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Laboratory Characterization and Leaching of Uranium and Hazardous Materials from Oak Ridge Y-12 Plant Wastes Contaminated with Depleted Uranium

J. L. Collins
W. L. Pattison
A. D. Kelmers

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Chemical Technology Division

LABORATORY CHARACTERIZATION AND LEACHING OF URANIUM AND HAZARDOUS MATERIALS FROM OAK RIDGE Y-12 PLANT WASTES CONTAMINATED WITH DEPLETED URANIUM

J. L. Collins
W. L. Pattison
A. D. Kelmers

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OAK RIDGE Y-12 PLANT
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prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
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CONTENTS

LIST OF FIGURES v
LIST OF TABLES vii
EXECUTIVE SUMMARY ix
ABSTRACT xiii
1. INTRODUCTION 1
1.1 PURPOSE AND SCOPE 1
1.2 LITERATURE REVIEW 3
1.3 METHODOLOGY DEVELOPMENT 4
2. MATERIALS AND METHODS 5
2.1 MATERIALS 5
2.1.1 Oak Ridge Y-12 Plant Wastes 5
2.1.2 Leach Solutions 6
2.1.3 Well Water and Artificial Shallow Groundwater Samples 7
2.2 METHODS 7
2.2.1 30-Gal-Size Leaching 7
2.2.2 2-L-Size Leaching 8
2.2.3 Analytical Methods 8
3. RESULTS 9
3.1 SELECTION OF SYNTHETIC GROUNDWATER COMPOSITION 9
3.2 URANIUM LEACHING 12
3.2.1 Production Trash 12
3.2.2 Composite Waste 17
3.2.3 Mixed Metal Chips 22
3.2.4 Air Filters 22
3.2.5 Uranium Oxide Powder from the UCOF 32
3.2.6 Redox Control by Metal Chips 43
3.3 HAZARDOUS MATERIAL LEACHING 47
3.3.1 Inorganic Elements 47
3.3.2 Organic Compounds 47
4. DISCUSSION OF URANIUM LEACHING 47
4.1 EFFECT OF WASTE TYPE 53
4.2 EFFECT OF LEACHANT USED 56
4.3 EFFECT OF LEACH TEST PROTOCOL 57
4.3.1 Batch vs Sequential Methodology 57
4.3.2 Liquid/Solid (L/S) Ratio 60
4.3.3 Leachate pH 61
4.4 EFFECT OF TIME 64
4.5 LEACHATE SAMPLE STABILITY 66
4.6 OVERVIEW OF URANIUM LEACHING FROM Y-12 PLANT WASTES 68
4.6.1 Bimodal Uranium Release 68
4.6.2 Possible Redox Control of Uranium Release Rate 69
4.6.3 Air Filters 71
5. ACKNOWLEDGMENTS 71
6. REFERENCES 72

APPENDIXES 75
APPENDIX A - DESCRIPTION OF WASTE SAMPLES 77
A.1 PRODUCTION TRASH 77
A.2 COMPOSITE WASTE 81
A.3 MIXED METAL CHIPS 86
A.4 AIR FILTERS 88
A.5 URANIUM OXIDE POWDER 91
APPENDIX B - METHODS FOR PREPARATION OF LEACH SOLUTIONS 93
B.1 SYNTHETIC GROUNDWATER 93
B.2 SYNTHETIC LANDFILL LEACHATE 94
APPENDIX C - ANALYTICAL DATA FOR WELL WATER SAMPLES AND SOIL SAMPLE LEACHATES 95
APPENDIX D - LABORATORY FACILITY AND PROCEDURE FOR 30-GAL-SIZE LEACH TESTS 99
D.1 DESCRIPTION OF LABORATORY FACILITY 99
D.2 PROCEDURE FOR 30-GAL-SIZE LEACH TESTS 107
APPENDIX E - LABORATORY PROCEDURE FOR 2-L-SIZE LEACH TESTS 113
APPENDIX F - DISCUSSION OF THE CHEMISTRY OF URANIUM PERTINENT TO THE Y-12 PLANT WASTE CONTAMINATED WITH DEPLETED URANIUM 117
F.1 THE SYSTEM URANIUM-OXYGEN (U-O) 118
F.2 THE SYSTEM URANIUM-OXYGEN-WATER 121
F.3 SOLUTION SPECIES INVOLVING ADDITIONAL ELEMENTS OR IONS 123
F.4 URANIUM OXIDE DISSOLUTION REACTIONS 125
F.5 URANIUM SOLUBILITY LIMITS 127
F.6 REFERENCES FOR APPENDIX F 129

