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)	0.0	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

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 3 indicates that strongly alkaline solution conditions (pH > 8.5) are necessary for substantial SO_4 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 SO_4 concentrations coincides with an increase in calcium 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 Tables 27 and 28 and in the lime/sodium bicarbonate data presented in Table 29 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 27 through 29 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 solution past pH = 8.5 to remove SO_4 . 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 SO_4 concentrations can result in the dissolution of Mo (as shown in Tables 27, 28, and 29) 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 averaged only 27%. Solution concentrations of molybdenum are plotted versus pH in Figure 4. The line labeled untreated tailings solution (long dashed line) in Figure 4 represents the concentration of Mo in the original acidic solution. The other line, labeled neutralized tailings solution (short dashed line), represents the molybdenum concentrations at each set pH after neutralization with hydrated lime (see Table 27). Molybdenum concentrations after neutralization with limestone and lime/sodium bicarbonate (see Tables 28 and 29) are not shown here, because the 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 neutral tailings solutions with high Ca 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

TABLE 29. Solution Chemistry: Neutralization of Lucky Mc Tailings
Solution Using $[\text{Ca}(\text{OH})_2/\text{NaHCO}_3]$

Parameter	Solution	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
TDS (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
Macro Ions (mg/L)						
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
Trace Metals (mg/L)						
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
Radionuclides (mg/L)						
U (total)	40.0	0.05	1.90	2.55	2.05	1.90

(a) NA = not analyzed.

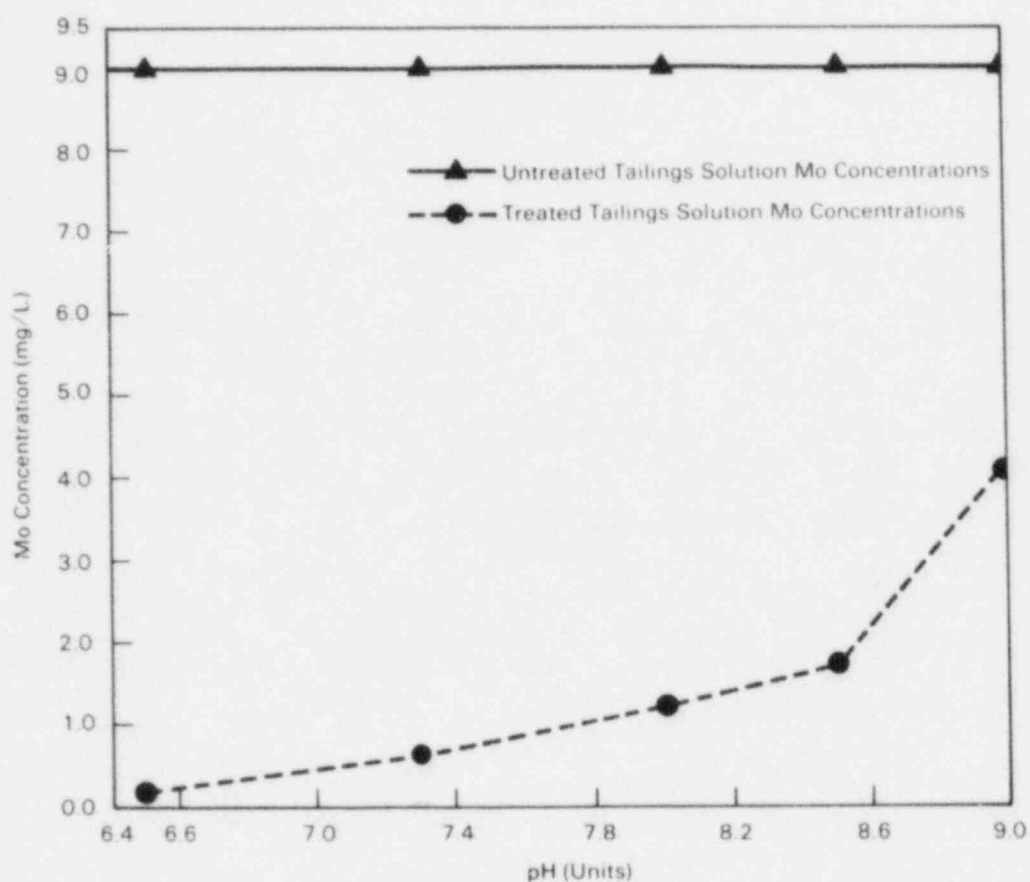


FIGURE 4. Comparison of Molybdenum Concentrations in Untreated and Neutralized Tailings Solution

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 solution 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.

Although 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 29. 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 U.

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 27, 28, and 29 were specified, the activity products of the various species were compared to the solubility products of these minerals (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 Doner 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. Because 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 solution 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). 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 were 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 27 and 29 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 of 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 8.0 or below, ZnSO_4 , 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 occurs, with $\text{Zn}(\text{CO}_3)_2^{2-}$ and ZnCO_3^0 predominating. Enough measured carbonate occurs 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 27, 28, and 29 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 pH ≤ 8.0 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 27, 28, and 29 suggest that for a set pH value, carbonate-bearing reagents allow higher zinc solution concentrations.

Trace metal concentrations in Table 29 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 pH = 6.5 and 99% removal at pH = 7.3 and greater). These results offer no explanation for the slightly greater solubility of cobalt observed in the 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. Because cobalt was not in the MINTEQA 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 solution, 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 5. 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 of 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 solution 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

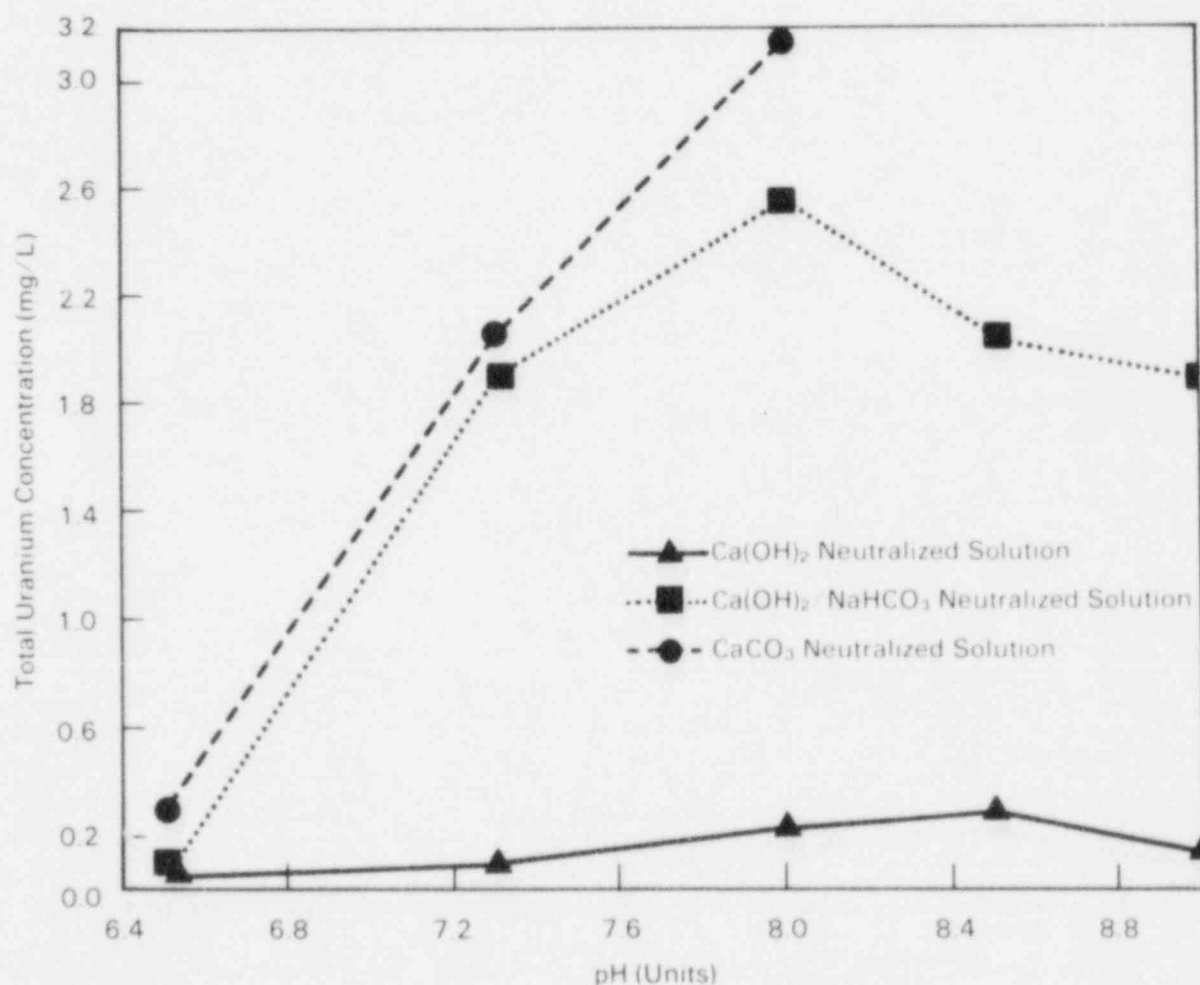


FIGURE 5. Total Uranium Concentration Comparison Between Hydrated Lime [Ca(OH)₂], Hydrated Lime/Sodium Bicarbonate [Ca(OH)₂], and Limestone-Neutralized (CaCO₃) Tailings Solution

contact with added carbonate reagents, the two most predominating species at the various pH values are shown in Table 30. 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 $\text{UO}_2(\text{SO}_4)_2^{2-}$. 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, CO_2 absorption from air does not occur rapidly enough to form the significant quantities of the highly soluble uranyl carbonates.