LIST OF FIGURES

Number		
3.1	Batch leach of production trash	14
3.2	Sequential leach of production trash	16
3.3	Batch leach of composite waste	19
3.4	Sequential leach of composite waste	21
3.5	Batch leach of mixed metal chips waste	24
3.6	Sequential leach of mixed metal chips waste	26
3.7	Batch leach of air filters	28
3.8	Sequential leach of air filters	31
3.9	Batch leach of uranium oxide from UCOF	34
3.10	Sequential leach of uranium oxide from UCOF	36
3.11	Percentage of initial uranium leached as a function of L/S ratio for certain uranium oxide powder tests which used synthetic landfill leachant	39
3.12	Sequential leaching of uranium oxide powder using TCLP leachant	41
3.13	Sequential leaching of uranium oxide powder using TCLP leachant (cumulative U leached vs cumulative L/S ratio)	42
3.14	Effect of adding iron chips to leachates containing soluble uranium	46
4.1	Log plots of the uranium leachate concentration vs pH for all five waste forms	58
4.2	Linear and log plots of the uranium concentration vs pH for all leachate samples	63
4.3	Plots of the fraction of uranium leached and the log uranium concentration of the leachates vs contact time for all the waste-type experiments	65

Number

A.1	Typical sample of production trash	79
A.2	Typical sample of composite waste	84
A.3	Typical sample of mixed metal chips waste	87
A.4	Typical air filter	90
A.5	Example of uranium oxide powder from the UCOF	92
D.1	Mixing rotator used in the 2-L-size leach tests . . .	100
D.2	Thirty-gallon-drum roller apparatus	101
D.3	Filtering apparatus used to filter samples of leachate for analytical analysis	102
D.4	Electronic scale used for large-scale weighing . . .	103
D.5	Vacuum filtration apparatus used to separate leachate from solids after leaching tests	105
D.6	Method for removing oily material from leachate to prepare leachate for disposal	106
D.7	Method of drying experimental solid waste	108
D.8	Teflon®-lined 30-gal drum and lids used in experiments	110

LIST OF TABLES

Number		
3.1	Comparison of uranium leaching from uranium oxide powder by three groundwaters and synthetic landfill leachate	10
3.2	Summary of batch leach data for production trash	13
3.3	Summary of sequential leach data for production trash	15
3.4	Summary of batch leach data for composite waste	18
3.5	Summary of sequential leach data for composite waste	20
3.6	Summary of batch leach data for mixed metal chips	23
3.7	Summary of sequential leach data for mixed metal chips	25
3.8	Summary of batch leach data for air filters	27
3.9	Summary of sequential leach data for air filters	30
3.10	Summary of batch leach data for uranium oxide powder from UCOF	33
3.11	Summary of sequential leach data for uranium oxide powder from the UCOF	35
3.12	Summary of batch TCLP leach data for uranium oxide powder from UCOF	37
3.13	Summary of TCLP sequential leach data for uranium powder from UCOF	40
3.14	Effect of adding iron chips to leachates containing dissolved uranium	45
3.15	Concentrations of cations and anions in production trash leach samples	48
3.16	Concentrations of cations and anions in composite waste leach samples	49

Number

3.17	Concentrations of cations and anions in mixed metal chips leach samples	50
3.18	Concentrations of cations and anions in air filters leach samples	51
3.19	Comparison of 24-h TCLP leach data of different wastes with EPA proposed toxicity characteristic levels	52
4.1	Uranium leached by day 7 for different waste	54
4.2	Fraction uranium leached and uranium concentration in the leachate as a function of liquid/solid ratio	62
A.1	Production trash	78
A.2	Composite waste	83
A.3	Mixed metal chips	86
A.4	Air filters	89
C.1	Artificial shallow groundwater and well water data .	97