TABLE 30. Percent of Predominate Uranium Carbonate Species at Specified pH Values

pH	Species	
6.5	51% UO_2CO_3^0	37% $\text{UO}_2(\text{CO}_3)_2^{2-}$
7.3	65% $\text{UO}_2(\text{CO}_3)_2^{2-}$	31% $\text{UO}_2(\text{CO}_3)_3^{4-}$
8.0	98% $\text{UO}_2(\text{CO}_3)_3^{4-}$	2% $\text{UO}_2(\text{CO}_3)_2^{2-}$
9.0	100% $\text{UO}_2(\text{CO}_3)_3^{4-}$	

MINTEQ was also used to calculate ion activity products for possible controlling uranium solids, schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$), β - $\text{UO}_2(\text{OH})_2$, 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 schoepite and β - $\text{UO}_2(\text{OH})_2$ 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 of uranium, 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 MINTEQ. At pH values 6.5 and 7.3, the observed solutions are oversaturated with these two minerals. At pH 8.0 the observed solution is undersaturated slightly with tyuyamunite and slightly oversaturated with carnotite. At pH values above 8.0, the solutions are undersaturated with 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 MINTEQ; 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 18A filter are given in Tables 31, 32, and 33. The selected solutions are the lime-only neutralized solutions of pH 6.5 and 7.3 (Table 31), the limestone-only neutralized solution of pH 6.5 and 7.3 (Table 32), and the lime/sodium bicarbonate solution of pH 7.3 (Table 33). Results show that, with the exception of solution zinc concentrations, no difference exists in solution chemistry because of solution filtering at 18A. The presence of elevated zinc concentrations in all filtered solutions suggests that even after performing a washing procedure on each filter before use, these filters are a source of zinc contamination. Therefore, the data presented in Tables 27, 28, and 29 do not appear to include significant quantities of colloidal material in the size range between 18A and 4500A (0.45 μm).

Sludge Characterization

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

As most of the sludge appears to be amorphous, the x-ray diffraction analyses provided little insight into the potential leachability of the sludges. Actual leach experiments described later will help evaluate the stability of the sludge generated during solution neutralization.

Characterization of the sludges generated from neutralization of acidic tailings solution provides data needed to determine potential sludge disposal problems. Of major importance are the weight of sludge generated, its residual moisture content and its leachability. The weight of sludge is directly proportional to the handling and disposal costs. Sludge moisture retention properties are a measure of the adhesive and cohesive (capillary) forces which bind water in the sludge. Sludge residual moisture content is related to the ease of handling, with high moisture content sludges being harder to handle. Sludge leachability determines the release of slightly soluble salts and potentially

TABLE 31. Solution Chemistry of Lime-Neutralized Lucky Mc Tailings Solution Before and After 18A Filtering

Parameter(a)	pH 6.5		pH 7.3	
	0.45 μ m Filtered	18A Filtered	0.45 μ m Filtered	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.

toxic trace metals and radionuclides. Mineralogical characterization was performed to give further information on chemical reactivity or leachability.

Results on the amount of sludge generated during neutralization appear in Table 34. Sodium hydroxide, Na₂CO₃, and MgO generated the lowest quantities of sludge. These reagents produced 4 to 7 g of dry sludge per liter of tailings solution neutralized for the Exxon Highland tailings solution and 11.8 to 14.6 g/L for the Lucky Mc tailings solution. All of the other neutralizing agents produced at least twice as much sludge on a dry weight basis. The other neutralizing agents contain reactive calcium and thus remove some sulfate from the acid tailings solution (see Tables 15 and 16), which increases the quantity

TABLE 32. Solution Chemistry of Limestone-Neutralized Lucky Mc Tailings Solution Before and After 18A Filtering

Parameter(a)	pH 6.5		pH 7.3	
	0.45 μ m Filtered	18A Filtered	0.45 μ m Filtered	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.

of sludge. Further, samples neutralized with fly ash appear to have unreacted solids present as part of the sludge. The fly ash reagents produced 27 to 32 g of dry sludge per liter of Exxon Highland tailings solution and about 60 g/L for the Lucky Mc tailings solution.

Measurements of sludge moisture retention versus capillary pressure are shown in Tables 35 and 36. Sludges formed by neutralization with MgO, Na₂CO₃, and NaOH contained substantially higher residual moisture contents over the entire pressure range. Values as high as 12 g of water per gram of solids were measured for these sludges. Fly sludges retain the least water of any samples tested (0.3 to 1.5 g of water per gram of solids over the pressure range

TABLE 33. Solution Chemistry of Lime/Sodium Bicarbonate-Neutralized Lucky Mc Tailings Solution 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.

studied). The undissolved solids remaining from the original ash contains little moisture and, hence, reduces the total moisture content of the fly ash sludges. Calcium carbonate and calcium hydroxide exhibit intermediate moisture contents of 1 to 3 g of water per gram of dry solids. The higher the moisture content at any capillary pressure range the more difficult the sludge will be to handle. Wet sludges also do not settle and consolidate well. The Exxon Highland Mill sludges for a majority of the treatments retain more moisture than the Lucky Mc Mill sludges at pressures >-10.2 m. For capillary pressures below (more negative than) -30.6 m, the two sludge's moisture retention are

TABLE 34. Total Dry Weight of Sludge Per Liter of Mill Tailings Solution Treated, g/L

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

TABLE 35. Capillary Pressure Versus Water Content Relationship for Lucky Mc Sludge Material

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

TABLE 36. Capillary Pressure Versus Water Content Relationship for Exxon Highland Mill Sludge Material

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

(a) NA = not applicable.

quite dependent on the neutralizing agent. These results show sodium reagents have the highest residual water content followed by MgO, Ca(OH)₂, CaCO₃, and the fly ash sludges have the lowest moisture content.

Together the total dry weight (see Table 33) and residual moisture content (see Tables 34 and 35) characteristics can be used qualitatively to project possible sludge handling and disposal problems. The noncalcium-containing reagents (MgO , Na_2CO_3 , and $NaOH$) produced much less sludge, but they may contain up to 10 times the residual moisture content of the calcium-containing reagents. The problems involved in handling and storing these sludges may be much more difficult than those of the low moisture content sludges. Of the calcium-containing reagents, calcium hydroxide produced the least sludge, but its sludges contained higher moisture content than the other calcium sludges. The fly ash sludges that were produced during neutralization had low moisture, but a total dry weight of nearly 60 g/L of Lucky Mc tailings solution neutralized. This sludge mass is 75% greater mass than the other calcium-based sludges produced. Thus, the hydrated lime, $Ca(OH)_2$, again appears to be a likely choice with its moderate sludge production and moderate moisture retention properties.

COLUMN STUDIES

Sludge Column Leaching Experiments

Results of the column leaching experiments using field-neutralized sludge material from both Lucky Mc and Exxon Highland mills are shown in Tables 37 and 38, respectively. The data are listed with respect to the number of effluent pore displacement volumes of synthetic ground water that had passed through the sludge column.

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

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

Many of the above-mentioned elements in both the Lucky Mc and Exxon sludge effluents showed dramatic decreases in solution concentration as solution continued to pass through the columns. The decrease in constituent concentration gradually approached the influent concentration as would be expected with continued leaching. The high initial effluent concentration of macro ions and some trace metals indicates a high soluble salt content left in the sludge material when dried. Moisture-retention values for sludges formed because of $Ca(OH)_2$ neutralization of acidic tailings solution range from ≈ 2.2 g of moisture per gram of sludge to 2.8 g/g for the Lucky Mc and Exxon sludges,

TABLE 37. Lucky Mc Sludge Column Leaching Data

	Effluent Sample Identification					Ground-Water Leachate
	1	2	3	4	5	
Pore Volume	0.65	4.0	5.37	6.1	7.4	
pH (units)	7.14	7.25	7.85	8.74	8.75	7.6
<u>Macro Ions (mg/L)</u>						
Al	<0.3 ^(a)	<0.3	<0.3	0.3	<0.3	<0.1
Ca	480	472	480	442	396	69
Fe	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mg	182	58	60	50	38	11
Mn	NA ^(b)	NA	NA	NA	NA	0.01
Na	2540	144	144	128	120	105
Si	1.4	<0.2	<0.2	0.2	<0.2	0.5
Sr	1.7	1.3	1.4	1.1	0.8	0.03
K	362	11.8	11.5	6.9	4.2	NA
Cl	2,200	150	147	100	80	44
NO ₃	480	11	9.4	6.1	3.3	3.3
SO ₄	6,000	1,600	1,590	1,590	1,290	300
<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	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cr	0.05	0.01	0.01	<0.01	<0.01	<0.01
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Mo	1.64	0.37	0.44	0.27	0.20	<0.01
Pb	<0.02	<0.02	<0.02	0.02	<0.02	<0.02
Se	0.52	0.11	<0.12	0.07	<0.05	<0.1 ^(c)
V	<0.1	<0.1	<0.1	<0.1	<0.1	<0.02
Zn	<0.01	<0.1	<0.1	<0.1	<0.1	<0.05
<u>Radionuclides (pCi/L)</u>						
²¹⁰ Pb	<75	<75	<75	<75	<75	<75
²²⁶ Ra	<75	<75	<75	<75	<75	<75
²³⁰ Th	<400	<400	<400	<400	<400	<400
²³⁸ U	<75	<75	<75	<75	<75	<75

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

(b) NA = not applicable.

(c) Analysis performed by Inductively coupled plasma.

TABLE 38. Exxon Highland Sludge Column Leaching Data

	Effluent Sample Identification				Ground-Water Leachate
	1	2	3	4	
Pore Volume	2.0	3.4	5.1	7.2	
pH (units)	11.23	11.48	11.08	10.34	7.6
<u>Macro Ions (mg/L)</u>					
Al	<0.3 ^(a)	<0.3	<0.3	<0.3	<0.1
Ca	624	644	602	597	69
Fe	<0.1	<0.1	0.4	<0.1	<0.1
Mg	0.5	0.6	0.6	0.9	11
Mn	NA ^(b)	NA	NA	NA	<0.1
Na	420	103	100	103	105
Si	4.4	1.5	1.6	2.0	0.5
Sr	2.4	2.1	1.7	1.4	0.03
K	97	11	4	6	NA
Cl	520	170	66	45	44
NO ₃	1.0	1.0	1.0	<1.5	3.3
SO ₄	1800	1450	1500	1440	300
<u>Trace Metals (mg/L)</u>					
Ag	<0.02	<0.02	<0.02	<0.02	<0.02
As	<0.02	<0.02	<0.02	<0.02	<0.02
Ba	<0.05	<0.05	<0.05	<0.05	<0.05
Cd	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.02	<0.02	<0.02	<0.02	<0.02
Cr	0.39	0.30	0.30	0.15	<0.01
Cu	0.04	<0.02	<0.02	<0.02	<0.02
Mo	0.02	0.01	0.01	0.01	<0.01
Pb	<0.02	<0.02	<0.02	<0.02	<0.02
Se	1.78	0.78	0.50	0.36	<0.1 ^(c)
V	<0.1	<0.1	<0.1	<0.1	<0.02
Zn	<0.1	<0.1	<0.0	<0.1	<0.05
<u>Radionuclides (pCi/L)</u>					
²¹⁰ Pb	<75	<75	<75	<75	<75
²²⁶ Ra	<75	<75	<75	<75	<75
²³⁰ Th	<400	<400	<400	<400	<75
²³⁸ U	<75	<75	<75	<75	<75

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

(b) NA = not applicable.