EXECUTIVE SUMMARY

Leaching tests were carried out in a radiochemical laboratory to study the solubilization or release of uranium from five Y-12 wastes contaminated with depleted uranium. This work was conducted both to support the design, operation, and data analysis of the planned field-scale Uranium Lysimeter Demonstration Project and to aid in the evaluation of potential future waste disposal options. These five wastes result from production operations at the Oak Ridge Y-12 plant that involve depleted uranium. The wastes studied were (1) production trash, waste generated by cleaning the buildings, and general trash found on the floors; (2) mixed metal chips, machine turnings and chips of nonuranium metals such as steel, iron, brass, and aluminum; (3) composite waste, a mixture representative of the combined Y-12 Plant wastes for disposal that are composed of production trash, mixed metal chips, and other wastes from highly contaminated areas; (4) air filters from building ventilation systems; and (5) uranium oxide powder from the uranium chip oxidation facility where uranium metal machining turnings and chips are burned to form an oxide waste. Two leachants were employed in the tests. One leachant was a synthetic groundwater representative of Conasauga-formation shallow groundwater that could intrude into disposed wastes in Bear Creek Valley or be employed in accelerated lysimeter tests. The other leachant was synthetic landfill leachate that simulated the acidic solution which forms as a result of biodegradation of organic materials in a landfill. Two leaching test protocols were employed: (1) batch contact of the waste and leachant at either 2:1 or 20:1 leachant:waste ratios, and (2) a sequential contact that produced a cumulative leachant:waste ratio of 62:1. Both protocols employed leachate sampling at days 1, 2, 3, 4, and 7. Uranium analyses were performed by the Analytical Chemistry Division of the Oak Ridge National Laboratory.

A novel leaching methodology was developed to allow leaching of bulk wastes on a large scale because meaningful, representative, small-size samples could not be prepared for more conventional 100-g-scale laboratory testing. The production trash, mixed metal chips, combined

waste, and air filters were leached in fluorocarbon-lined 30-gal stainless steel drums. The leachate was recovered by a suction-filtration technique. The uranium oxide powder was leached in 2-L borosilicate glass bottles generally following the proposed EPA Toxicity Characteristic Leach Procedure.

The following significant findings resulted from this work.

Bimodal Uranium Release. A bimodal response of uranium leached as a function of time was observed in the batch contact tests. In some tests, the uranium concentration in the leachate or the fraction of the initial uranium leached increased with time and did not reach a steady-state limit or constant value in 7 d (the last time point). Such behavior could be consistent with slow leaching kinetics. In other tests, the uranium concentration or fraction released maximized on day 1 (the first data point) and then decreased to low values by day 7. Such behavior could result from sorption or precipitation of initially solubilized uranium. (Sequential leach tests never showed a decreasing mode because the leachate was removed after each contact.) Bimodal uranium leaching behavior has been reported previously in tests to study uranium leaching from wastes at the Portsmouth Gaseous Diffusion Plant. The existence of bimodal uranium leaching behavior may complicate extrapolation of these 7-d tests to the longer times associated with the field lysimeters or to the prediction of the performance of disposal options.

Possible Redox Control of Uranium Release Rate. A number of experimental observations are consistent with the development of reducing redox conditions in the leaching vessel. The most likely reductant for these tests is the mixed metal chips component of the various wastes. These metals can react with water to form strongly reducing conditions. Under such reducing conditions, any solubilized uranium would be reduced to the 4+ valence state, and it is well known that the corresponding uranium(IV) oxide, UO_2, has a very low solubility in aqueous solutions. A reasonable working hypothesis is that the redox state of the leaching test (or waste disposal situation) may be the single most important variable in controlling the leaching or release of

uranium from the waste. It would be interesting to test this hypothesis in a series of controlled leach experiments.

Rapid Release of Uranium from Air Filters. Of the five wastes tested, the air filters were unique in that large fractions (as much as 68% in one test) of the uranium were rapidly leached by the synthetic groundwater or the synthetic landfill leachants. This finding suggests that air filters might be better candidates for a more isolated disposal option than the other wastes.