(c) Analysis performed by inductively coupled plasma.

respectively (Sherwood and Serne 1983a). The moisture retained in the sludges from both mills has the same constituent makeup as the respective neutralized tailings solution shown in Table 14. Those solutions are the filtered fraction of the solution/sludge slurry after neutralization. The data in Table 14 show similar high concentrations of macro ions such as Ca, K, Na, Cl, SO_4 , and trace metals such as Mo and Se. Prior to the column-packing steps, the sludge material was oven dried to ensure that the desired packing densities are met and to facilitate handling. The moisture normally retained within the sludge was driven off leaving the residual solution evaporites comprised of the above elements normally soluble in neutral tailings solutions. On contact with the laboratory-prepared ground water used as leachate, the evaporites redissolve and pass through the column and are collected in the first effluent. Once dissolution of the evaporites or soluble salts is complete, the effluent solution constituent concentrations gradually approach that of the influent synthetic ground water. The only evident exceptions to this for the Lucky Mc solution are the macro ions, Ca and SO_4 , which seem to decrease but at a slower rate than other constituents. For the Exxon sludge effluents, similar trends were seen over the period of contact with the 6.5 pore volumes of leachate. Calcium and SO_4 ions show the slowest decrease in solution concentration caused by the dissolution of gypsum formed during the addition of $\text{Ca}(\text{OH})_2$ during the in-field neutralization. The excess addition of lime in the field resulted in column effluent solution pHs ranging from pH = 11.1 to pH 11.6 for the Exxon sludge column. The most notable trace metals showing significant solubility is selenium with a concentration of almost 1.8 mg/L and chromium at 0.36 mg/L during the second pore volume of leaching. By the time the Exxon sludge has contacted 6.5 pore volumes of ground water, the selenium value had dropped to 0.36 mg/L and chromium to 0.15 mg/L. This is approximately an 80% reduction for selenium and 58% for chromium in solution concentration after 6.5 pore volumes, still substantially higher than the MPC value in drinking water of 0.01 mg/L and 0.05 mg/L for selenium and chromium, respectively, (see Table 13) and the influent concentrations of the synthetic ground water used for leaching. Several investigators (Rai and Zachara 1984; Lindsay 1979; Bohn, McNeal and O'Connor 1979) have found increased solubilities of certain species of chromium and selenium (particularly chromite and selenite) in highly alkaline (pH 11) solutions such as these. For elements such as selenium and chromium, an additional solution treatment such as specific ion removal may be necessary to reduce the solution concentration to acceptable limits. Alternatively, at more realistic pH values of 7.0 to 8.0, selenium or chromium might not be mobile as evidenced by the Lucky Mc sludge results.

Tailings Leaching Studies

In order to evaluate the effectiveness of neutralizing the solid portion of uranium mill waste, tailings leaching studies were performed. Samples of untreated acidic and neutralized uranium mill tailings were leached with laboratory-prepared ground water. The results of those tests are described below.

Acid Tailings Leaching Results

Results of the solid acidic tailings leaching experiments are shown in Tables 39, 40, and 41 for the Lucky Mc and the Exxon untreated tailings, and Tables 42 and 43 for the neutralized tailings. For the untreated (acidic) tailings from both mills (Tables 39, 40, and 41), 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 6, 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 6 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 earlier in the section on tailings solution characterization.)

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 32. 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 MPC for various water types shown in Table 13, 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 14). 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

(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 39. Column Effluent Solution Chemistry of Untreated Lucky Mc Tailings-Extended 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
Macro Ions (mg/L)						
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
Trace Metals (mg/L)						
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
Radionuclides (pCi/L)						
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 40. Column Effluent Solution Chemistry of Untreated Exxon Highland Tailings-Extended 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 41. Column Effluent Solution Chemistry of Untreated Exxon Highland 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
Macro Ions (mg/L)						
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
Trace Metals (mg/L)						
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
Radionuclides (pCi/L)						
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.

TABLE 42. Column Effluent Solution Chemistry of Neutralized Lucky Mc Tailings-Extended 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 42. (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 43. Column Effluent Solution Chemistry of Neutralized Exxon Highland 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 43. (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	561	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 43. (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.

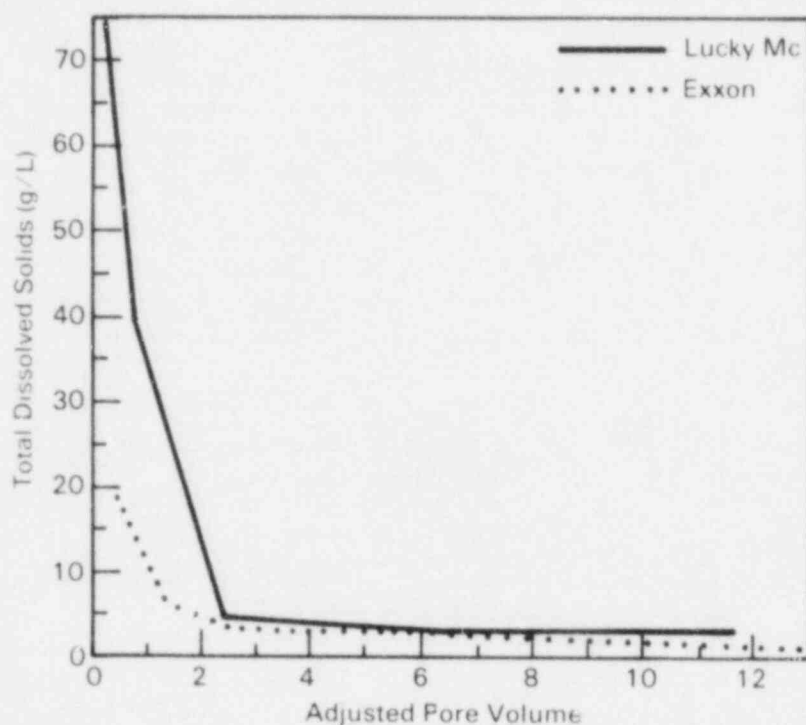


FIGURE 6. Lucky Mc and Exxon Highland Acidic Tailings Total Dissolved Solids Versus Adjusted Pore Volume

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 33 shows that the first two samples of eluant have larger solution concentrations of Al, Fe, Mg, Na, Cl, NO₃, SO₄, As, Co, Cr, Cu, Zn, and ²³⁸U 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, ²¹⁰Pb, and ²³⁰Th than the slurry leaving the mill. The increase in Mg, Na, Cl, NO₃, and SO₄ 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 tailings column (see Tables 40 and 41) 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 tailings column eluants are quite similar to the Lucky Mc tailings column eluant data. The lowest pH observed for the Exxon Highland tailings column effluent was 3.0, 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 39) 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 39). 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 6. 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 40 and 41. 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 40 and 41^(a)]. The TDS content of the second collected effluent (see Table 41) was reduced to 6.04 g/L after 1.39 pore volumes of tailings leaching. The dotted line in Figure 4 shows a gradual

(a) The data presented in Table 41 are similar in nature to that presented in Table 40 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.

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 Highland tailings. Since both mills employ a sulfuric acid leaching process, high sulfate concentrations are not unusual. As can be seen in Tables 39, 40, and 41, 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 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) suggest gypsum is depleted after about 16 pore volumes of leaching. Tables 39 and 40 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 Highland 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 solutions. Note that even though several pore volumes of leachant had contacted the acidic tailings, several constituents still exceed MPC limits for various water types. For example, Al, As, Fe, and SO_4 all exceed certain specified water limits as shown in Table 13. In addition, Ra and Se may also exceed the MPC; however, the detection limits of the analytical instruments were higher than some MPCs, and definite conclusions cannot be made.

Neutralized Tailings Leaching Results

Tables 42 and 43 show the results of the neutralized tailings leaching experiments. Subsamples of the same solid tailings material from both the Lucky Mc and Exxon Highland 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 solution 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 solution. The macro ions contribute significantly to the TDS content of acidic tailings solutions. 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 7. The solid line in Figure 7 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 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 was 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 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 13) of 5 pCi/L and remained above the MPC for most samples collected throughout the experiment.