Comparison of Uranium Leaching by Synthetic Groundwater vs Synthetic Landfill Leachate. It was anticipated, based on a general knowledge of uranium chemistry, that the synthetic landfill leachant (a 0.1 M acetate buffer at pH 4.9) would be a more aggressive leachant for uranium (i.e., leach more uranium faster) than would be the synthetic groundwater (a very dilute Na^+, Cl^-, HCO_3^- solution at near-neutral pH). The test results indicated that the initial acidity (pH) or acid capacity (buffering) of the leachant was not important in controlling the leaching of uranium from most of the wastes. (The uranium oxide powder was the only waste which seemed to fulfill that anticipation.) This is a surprising finding and suggests that simple dissolution reactions involving higher-valence uranium oxides may not be controlling the release of uranium from most of the wastes. By default, then, reactions involving other waste components may be dominating the solution chemistry; potentially slow reactions, such as oxidation of uranium metal or insoluble UO_2 to soluble uranium(VI) species, and/or sorption/precipitation reactions involving uranium(VI) species may be the important release-rate-controlling reactions.

Inorganic Elements and Organic Compounds. Limited data on the inorganic element and organic compound content of some leachates were obtained. Appreciable differences, both between samples of the same waste type and between waste types, were observed.

ABSTRACT

Batch and sequential contact leaching tests were conducted to study the solubilization of uranium from five different waste types that are generated in the production operations at the Oak Ridge Y-12 plant. These data were needed to support the design, operation, and data analysis of the planned field-scale Uranium Lysimeter Demonstration Project at Y-12 and to aid in the evaluation of potential future waste disposal options. Two different leachants were employed in the tests. One leachant was a synthetic groundwater representative of Conasauga-formation shallow groundwater that could intrude into disposed wastes in Bear Creek Valley or be employed in accelerated lysimeter tests. The other leachant was synthetic landfill leachate that simulated the acidic solution which forms as a result of biodegradation of organic materials in a landfill.

A novel leaching methodology was developed and employed that allowed leaching of production and trash-type wastes on a large scale (30 gal). Because of the complexity of these wastes and the need for representative samples, small-scale, bench-top leaching was not applicable in four of the five waste types tested.

The percentage of the initial uranium leached from the different waste types in a 7-d period varied from 0.00002 to 68%. The most soluble uranium was that on the HEPA air filters; the least soluble was that on mixed metal chips of iron and aluminum. Uranium leaching from the waste containing mixed metal chips was bimodal: in some cases, the function of uranium leached increased with time; while in others, the uranium concentration in the leachate would initially increase the first day of leaching but decrease subsequently. The decrease in uranium concentration probably was caused by reduction of soluble uranium (VI) species to insoluble uranium (IV) species which were sorbed by the gelatinous sludge. Hydrous iron and aluminum oxides also are good ion exchangers and are capable of removing the (VI) species by ion exchange. Additional tests were conducted where iron and aluminum chips were added to leachates containing known amounts of soluble uranium. These tests confirmed the limiting and controlling effect of the metal chips on uranium solubility; in each test the uranium concentration decreased rapidly.

Limited data on the inorganic element and organic compound content of some leachates were obtained. Appreciable differences, both between samples of the same waste type and between waste types, were observed.

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1. INTRODUCTION

1.1 PURPOSE AND SCOPE

The work described in this report was performed under the Laboratory Characterization Task of the Uranium Lysimeter Demonstration Project (ULDP), an activity of the Low-Level Waste Disposal Development and Demonstration Program (LLWDDD) in the Chemical Technology Division's Waste Management Technology Center at the Oak Ridge National Laboratory (ORNL). The task was supported by the Oak Ridge Y-12 Plant Waste Transportation, Storage, and Disposal Department. The purpose of this work was to develop data to support the evaluation of disposal options and the analysis of disposal scenarios for the wastes generated by production operations at the Oak Ridge Y-12 Plant that are radiologically contaminated with depleted uranium.

The task had three overall goals: (1) to supply uranium leaching information for the LLWDDD Environmental Data Package (EDP); (2) to support the planned field-scale activities by characterizing the wastes that may be placed in the lysimeters under the ULDP by aiding in the prediction of waste performance in the lysimeters over time, and helping in the interpretation of the lysimeter data when they become available; and (3) to collect exploratory information on hazardous materials content (if any) and leaching.