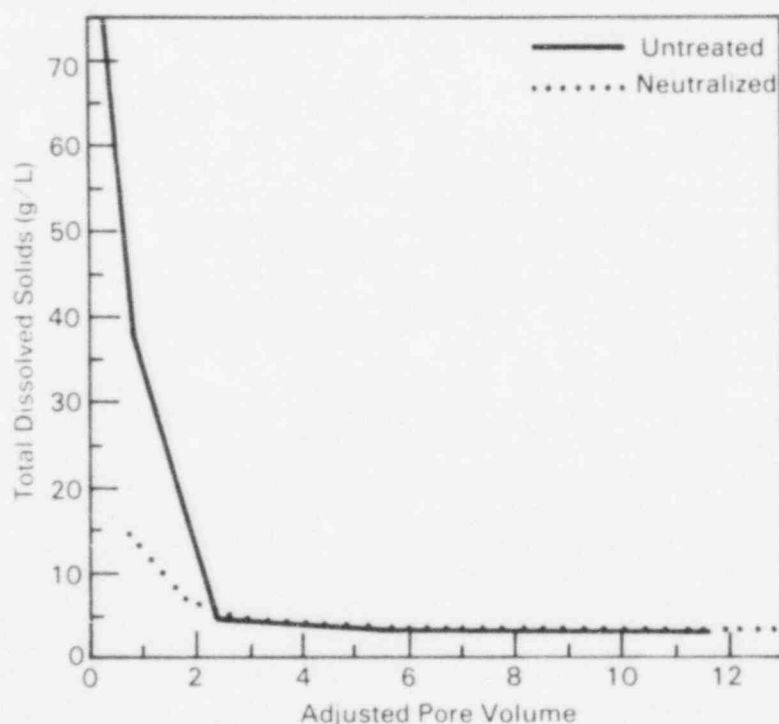


FIGURE 7. Lucky Mc Neutralized and Untreated Tailings Total Dissolved Solids Content Versus Adjusted Pore Volume

As laboratory leachant continued to contact the neutral tailings for ~10 more pore volumes, the column effluent pH remained between pH 7.4 and 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 43. 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 TDS content versus the adjusted pore volume from both the untreated and neutralized Exxon tailings columns is shown in Figure 8. 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

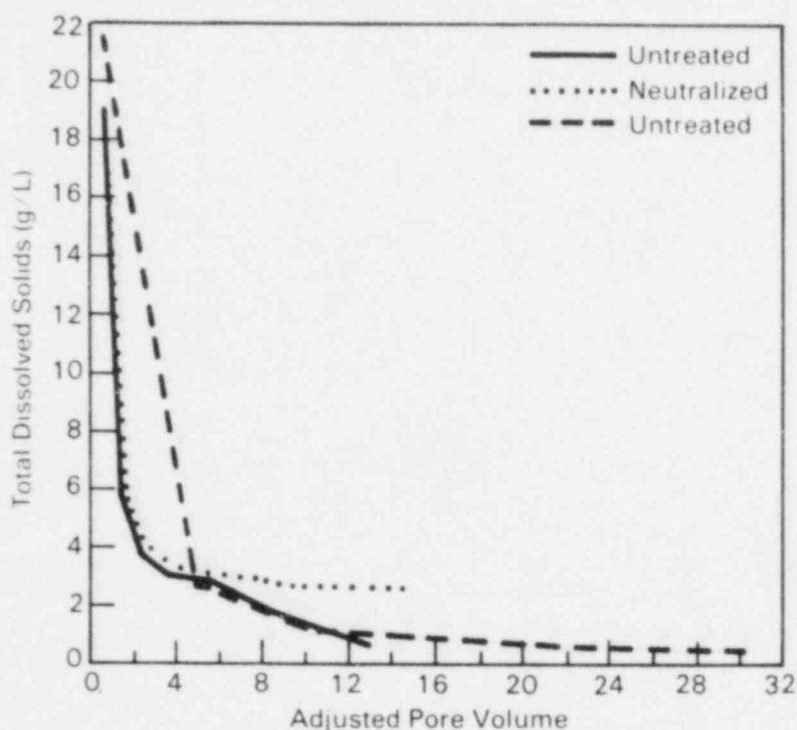


FIGURE 8. Exxon Highland Tailings Neutralized and Untreated Total Dissolved Solids Content Versus Adjusted Pore Volume

matrix was almost complete at the end of the study. Once all the gypsum was dissolved in the neutralized column, we would expect a similar drop to ~0.5 g/L.

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 the Tailings Solution Characterization section). 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 composed 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.

Radium Attenuation Experiments

The results of the radium attenuation experiments comparing the untreated tailings with the amended tailings are shown in Figure 9. The first sample collected from the untreated acidic tailings at an adjusted pore volume of 0.51 contained 3345 pCi/L of soluble radium. As local ground-water contact continued, the activity of the radium leached from the acidic tailings decreased to 1218 pCi/L after 1.6 pore volumes of leaching. The final sample collected in these experiments contained 570 pCi/L at an adjusted pore volume of 2.8, still over two orders of magnitude higher than EPA's drinking water limit of 5 pCi/L total radium. The amended tailings column (neutralized with Ca(OH)_2 plus BaCl_2 added) displayed a high degree of radium attenuation throughout the duration of the experiment. The initial radium activity in the sample collected at an adjusted pore volume of 0.6 was 1.7 pCi/L. This represents a reduction in total radium activity of greater than three orders of magnitude compared to the first sample collected from the untreated acidic tailings. With further leachant contact, the radium activity showed a further reduction to 1.1 pCi/L at 1.72 adjusted pore volumes. The last sample collected from the amended tailings column displayed a slight increase in radium activity. At an adjusted pore volume of 2.8, 6.1 pCi/L of soluble radium were detected in the column effluent. Although the final sample collected from the amended tailings column was 1.1 pCi/L higher than EPA's drinking water limit, a value of 6.1 pCi/L represents a decrease of nearly two orders of magnitude over the untreated tailings column at similar leaching volumes.

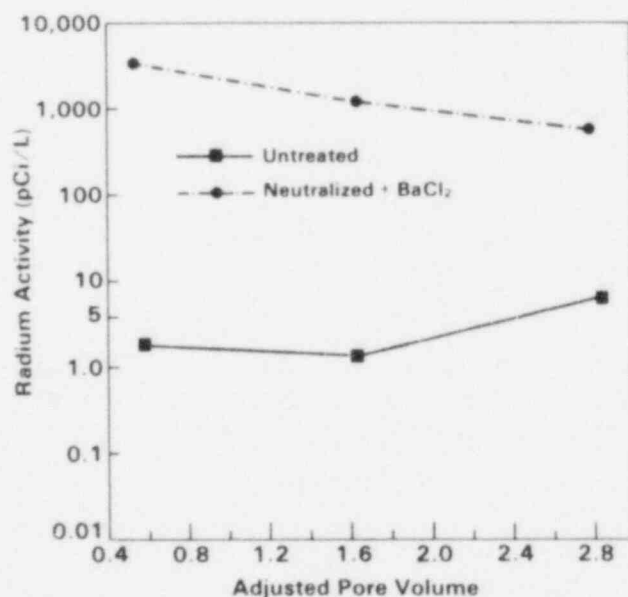


FIGURE 9. Results of Treated and Untreated Tailings Experiments

The mechanism that accounts for the removal of soluble radium from the tailings effluent solution is assumed to be coprecipitation. The reactants in the amended tailings material are BaCl_2 and radium from the acidic tailings. The reaction is shown in Equation (1) and is probably the most common method for radium removal from solution (Moffett 1976, Hostetler and Sherwood 1985^(a)).



As barium sulfate is precipitated, radium is effectively removed from solution by adsorption onto the precipitate surface or is incorporated into the lattice structure of the solid precipitate. Radium removal is very much dependent on the solution parameters associated with the precipitation reactions. For example, there must be an excess of sulfate in solution and the kinetics of the coprecipitation reaction are sometimes slow, so adequate column residence time or reaction time (ranging from hours to days dependent on conditions) is necessary (Moffett 1976; Levins 1983). Since most U.S. mills use a sulfuric acid leach cycle, excess sulfate is typically present. Furthermore, by neutralizing the acidic tailings, the reactants (BaCl_2 and radium) are retained in the column long enough for the reaction to occur. Tailings neutralization causes the pH-dependent ions to precipitate in the pore spaces within the column. The solids formed plug the pathways through which solution normally travels, reduces the flow rate of leachant through the neutral tailings, and therefore increases the residence time for reactions. Further specifics of the effects of tailings neutralization are discussed in the section on effluent solution chemistry.

Effluent Solution Chemistry

The chemical composition data from the effluents collected from both the untreated acidic tailings and the amended tailings columns are shown in Table 44. The data indicate that in addition to a substantial reduction in total radium activity, similar reductions were detected for several of the macro cations, trace metals, and sulfate in the column effluents. Elements such as Al, As, Cr, Cu, Co, Fe, Si, Zn, and SO_4 exhibited large decreases relative to their original concentration in the untreated tailings column effluents. These reductions are attributed to the change in solution pH (acidic to neutral) when the solubility of the above elements is exceeded resulting in precipitation reactions. The reaction products that form are probably metal hydroxides from the added $\text{Ca}(\text{OH})_2$ and the sulfate salts, as indicated by the large decrease in soluble SO_4 detected in the effluents (Table 44). As mentioned previously, the metal hydroxide and sulfate precipitates plug the solution pathways and reduce the flow rate of leachant through the neutral tailings. The flow reduction allows a longer reaction time for the barium and radium reactions to occur and also limits the total volume of

(a) Hostetler, C. J., and D. R. Sherwood. 1985. Personal Correspondence, Pacific Northwest Laboratory, Richland, Washington 99352.

Table 44. Solution Composition of Untreated and Amended Tailings Effluents

Parameter	Untreated(a)			Amended(a)		
	1	2	3	1	2	3
pH	2.40	2.65	2.77	6.52	7.31	7.66
Adjusted pore volume	0.52	1.64	2.77	0.60	1.72	2.84
Total dissolved solids (g/L)	7.22	2.46	1.70	3.25	1.35	1.04
Total radium (pCi/L)	3,345	1,218	570	1.7	1.1	6.1
Macro Ions (mg/L)						
Al	2,100	570	300	<10	<10	<10
Ca	610	560	610	1,020	660	660
Fe	1,400	390	240	<10	<10	<10
Mg	1,740	472	254	1,120	391	202
Mn	197	50	26	36	19	14
Na	1,000	360	230	1,070	280	160
Si	60	34	30	<10	5	6
Sr	2		0.9	<1	<1	<1
Zn	32	7.8	<5.0	<5	<5	<5
Cl	510	170	90	3,860	565	140
NO ₃	<20	<20	<20	<20	<20	<20
SO ₄	25,600	8,100	5,000	3,430	2,780	2,630
Trace Metals (mg/L)						
As	2.82	0.76	0.43	<0.02	<0.05	<0.02
Ba	<0.06	<0.02	<0.02	<0.04	<0.02	<0.02
Cd	0.27	0.08	0.04	0.02	<0.01	<0.01
Co	5.33	1.22	0.83	0.06	<0.02	<0.02
Cr	2.70	0.89	0.55	<0.01	<0.01	<0.01
Cu	2.69	0.76	0.34	<0.02	<0.02	<0.02
Pb	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Se	0.24	<0.03	<0.02	0.22	<0.05	<0.05

(a) Effluent numbers.

leachant to contact the tailings. By limiting or reducing the solution flow through tailings, the leaching of contaminants not attenuated by either neutralization or barium addition is also reduced (Opitz, Dodson and Serne 1985).

Reagent Efficiency and Costs

The total weight of dry reagent added to each 400-mL batch contact experiment was compared to the theoretical amount based on the reagent's equivalent weight needed to neutralize the measured total acidity. This ratio expressed

as a percentage is called the reagent efficiency. Because the fly ash has no theoretical weight, an efficiency for tailings neutralization cannot be calculated. If quantitative estimates of the lime and periclase in fly ash were available, we could calculate a theoretical equivalent weight solely on their composition and then compare that weight with the actual weight of fly ash used. The actual weight of reagent used to neutralize the 400-mL tailings solution, the theoretical weight needed, and the efficiency of the reagent are shown in Table 45. Fly ash results suggest that large quantities of these reagents would be required to treat the acid tailings solutions tested. Most of the other reagents tested required less than half the weight necessary with fly ash treatment. Magnesium oxide and calcium hydroxide neutralization used the smallest quantity of reagent for each of the tailings solutions.

Neutralization efficiency results show that sodium hydroxide and calcium hydroxide are the most efficient reagents tested. Each of these reagents had efficiencies of greater than 89% on each tailings solution with a maximum of 98% for the Lucky Mc tailings solution and sodium hydroxide. The lowest calculated efficiency was for calcium carbonate and Exxon Highland Mill solution (62%).

TABLE 45. Reagent Usage and Cost Data for Several Reagents

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

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

(b) No efficiency could be calculated.

(c) 1982 costs.

Table 45 also lists the reagent costs to neutralize the tailings solution per ton of ore processed. This value is obtained by assuming that 500 gal (1892.7 L) of tailings solution is produced per ton of ore processed and that all the tailings solution requires neutralization. The measured quantity of reagents used to neutralize 400 mL is converted to pounds of reagent/500 gal of tailings solution (1 ton of ore); thus, a reagent cost per ton of ore can be calculated.

Calculated reagent costs for leachate neutralization suggest that CaCO_3 , Ca(OH)_2 , and MgO would be the least expensive of the neutralizing agents tested. In addition, the total acidity of the leachate (see Table 14) is directly related to the cost of the treatment. High total acidity values as in the case of the Lucky Mc tailings solution may triple the cost of treatment over that of one with low acidity such as Exxon Highland tailings solution. These tests can only be used to predict costs on a laboratory scale, but both reagent choice and leachate acidity do influence total treatment costs. Other factors such as shipping charges, capital equipment requirements, and operating expenses must also be considered when evaluating neutralizing agents. These factors are best addressed under actual field conditions at each specific mill. On the other hand, generalized data contained in the neutralization literature review (Sherwood and Serne 1983b) suggest that lime and limestone or a combination of the two are cost competitive at Canadian uranium mills and AMD sites in the United States.

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

The reagent usage and cost data for the limestone/lime neutralization are presented in Tables 21 and 46 for the Lucky Mc and Exxon Highland tailings solutions. For comparison with the limestone/lime neutralization studies, cost data generated during the pH optimization experiments using Ca(OH)_2 alone are taken from Table 21. The calculations show limestone/lime neutralization of acidic uranium mill tailings to be less expensive than incorporating a lime-only solution neutralization. In addition, the data indicate that CaCO_3 neutralization to an intermediate pH of 4.0 is less expensive than initial CaCO_3 neutralization to pH 5.0. This includes, in both cases, the final lime neutralization to pH 7.1. The lower treatment cost is due to the lower CaCO_3 reagent efficiency at solution pHs above pH 4.0. Furthermore, Ca(OH)_2 is extremely efficient for solution neutralization up to pH 7.0 to 8.0. The higher efficiency of lime from pH 4.0 to 7.2 outweighs its higher cost. The additional CaCO_3 required to raise the solution from pH 4.0 to 5.0 costs more despite the lower unit cost of limestone.

TABLE 46. Reagent Usage and Cost Data for Limestone/Lime Neutralization

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

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

(b) Lime-only solution neutralization directly to pH 7.2 or pH 7.3 for the respective solution from pH optimization data (Table 20).

The combination reagent treatment cost of \$0.21/t of processed ore for the Exxon Highland solution and \$0.59 for Lucky Mc solution is the least costly solution treatment tested during the course of this laboratory study.

CONCLUSIONS

SUMMARY OF NEUTRALIZATION PROCESSES

Of the six reagents studied (lime, limestone, caustic soda, soda ash, combined limestone/lime and combined alumina/lime/soda), a combined treatment of limestone and lime appears best, especially for uranium mill tailings containing ferric iron. The limestone economically neutralized the tailings acidity while the lime increases the pH to 8.0, an optimum level for heavy metal removal. For those uranium mill tailings containing ferrous iron, lime alone would be most economical and efficient. Neutralization with these calcium-based reagents are capable of removing acidity, trace metals, and radionuclides from acid mine drainage and Canadian uranium mill tailings. Removal of radionuclides and trace metals from U.S mill tailings has not been documented, but because of their similarity to AMD and Canadian mill tailings wastes, we expect neutralization techniques to be quite effective for most radioactive and trace metal potential contaminants.

Neutralization may not remove all potentially mobile contaminants. The available literature concentrates on its ability to remove transition metals (e.g., Fe, Cu, Zn, Cd), selected radionuclides (U, Pb, Th, Ra), and sulfate. For other constituents such as alkaline earth metals, NH_4^+ , and NO_3^- , data are sparse.

Summary of Fixation Processes

In general, fixation processes are not well suited for uranium mill tailings because they increase volume and weight of the waste (Table 11 describes the advantages and disadvantages of the various processes). For example, some of these treated solids contain as little as 40% of the original waste, which significantly increases the waste volume. An effective lime-based solidification process, such as Pos-O-Tec, costs between \$10 to \$17/ton of tailings. An effective cement-based solidification process has an estimated cost of \$7/ton of tailings. The bitumen-based solidification process works only on dried tailings and is exceedingly costly: \$140 to \$420/ton of tailings treated. For comparison with the neutralization costs discussed in the previous section, we converted the 1000-gal-based costs to per-ton costs. Neutralization using lime or limestone would cost \$0.30 to \$0.17/ton of tailings (assuming a specific gravity of slurry of 1.4) or ~1% of the solidification costs. Thus, applying fixation processes to uranium mill tailings waste treatment should be limited and, if used at all, only on the most toxic fraction of waste stream, such as concentrated slimes. Strictly limiting the volume of tailings treated may make this technique feasible.

Summary of Ore and Tailing Solids Treatments

Other ore milling technology and tailings leaching that remove potential pollutants prior to disposal are in their infancy. In general, the acid or salt lechants require more complex process steps, new capital equipment, and often produce waste streams with the same or greater potential hazard as the

conventional sulfuric acid leach process. For tailings treatment, long-term hazards reduction via radium-226 removal will require removing thorium-230 also because of the ingrowth of radium-226 daughters. After 1000 years, ingrowth reaches 35%, and after 10,000 years, 100% of the existing thorium-230 activity. Radium-226 represents the largest potential radiation hazard in tailings and thus is the focus of most treatment schemes.

The most promising alternative ore processing technique reviewed uses ore preconcentration via flotation to remove sulfide minerals and high-intensity magnetic separation to remove radionuclide-laden minerals. The two concentrates combined represent only 33% by weight of the original ore yet contain 97% of the uranium, 98.5% of the radium, 92% of the thorium, and 98.5% of the pyrite. The bulk tailings contain only 25 pCi/g radium-226 and are environmentally acceptable for mine backfill or uncontrolled pit disposal. The concentrates may be uranium extracted by conventional sulfuric acid leach to yield 1/3 the typical amount of waste. The same process may be used on spent tailings to remove residual sulfide minerals and radionuclides to produce a bulk tailings, ~2/3 of which have very low hazard potential and 1/3 of which contain the concentrated radioactive waste. Removal of pyrite also reduces the risk of tailings pile re-acidification upon pyrite oxidation, which is a demonstrable problem in Canada.

Summary of Effluent Seepage Treatments

The adsorptive reactions of several clays, zeolites, hydrous oxides, and soils/sediments for the radionuclides uranium, thorium, and radium were reviewed. Uranium is only moderately adsorbed because of its high solubility under oxidizing conditions and strong anionic carbonate complexes. Thorium is insoluble in neutral pH environments and readily retained in soils. Radium appears to adsorb readily to clays, soils, and sediments via ion exchange-like processes.

Ion-exchange resins have been used to remove radium from low-quality municipal and drinking water sources and mine wastewaters. Common cation exchange resins are of limited use as calcium, magnesium, and other multivalent cations load the exchange sites and compete too strongly. Other specialized resins show good radium selectivity from low TDS neutral mine waters, but column regeneration is a problem. Without good column regeneration the cost for treatment is high.

At best ion exchange appears useful for removing radium from only neutralized, low-TDS waters. For direct application to acidic tailings liquids with the 15,000 to 35,000 ppm TDS, more testing is needed. No specific costs for ion-exchange removal of radium for mine waters are available, but for a 1000 gal/min drinking water plant using conventional strong acid cation resins, the capital costs are estimated at \$2,000,000 (1976 dollars) and 20¢/1000 gal for operating costs. The capital costs greatly exceed those for BaCl_2 treatment but the operating costs are 3.5 times less.

Summary of Other Treatments

Less common treatment techniques to remove radionuclide and trace metals from uranium mine and mill-related wastes include biological treatment (adsorption onto algae), solvent extraction, reverse osmosis, and selective membrane mineral extraction. The techniques are not well studied, but aside from selective membrane mineral extraction, they appear to be of limited use for practically treating high-acid high-salt mill tailings solutions. Biological growth is probably inhibited in these solutions and reverse osmosis would probably be only 85 to 95% efficient for most constituents. More information on the proprietary selective membrane mineral extraction technique is needed to assess its usefulness.