The primary task milestone was the development of the uranium leaching information on schedule (June 30, 1988) for the EDP. The uranium data in the EDP will be used in the planned Environmental Impact Statement (EIS) for Y-12 waste disposal alternatives and may be used to help evaluate, model, and/or select future waste disposal options for

Y-12 Plant wastes. Modeling or predicting the performance of future disposal options requires quantification of the uranium releases from the wastes over time for various potential disposal scenarios, and the task was designed to help generate such information. The task also supports the ULDP by (1) providing information to assist in choosing wastes for field-scale testing and (2) developing short-term laboratory data that will be useful in interpreting the longer-term and larger-scale lysimeter results. To this end, the wastes were chemically and physically characterized. In addition to the uranium data, information was collected on the leaching of both organic compound and inorganic element hazardous materials.

The task was primarily a laboratory-scale activity. Work on a relatively small scale (compared to field lysimeters or actual disposal operations) was essential in maintaining the task schedule and in allowing control of test parameters which could simulate accelerated time (i.e., conduct the laboratory study in a few days of leaching events that will take longer times in the lysimeters or full-scale disposal options). Because of the heterogeneous nature of most of the Y-12 Plant wastes studied, many of the laboratory leaching tests were done on a 30-gal scale. The development of this 30-gal-scale leaching methodology is discussed below.

The Y-12 Plant Waste Transportation, Storage, and Disposal Department identified priority waste streams for study in this task that result from production operations involving depleted uranium. Most of these waste streams are bulk- or trash-type wastes that are very heterogeneous both in bulk waste components and in uranium contamination. Because much of the uranium contamination results from operations involving fabrication of uranium or uranium-alloy metal parts, it seemed likely that much of the uranium contamination in many of the wastes would consist of chips or turnings of elemental uranium rather than uranium oxides. Five wastes were investigated during this task: production trash, composite waste, mixed metal chips, air filters, and uranium oxide powder. These wastes are described in Sect. 2.1 and in detail in Appendix A.

1.2 LITERATURE REVIEW

One of the first task activities was the selection of a uranium leaching methodology that would be applicable to the types of wastes generated by the Y-12 Plant. A literature search was undertaken to identify published information on methods for the leaching of uranium from low-level wastes or general methods for leaching contaminants from bulk-type wastes. Emphasis in the search was on prior laboratory work to predict long-term waste or waste facility performance.

The literature review was conducted by searching the DOE Energy Database in the Dialog computer-based information system[1] and by scanning the indices for the last several years of appropriate journals, such as Nuclear and Chemical Waste Management and Radioactive Waste Management and the Nuclear Fuel Cycle. The search was directed toward reports or papers that describe methods for characterization of the leaching of uranium from bulk wastes or trash. No articles describing investigations or methods relevant to the task work with Y-12 Plant wastes were identified. The literature review showed that little attention has been directed in the past to the study of the leaching of uranium from low-level radioactive wastes. Most studies of low-level wastes have focused on fission products such as cesium, strontium, and cobalt or on transuranics such as plutonium or neptunium. These elements are generally considered to be the more environmentally hazardous radionuclides in low-level waste. Studies of garbage or sanitary landfill wastes have focused on hazardous elements, such as cadmium, lead, and silver, or on organic contaminants and have not addressed uranium. Also, few laboratory-scale studies have attempted to deal with heterogeneous bulk or garbage wastes. Prior laboratory waste-leaching work has been primarily limited to prepared or monolithic waste forms; much of the work has been with cast concrete waste forms. Standard or generally accepted leach methods for heterogeneous or "garbage-type" wastes do not seem to exist, and it was concluded that there is little prior experience with uranium leaching from low-level wastes to draw upon for the leaching and characterization of the Y-12 Plant wastes.