Summary of Nonradioactive Selective Extraction Techniques

Techniques such as sulfate precipitation via barium chloride treatment, sulfate removal by anion exchange, nitrate removal by biological denitrification, nitrate removal by anion exchange, ammonium removal by ammonia stripping, biological nitrification, and cation exchange on clinoptilolite were discussed but no operating data or costs for such specific removal techniques are available for uranium mill effluents.

The most mobile constituents in tailings effluents will probably be the anions SO_4^{2-} and NO_3^- , both of which can exceed drinking water and irrigation/livestock concentration limits by several orders of magnitude.

Treatment Effectiveness and Recommendations

The use of neutralization processes to treat uranium mill tailings leachate appears to significantly reduce contaminant mobility based on experience with AMD and other industrial-generated acidic solutions. Because of the high concentrations of certain contaminants, it is possible that neutralization will not be as effective as it would be for AMD. Contaminants that do not appear to be effected by neutralization techniques include nitrate and ammonia. Sulfate concentrations are only reduced if calcium based reagent are used as neutralizing agents. Manganese and iron may remain slightly insoluble if they are not present in oxidized forms. The high iron concentrations present in uranium mill tailings solutions may require long residence times in the aeration vessel to ensure the total oxidation of ferrous iron. If the iron is present in the ferric oxidation state, treatment of the solution is rapid with only short residence times. Pretreatment oxidation or long storage times prior to treatment would both allow the iron to oxidize and make the neutralization process more efficient.

At U.S. mills, five specific situations are foreseen where the neutralization processes might be beneficial. These scenarios are

1. to hasten the closure process at the time of mill decommissioning; excess solution present in the tailings impoundment or in an evaporation pond may be treated

2. to avert the possibility of an uncontrolled discharge of acid leachate, as an emergency measure
3. to protect the quality of a near-surface ground-water resource
4. to reduce the volume of leachate present in a tailings impoundment thereby increasing the usable disposal capacity
5. to mitigate the effects of a release of acidic solution through surface seeps adjacent to tailings disposal areas.

Neutralization of uranium tailings leachate with calcium alkalies appears to be the preferred technique. A two-stage combination limestone-lime treatment would be the optimum process for ferric iron uranium mill tailings solution. The majority of the solution acidity would be buffered by inexpensive limestone in the first stage of the process. The second stage would take the pH to approximately 8 with lime which is the optimum pH for removal of heavy metals from AMD. Another advantage of the limestone-lime process is that the sludge generated has a high percentage of solids. This makes handling and sludge disposal relatively easy.

For the treatment of ferrous-iron-rich uranium tailings solution, we recommend lime treatment. The high pH generated in the lime process speeds the oxidation of the iron which is more rapid at elevated pH values (pH 8 or higher). This process would be slightly slower than the combination process at neutralizing ferric uranium tailings solution, but far quicker when it comes to ferrous tailings leachate.

The limestone-only process is not recommended for solutions containing high iron concentrations. For this reason a single-stage limestone process should only be used in emergency situations to avert spills of acidic leachate. Sodium reagents should also only be used under emergency conditions. The high quantity of sodium alkalies required to neutralize extremely acidic uranium mill tailings solution adds hazardous concentrations of sodium to the treated water.

The alumina-lime-soda process has not been studied in depth. The performance of this process in reducing trace element concentrations is unknown. Use of this process is the most expensive of the six neutralizing techniques reviewed.

Fixation techniques reviewed for this paper had one common problem: these techniques can represent a major expenditure. Prices for solidification ranges from \$1.50 to \$420/ton of tailings. In terms of product value to solidification cost, the processes reviewed cost from 5 to 1400% of the uranium price. This was calculated based on the recovery of 1 lb of uranium at \$30/lb for each ton of tailings solidified. The use of these type of treatments is only feasible if the waste to be processed is highly toxic and the volume is relatively small.

Specific constituent removal processes need careful cost/benefit analyses. The cost of radium removal from Canadian uranium mill waste effluents using BaCl_2 treatment is similar to the cost of neutralization (\$0.68/1000 gal versus \$0.20 to \$1.00/1000 gal). In Canada the mill sites are often located in areas with little soil, high water tables and close to surface water bodies. Thus, the natural sediment/soil radium retardation processes are not effective and man-induced immobilization required by government agencies. For typical U.S. mill sites where natural soil/sediment neutralization processes are prevalent and ground-water supplies usually distant from the disposal pits, no general statement on cost effectiveness is possible. We recommend additional field studies and long-term consequence modeling using developing sophisticated coupled hydrologic-chemical predictor codes to better assess the need for mill tailings waste treatment and/or new disposal schemes. To evaluate the most economical and practical treatment/disposal schemes, one must consider the natural ability of soils and sediments to neutralize acid mill wastes and retard the migration of potential contaminants.

Multi-Reagent Batch Neutralization Study

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

Results of the crystalline mineralogical analysis have provided limited information on the chemistry of the solids formed during neutralization. Crystallization of gypsum must occur rapidly under test conditions. No other crystalline substances were identified but other amorphous Fe, Al, SiO_2 , and Mn compounds are probable. Formation of such amorphous compounds are common in acidic soil systems when neutralized.

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

Hydrated lime neutralization removed 62 and 54% of the total dissolved solids content of the Lucky Mc and Exxon Highland tailings solution, respectively. For the elements Al, Fe, Si, Co, Cr, Pb, V, and ^{230}Th for both solutions the hydrated lime removed >95% from solution. Greater than 90% of the Mn, As, Cu, and ^{238}U and <80% of the Cd, Mo, Zn, and Ra were removed from

the solutions when neutralized with hydrated lime. Less than 20% of the Ca, Na, K, NO_3 , Cl, and Se present in the tailings solutions was removed when neutralized.

Based on water quality guidelines that to date have been used to regulate wastewater disposal activities, our laboratory observations suggest that selenium, sulfate, and TDS will still exceed maximum control limits by ten to a hundred times. As sediment sorption is not high for these constituents under oxidizing conditions and neutral to slightly basic pH values, substantial ground-water dilution may be required.

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

pH Optimization Study

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

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

Limestone/Lime Neutralization Study

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

initial neutralization to pH 5.0 was effective in reducing the contaminant concentrations in solution, it was calculated to be more costly and resulted in nearly the same end product.

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

Treated effluent quality data support the premise that additional solution treatment (i.e., specific ion-removal techniques) will be necessary for ions such as Mo, Se, and sulfate, and for TDS content. These constituents in neutralized solution still exceed EPA's MPC contaminant levels by ten to one hundred times. Other constituents of concern include Na, Cl, and Co and should be considered on a case-by-case basis, since their concentrations in acidic tailings solutions vary dramatically from site to site.

Contaminant Complexation Study

Neutralization of acidic uranium mill solutions with either solid limestone or hydrated lime can substantially improve solution quality. At the optimum pH for neutralization (pH = 7.3), the TDS solids 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 solution beyond 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 (pH 6.5 to 9.0). Thermodynamic calculations suggest that the carbonate

should only affect zinc solution concentrations above pH 8.5. Neutralization with limestone and hydrated lime proved ineffective in removing Na, K, or the anions Cl and NO₃.

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 pH = 7.0 but under 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 CO₂ 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 solution 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.

Sludge Leaching Study

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

The tailings solution characterization data enforces the fact that neutralization studies need to be performed on a case-by-case basis. Both mill tailings solutions studied employed a sulfuric acid solution as the primary leachate. Despite this fact, the Lucky Mc solution contains roughly three times more mass of constituents as compared to the Exxon solution. This includes macro ions such as Al, Fe, Mg, Mn, Cl, and SO₄, TDS content, and total acidity values. The quantity of reagent required to neutralize different tailings solutions is very much dependent on the factors mentioned above.

The results presented in this progress report for the Lucky Mc and Exxon tailings solution neutralization consider a rather wide range of tailings solution constituent concentrations and solution properties. Acidic tailings

solutions from many other mill sites should fall within the range of solution parameters presented here. In that sense, neutralization is an efficient and cost-effective means of controlling or reducing many contaminant concentrations in acidic uranium mill tailings solutions. But for all solution parameters to meet water quality guidelines, further treatment may be necessary for those constituents not effectively removed by neutralization such as Mg, Na, Cl, SO₄, and Se and in selected cases Mo, Co, and Cd.

Tailings Leaching Study

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 solids 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 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. They 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 for the molybdenum concentrations from Lucky Mc tailings. For some constituents, such as selenium and radium-226, additional solution treatment (i.e., specific ion removal techniques) may be necessary to meet EPA drinking water regulations. In neutralized solutions, these constituents still exceed the EPA MPC 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).

Radium Attenuation Study

The results of the radium attenuation tests indicate that adding barium chloride to tailings can be an effective means of limiting the amount of soluble radium leached from acidic uranium mill tailings. Initial radium activities in the untreated acidic tailings (0.52 pore volumes) were greater than 3300 pCi/L. After 2.8 pore volumes of leaching, the radium activities were 570 pCi/L, still greater than two orders of magnitude higher than EPA's drinking-water standard of 5 pCi/L. At similar pore volumes, the radium activity of the barium treated tailings was 1.7 pCi/L (0.60 pore volumes) equivalent to a reduction by a factor of greater than 1900. At 2.8 pore volumes, the radium activity was 6.1 pCi/L or 1.1 pCi/L higher than EPA's drinking-water standard but still a reduction of nearly two orders of magnitude.

Macro cation and trace metal reductions also occurred in the effluents from the neutralized and barium-treated column. This reduction was generally indicated by the reduction in the effluent total dissolved solids content in the amended tailings column, 7.22 g/L in the untreated tailings column effluent (0.52 pore volumes), compared with 3.25 g/L in the amended tailings column effluent (0.60 pore volume).

A tailings amendment technique such as this barium chloride/hydrated lime treatment effectively reduces the amount of soluble radium, macro ions, and trace metals that can be leached from acidic tailings. Using tailings treatment techniques, such as the one described above, appears to be an effective method for preventing the migration of radium acidic tailings.

Reagent Costs

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

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

SUBTASK C. FIELD TESTING

INTRODUCTION

The objective of this study was to investigate the use of selected neutralizing agents and techniques to evaluate their effectiveness, benefits, and costs in neutralizing acidic uranium mill tailings solution on a field site scale.

The step-wise approach suggested for this project was to first carry out laboratory studies to identify the most effective neutralizing reagents (e.g., lime or limestone) to immobilize and reduce the potential leaching of toxic trace metals, radionuclides, and macro ions from uranium mill tailings and tailings solution. The second step was to demonstrate the use of the most effective reagents under larger-scale field demonstrations.

The acidic uranium ore-leaching process used by the majority of uranium-processing plants is a sulfuric acid-based leaching cycle. The acidic solution used for leaching the uranium-bearing ore also dissolves other constituents present in the ore. These constituents include trace metals, such as arsenic, selenium, lead, cadmium, chromium, and molybdenum. In addition, radionuclides besides the desired uranium are also dissolved and include, among others, lead-210, thorium-230, and radium-226.

Upon discharge to the disposal facility, the uranium mill tailings solution remains in the acidic, low pH range (pH 1.2 to 2.5), and contains a high TDS content (10 to 40 g/L), high ionic strength, high concentrations of cations (Al, Fe, Ca, Mg, and Na) and anions (Cl, NO₃, and SO₄) along with the elevated concentrations of the previously mentioned trace metals and radionuclides.

The concentrations of various constituents in two typical acidic uranium mill tailings solutions are shown in Table 14. Also shown in Table 14 are the results of analyses performed on the same tailings solutions after neutralization with lime [Ca(OH)₂] to a pH of 7.5. By comparing the results of the analyses of the acidic tailings solutions and the neutralized tailings solutions, many elements with high concentrations at low pH dropped below detectable limits as the pH increased to pH 7.5. The maximum concentration of many of these potential contaminants is limited by their solubility. In turn, the solubility of these elements in many cases is pH dependent. Several contaminants in the tailings solutions are less soluble at higher pHs; thus, as the acidic tailings solutions are neutralized, precipitation reactions occur and reduce the solution concentration of numerous major and trace elements.

The MPCs for primary and secondary drinking water as set by the U.S. Public Health Service and EPA are shown in Table 13. In the low pH acidic uranium mill tailings solutions, several elements have concentrations higher than those listed in Table 13. After neutralization, many of the constituents' concentrations have either decreased below the drinking water standards or are below detectable limits for analysis.

The results of this project will assist in evaluating the cost benefits and the need for treatment via neutralization of acidic uranium mill waste solutions. Treatment of uranium mill wastes as they are generated may prove to be more cost effective than long-range remedial action measures necessary at many sites to ensure contaminant immobilization.

To effectively demonstrate the usefulness of neutralization on a more realistic scale than previous laboratory studies, a field-scale demonstration plan is presented, which allows an evaluation of the benefits, costs, and usefulness of neutralization of acidic tailings solution.

FIELD DEMONSTRATION OBJECTIVES

The work described in this program plan for conducting field-scale experiments on acidic tailings solution neutralization has three main objectives:

1. to demonstrate the effectiveness of neutralization to reduce contaminant concentrations in acidic uranium mill tailings solution.
2. to determine the degree of contaminant removal of selected trace metals and radionuclides from neutralized uranium mill tailings solution under field-scale conditions for comparison with laboratory results.
3. to develop operational safety procedures for tailings solution neutralization so that they may be incorporated at other mill sites where applicable.

The demonstration plan proposed to meet these objectives includes several key elements. Among these are studies involved in the selection of most efficient neutralizing reagent or reagents. Reagent selection is based on criteria such as amount of generated waste product, ease of reagent handling, reaction rates, cost, and reagent efficiency. In addition, studies that determine the optimum pH for solution neutralization will be valuable for choosing the most cost-effective neutralization technique. The optimum pH is defined as the point where continued addition of a neutralizing reagent (thereby increasing the solution pH) does not further reduce contaminant concentrations significantly. Furthermore, leach testing of the sludge material generated on neutralization of acidic tailings solution will be performed to assess the sludge's long-term contaminant attenuation properties.

FIELD DEMONSTRATION DESCRIPTION

The concept for neutralization of acidic uranium mill tailings involves adding an intermediate step between the time the acid solution/slurry exits the milling process and prior to its discharge into an evaporation or drainage pond. During the intermediate step, the acid tailings solution will be reacted with a neutralizing reagent(s) in a large capacity mixing apparatus until a preset solution pH is reached (determined by laboratory experiments as most desirable). The slurry is then discharged into the disposal pond. The primary interest of this demonstration plan is to represent a full-scale disposal

scenario as opposed to smaller-scale laboratory studies. The following alternatives describe the activities necessary to perform the larger field-scale treatment of acidic tailings solution and to meet the demonstration objectives identified earlier.

Alternatives

The field demonstration of neutralization techniques and selected neutralizing reagents will be one of three alternatives considered below:

Alternative A - The outright purchase of the necessary equipment for neutralization of a specified volume ($\approx 10^6$ L) of tailings solution using one reagent or a combination of more than one reagent as determined by laboratory experiments as most beneficial for the selected demonstration site.

Alternative B - The use of existing equipment and facilities at a milling site that currently neutralizes the acidic solution via incorporation of our chosen reagent or a combination of more than one reagent as determined by laboratory experiments as most beneficial.

Alternative C - Analysis and evaluation of the efficiency, costs, and benefits of an existing neutralization technique and reagent(s) in use at a mill site that currently treats acid tailings solution.

The criteria involved in selecting one of these three alternatives for fulfillment of the demonstration program is based primarily on 1) sponsor concurrence, 2) mill site owner/operator concurrence, 3) time allocated and funding availability for project completion and 4) site location and equipment availability.

TECHNICAL SCOPE

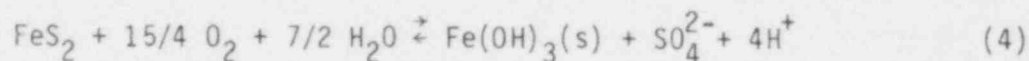
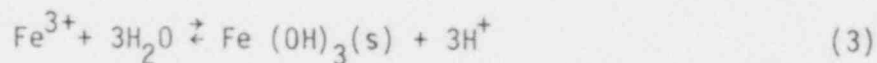
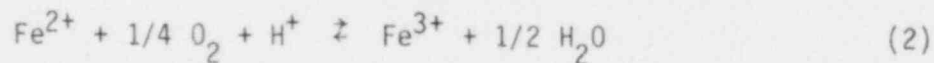
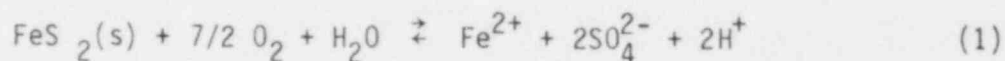
Regardless of which one of the three above alternatives is chosen, the following common activities are necessary: 1) site characterization and 2) mill production and discharge evaluation.

Site characterization will evaluate the physical and chemical aspects of the feed material, the discharged tailings, tailings solution, mill process water, and the sediment in and around the disposal facility. Tests on the following materials and solutions will include the following:

Local Sediments	Saturated paste or 1:1 extract pH, Eh, and electrical conductivity
	Cation exchange capacity
	CaCO ₃ content
	Moisture content
	Acid-buffering capacity
	Permeability of hydraulic conductivity

Local Sediments	Particle-size distribution Particle density
Tailings (Solid)	Particle-size distribution Moisture retention Radionuclide content 1:1 extract pH, Eh, and electrical conductivity 1:1 extract analysis for cations, anions, and radionuclides
Tailings Solution	pH, Eh, and electrical conductivity TDS Total suspended solids Cation analyses Anions analyses Ammonia analysis Radionuclide content Total acidity
Mill Process Water	pH, Eh, and electrical conductivity TDS Cation analyses Anions analyses Radionuclide content Ammonia analysis

Another important factor necessary for adequate site characterization is determination of pyrite content in the feed material and the discharged tailings. Pyrite (FeS_2) oxidation releases ferrous and sulfate ions and acidity into the pore water of the tailings as shown in Reaction (1) of the following reactions:



The ferrous ions produced in Reaction (1) may then be oxidized to ferric (Fe^{3+}) ions as shown in Reaction (2). Ferric ions are much less soluble than

ferrous ions which then, upon hydrolysis, can precipitate out of solution to form insoluble ferric hydroxide releasing more acidity into solution as illustrated in Reaction (3).

The overall reaction [shown in Reaction (4)], illustrates how the low solubility of Fe^{3+} makes this one of the most acidic of all weathering reactions (Stumm and Morgan 1981).

This slow oxidation to produce hydronium ions can eventually consume the hydroxides added in the neutralization step and result in a gradual reduction in pore water pH. Pyrite oxidation is a slow process and predominately a problem in Canadian ores because their pyrite content is higher than typically found in uranium ore in the United States (Cherry et al. 1980). However, the pyrite content of the ore and tailings at the chosen demonstration site will be necessary for assessing the long-term effectiveness of acid solution/slurry neutralization.

The mill production and discharge evaluation will provide insight into the types and quantity of materials and chemicals added to leaching solution for uranium extraction. By knowing in greater detail the constituents used in uranium production, better predictions on long-term stability of the generated waste and contaminant attenuation may be formulated. These types of analyses will provide the basic groundwork necessary for the eventual selection of neutralization techniques and reagents.

TECHNICAL APPROACH

Implementing the three previously mentioned field demonstration alternatives will commence depending on approval and funding availability from the NRC. If alternative C is chosen, the emphasis will be on reviewing existing neutralization processes at mill sites for their effectiveness, costs, and benefits for treating acidic tailings solution. The long-term integrity of solution treatment will be evaluated by performing analyses on the neutralized solution and the sludge materials that result from solution neutralization. If possible, treated samples with the longest residence time in the neutralized solution/slurry disposal impoundment will be collected and subsequently evaluated for their contaminant attenuation properties. In addition, a comparison of the treated and untreated uranium mill tailings solutions will be performed to determine the degree of contaminant removal after solution neutralization. Furthermore, discussions with mill owner/operators would provide insight and suggestions for operating and maintaining a solution treatment facility.