Four generally accepted leaching methods are designed either as pass/fail regulatory tests or for the study of releases from monolithic waste forms. The proposed EPA Toxicity Characteristics Leaching Procedure (TCLP),[2] the EPA Solid Waste Leaching Procedure,[3] the Materials Characterization Center Leach Test MCC-1,[4] and the American Nuclear Society Leach Test ANSI/ANS-16[5] have been developed by others and widely used to characterize hazardous and/or radioactive wastes with respect to the leaching of contaminants or radionuclides. Some of these methods are used to grade wastes on a relative scale and, by varying test parameters, to give indications of waste behavior under diverse disposal scenarios. However, pass/fail tests use a single test time and/or arbitrary test conditions to establish a regulatory screening criteria and, thus, will not yield leaching data which can be extrapolated over the times of interest for the Y-12 Plant waste lysimeters or disposal options. Also, test methods designed for monolithic solid specimens cannot be applied to the Y-12 Plant bulk or powdered wastes. Therefore, an early finding in the evolution of the task planning was the need for a methodology development phase, and methods development become the first task activity.

1.3 METHODOLOGY DEVELOPMENT

The heterogeneous nature of the bulk- or trash-type Y-12 Plant wastes precluded work in the laboratory with small samples, such as the 100-g samples used in the 2-L-scale EPA proposed TCLP, and necessitated the development of a larger-scale method of contacting wastes with leachants and subsequently recovering the leachates. After some experimentation, the following method was selected (the method is described in Sect. 2.2.1, and a detailed laboratory procedure is given in Appendix D). The use of 30-gal drums was chosen to allow working with substantial samples of given waste streams. Lined stainless steel drums were rotated on drum rollers to contact the wastes and leachants. A vacuum-filtration method was devised to recover clarified leachate

after the desired contact time. After completion of the 30-gal-scale methodology phase of the task, the leach tests described in this report were carried out.

2. MATERIALS AND METHODS

A general description of the materials and methods used in this work is given in this section. Detailed records of the waste samples, formulae for the leachates used in the various tests, and detailed laboratory procedures for both the 30-gal-size and 2-L-size leaching methods are given in the Appendixes.

2.1 MATERIALS

2.1.1 Oak Ridge Y-12 Plant Wastes (details in Appendix A)

Five wastes which contain depleted uranium were identified by the Y-12 Plant Waste Transportation, Storage, and Disposal Department as priority wastes for investigation. These wastes were:

1. Production trash. Waste generated by the cleaners in cleaning and protecting the floors, resulting from efforts to minimize the spread of contamination, and general trash found on the floors. Production trash samples consisted of a very wide variety of components. Samples frequently contained floor sweepings, paper, metal scrap or parts, Hot Hogs (an adsorbent in a cloth tube), oily cloths, plastics, etc.

2. Mixed metal chips. Mixed metal chip samples were primarily mixtures of turnings and machining chips of various nonuranium metals, such as aluminum, iron, stainless steel, copper, and brass. Most samples were quite oily.

3. Composite waste. This waste was an assortment that contained 1/3 production trash, 1/3 mixed metal chips, and 1/3 general trash from highly contaminated areas. This composite waste is representative of the overall mixture of Y-12 Plant wastes for disposal. Composite waste samples were a mixture of the

components in the first two waste types plus a wider variety of cloth, leather, and plastic materials. These components sometimes were coated with a red, oily liquid.

4. Air filters. These are contaminated air filters from building ventilation systems throughout the Y-12 Plant. They were standard HEPA (High-Efficiency Particulate Absorber) air filters. The filter medium is constructed of fiberglass with aluminum separators and is supported on both sides by galvanized steel wire-guards inside a steel frame (2 × 2 × 1 ft). Appreciable amounts of an easily dispersed, yellow-green, uranium-containing powder was observed on all filters. The filter medium was cut from the metal frames and used in the leaching tests. The frames were discarded because they were too large to fit into the 30-gal leaching drums.

5. Uranium oxide powder. This waste is a powder from the uranium chip oxidation facility (UCOF) where uranium metal turnings and chips are burned to a mixture of uranium oxides.[6] One sample was obtained and homogenized for use in all uranium oxide tests. X-ray diffraction analysis showed the sample to be primarily UO_2 with a small amount of U_3O_8.