If Alternative A or B is chosen, reducing contaminant mobility by using neutralizing reagents and techniques will be investigated by conducting two tasks. The first task, performed in conjunction with the site characterization studies, is a critical review of the properties of the uranium mill tailings solution from the selected demonstration site. If the mill tailings solution from the demonstration site has similar or identical characteristics (e.g., pH, total acidity, TDS content) as the tailings solutions previously studied in the laboratory, then implementation of the most promising neutralization technique may commence. Based on initial laboratory studies with representative

solutions, the most promising technique for contaminant reduction in uranium mill tailings solution is, first, the addition of CaCO_3 to pH 4.0 to 4.5 followed by Ca(OH)_2 addition to the desired optimum pH. Should the tailings solution from the demonstration site possess characteristics unlike the previously evaluated solutions, laboratory studies will be necessary to determine the most cost effective and beneficial means of solution treatment.

The second task consists of studies including techniques and reagent testing on a large scale in field tests at the selected tailings site. The most promising, cost-effective contaminant attenuation procedure will be determined based on the site-specific tailings solution characteristics and then field demonstrated. The benefits of neutralization will be studied including solution treatment quality and contaminant retardation. The long-term effectiveness of this method of acidic solution treatment will be established by periodic monitoring of the treated solution/slurry over time. The criteria needed for carrying out full-scale neutralization at a selected milling operation will also be established from the results achieved in this intermediate-scale neutralization demonstration.

Task 1: Laboratory Testing

The ability of selected neutralizing reagents to immobilize trace metals, macro ions, and radionuclides will be determined. The use of more than one reagent (i.e., limestone to pH 4.0 followed by lime addition to optimum pH) will also be evaluated on tailings and tailings solution from the selected field site. The optimum neutralizing pH for the site specific solution will be determined based on the rate of removal of contaminants in the tailings solution. Preliminary studies on the long-term stability of the methods and reagents will be assessed with the laboratory tests and eventually the field test results. Long-term contaminant attenuation will be estimated by batch and flow through column-leaching experiments of the sludge and subsequent contact of leachate with sediments.

Task 2: Field Studies

Current Technology

The technology and equipment for implementing the neutralization field project will be reviewed if Alternative A is chosen. Equipment similar to that currently used will be evaluated for its ability to resist mechanical degradation caused by the corrosive nature of acidic solutions. The most promising implementation technique will be identified for use in the field test. If Alternative B or C is chosen, the review will be strictly limited to the technology and equipment in use at mill sites that currently neutralize acidic tailings solution.

Field Test

Exercising one of the three alternatives (A, B, or C) will depend on funding allocated for the field demonstration and NRC approval. The neutralization field demonstration will be conducted after owner/operator concurrence and the necessary permits are obtained.

Alternative A Description. Alternative A would require the acquisition of the necessary equipment to neutralize a specified volume of acidic tailings solution using either one reagent or a two-component neutralization scheme. This option is the most costly of the three because of the equipment purchase for the field demonstration. Once the equipment is acquired, the costs of Alternatives A and B will be very similar. The size of the field demonstration study will be dictated by the requirements of the equipment to be used. Efforts will be made to minimize the expenditures on equipment that will in turn result in smaller disposal facilities required for the neutralized solution. For this reason, lower capacity equipment is optimum for this study. Preliminary estimates on the neutralized solution disposal facility size are 25 m x 25 m x 3 m deep. Once again the size will be dictated by the equipment, but every effort will be made to purchase equipment that can neutralize enough tailings slurry to fill a pit with the above dimensions. Contouring and site preparation will be accomplished with standard construction equipment to minimize costs. After installing the neutralizing equipment, the neutralizing reagent(s) will be incorporated into the system and contacted with acidic uranium mill tailings solution. Factors such as reaction rates, solution/reagent contact time, reagent consumption, and waste material production rate will be used for evaluating the effectiveness, cost, and benefits of acid solution neutralization. Onsite analysis of solution pH, electrical conductivity, and sludge volume will occur at periodic intervals. Furthermore, samples of solution and sludge material will be collected at various intervals and will be characterized for solution constituent content (i.e., cations, anions, and radionuclides) and sludge properties (i.e., moisture retention, radionuclide content, and contaminant immobilization) through a series of batch and column leach tests. Parameters to be analyzed on the leachate and sludge include those listed in the site characterization section for the tailings solids and tailings solution. These tests will aid in the evaluation of the long-term stabilization of the contaminants associated with the uranium mill tailings solution.

Alternative B Description. Alternative B involves using existing neutralization equipment and facilities at a milling operation that currently neutralizes or plans to start neutralizing acid solution at the time of the field study. This option involves incorporating the most promising neutralizing reagent(s) as determined by the site characterization and laboratory evaluation task outlined previously into the current treatment facility, provided the reagents and techniques are compatible with existing equipment. In the event that the most promising neutralizing technique and reagent(s) differ from that currently employed at the site, a review of existing procedures will be made for comparison. The review will include costs and benefits of both techniques. Post-treatment analyses will include the same characterization as outlined in the Alternative A description.

Alternative C Description. Alternative C deals strictly with the review, analyses, and evaluation of a current acid solution treatment facility. This alternative is estimated to be the least costly of the three alternatives described. Alternative C would emphasize post-treatment characterization as outlined in the Alternative A description and would look into factors such as treatment effectiveness over time, benefits of solution treatment, sludge handling practices, treatment cost analysis, and identification of problems resulting from implementing solution neutralization.

TECHNICAL PROGRESS

First Year (Expected Results)

The criteria for optimum benefits, costs, and effectiveness will be established in the laboratory. The optimum neutralization pH, above which contaminant removal does not increase significantly, will be determined. The most promising neutralization technique and reagent(s) will be determined and selected for the field test based on site-specific details. Current studies indicate that limestone (CaCO_3) addition to pH 4.0 to 4.5 followed by hydrated lime (Ca(OH)_2) addition to an optimum pH of ≈ 7.2 is the most cost effective for several tested tailings solutions. In addition, the stability of the generated waste product (sludge) will be evaluated for its ability to immobilize contaminants during leach testing with neutralized solution or ground water.

A full-scale demonstration is planned to show the overall effectiveness and benefits of the chosen neutralization procedure. This demonstration will include treating a specified volume ($\approx 10^6$ L) of acidic uranium mill tailings at a selected site. This site will be characterized prior to the field demonstration and monitored after the field demonstration in order to establish the overall effectiveness of the neutralization procedure.

Second Year (Expected Results)

During the second year, the waste products and treated solution generated during the first year will be monitored. Monitoring results will be used to assess the initial effectiveness of acid solution neutralization. From this information, plans can be developed for application of this procedure to additional sites if field results confirm the laboratory experiments on the effectiveness of acid solution neutralization. In addition, plans for field site closure will be drawn up during the middle of this year.

Third Year (Expected Results)

The plans for field site closure drawn up during the second year will be implemented in the third year and carry over into the beginning of the following year. Also during the third year, the field site closure and decommissioning will be completed. During the closure procedure, the neutralized material will be monitored for a final time to aid in the overall evaluation of the

long-term integrity of neutralized uranium mill tailings solution. A final report on the field demonstration and laboratory studies will be submitted during the fourth quarter of the final year.

Milestone Schedule

For a description of the key milestones for the field demonstration program on acidic uranium mill tailings solution neutralization, see Opitz and Serne (1983).

Field Demonstration Program Budget

A breakdown of the budgets required for each year for each alternative as of 1983 can be found in Opitz and Serne (1983). Implementing any one of the three alternatives in future years would require a thorough reevaluation of funding requirements for the period of time that the project would cover.

SAFETY

A safety analysis and review will be performed before implementing one of the three alternatives at the selected site. The review will evaluate and determine that:

- potential hazards are clearly identified
- reasonable measures to eliminate or control potential hazards have been taken
- radiation work procedures have been developed
- site-specific rules and procedures are followed to ensure compliance with state and federal regulations.

To ensure that precautionary measures are followed at all times and to minimize risks during the field demonstration, one member of the onsite technical staff will be designated as site safety officer. Prior to the actual demonstration, the designated safety officer will review all established working procedures to be implemented over the course of the program with PNL's departmental safety officer. In addition, coordination with PNL's Hazardous Materials Transportation Officer will be initiated prior to transporting any materials or samples that may be considered radioactive or hazardous.

PROGRAM CONTROL

The actual technical direction of the demonstration program will be performed by Brian Opitz, Task Leader for Tailings Neutralization, Alternatives for Immobilizing Toxic Materials in Tailings. Principal investigators for the demonstration program include R. J. Serne, a Technical Leader for numerous URR Programs, D. R. Sherwood, and W. J. Martin.

All coordination of contractors for construction work and equipment will be administered by the task leader through PNL's subcontracts and procurement department.

Quality assurance procedures and requirements will be followed throughout the project. The quality assurance plan developed for ongoing NRC work at PNL will be adapted for this project.

For a complete description of the field demonstration plan see Opitz and Serne (1983).

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13. ABSTRACT (200 words or less)

This final document, in a series of six, summarizes research completed since the beginning of the project. Three subtasks are included: Subtask A - Neutralization Methods Selection; Subtask B - Laboratory Analysis; and Subtask C - Field Testing.

Subtask A reviews treatment processes from other industries to evaluate if current waste technology from other fields is applicable to the uranium industry. This task also identifies several reagents that were tested for their effectiveness in treating acidic tailings and tailings solution in order to immobilize the contaminants associated with the acid waste.

Subtask B describes the laboratory batch and column treatment studies performed on solid waste tailings and tailings solution over the course of the project. The evaluation of several reagents identified in Subtask A was based on three criteria: 1) treated effluent water quality, 2) neutralized sludge handling and hydraulic properties, and 3) reagent costs and acid neutralizing efficiency.

Subtask C presents a field demonstration plan that will evaluate the effectiveness, costs and benefits of neutralizing acidic uranium mill tailings solution to reduce the potential leaching of toxic trace metals, radionuclides and macro ions from a tailings impoundment.

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