2.1.2 Leach Solutions (details in Appendix B)

Two leachants were used in the tests. The acidity of these leachants bracket the acidity of solutions that might contact waste in numerous disposal situations. One solution was a synthetic groundwater that was prepared in the laboratory. The synthetic groundwater composition was adjusted to simulate the low Na^+, Cl^-, and HCO_3^- content and the acidity (pH 7.3) of a Conasauga saprolite water sample. This composition represents near-surface groundwater that could enter waste emplaced in below grade in the soil or in a tumulus in the Conasauga formation at the Y-12 site. The other solution was the synthetic landfill leachate specified in the proposed EPA TCLP.[7] The TCLP solution is a 0.1 M sodium acetate - acetic acid buffer at pH 4.9, which was specified by

the EPA to simulate the carboxylic acid solution formed by the biological degradation of organic wastes in a sanitary landfill. Because the solubility of 6+ valence uranium species is known[8-11] to be highly dependent on solution pH, it was assumed that these two leachates would bracket the aggressiveness of potential leachants and that the synthetic landfill leachate would be much more aggressive (leach much more uranium) than the synthetic groundwater. (This assumption was not substantiated by the experimental results, as discussed in Sects. 3 and 4.)

2.1.3 Well Water and Artificial Shallow Groundwater Samples (details in Appendix C)

Samples of water from two wells in the Y-12 site were obtained and analyzed. These wells could be sources of water for the planned accelerated lysimeter leaching tests. These two water samples were relatively high in pH and total alkalinity, and it was assumed that the waters were in communication with limestone or dolomite. It was decided not to use these well waters in the waste-leaching work because their composition was representative of deep or standing groundwater rather than of near-surface or shallow groundwater. Samples of three different types of soil from the Y-12 site were obtained and leached with deionized water to prepare artificial shallow groundwaters for analysis. Artificial waters from these soils were prepared because no samples of perched water table or shallow groundwater were available from the Y-12 site. The composition of the Conasauga saprolite sample was chosen to represent near-surface groundwater that could intrude into emplaced waste.

2.2 METHODS

2.2.1 30-Gal-Size Leaching (details in Appendix D)

The bulk wastes were leached in fluorocarbon-lined 30-gal stainless steel drums mounted on drum rollers. The waste sample and leachant selected for a given test were placed in the drum, and the drum was sealed and rotated for a specified contact time at ambient temperature.

After contact, the drum was opened and the leachate was sampled and/or removed by a vacuum-filtration procedure. Laboratory measurements (pH and temperature) were promptly made, and analytical and archive samples of the leachate were stored in a refrigerator. Two types of leaching protocols were followed: sequential or batch. For the sequential leaches, the leachate was removed, sampled, and replaced with fresh leachant at 1, 2, 3, 4, and 7 d. In addition, the volume of leachant was geometrically increased to yield a series of liquid/solid ratios of 2, 4, 8, 16, and 32 for the five replacement times. This sequence yielded a cumulative liquid/solid ratio of 2, 6, 14, 30, and 62 for the sequential leach protocol. For the batch leach protocol, a single leachant contact at a liquid/solid ratio of either 2 or 20 was employed. The leachate was sampled (but not replaced) on days 1, 2, 3, 4, and 7. All leachate samples were analyzed for uranium by the ORNL Analytical Chemistry Division (ACD). In addition, selected samples were analyzed by ACD for hazardous materials (inorganic elements and organic compounds), anions, radioactivity (gross alpha and gross beta), alkalinity, and organic carbon.

2.2.2 2-L-Size Leaching (details in Appendix E)

The uranium oxide powder was leached in 2-L glass bottles with Teflon®-lined lids. The bottles were rotated end-over-end to achieve contact of the powder and leachant. The same batch and sequential leaching protocols were followed as in the 30-gal-size tests with bulk wastes. After the desired contact time, the leachate was recovered by filtration through microfiber glass filter medium. The same laboratory measurements and analytical information were obtained as for the 30-gal-size experiments.

2.2.3 Analytical Methods

All chemical analyses for the well water samples, artificial shallow groundwater samples, and test leachate samples were performed by ACD in accordance with its standard laboratory procedures and quality assurance plan. Uranium was analyzed by Davies-Gray or fluorometric

methods. Inorganic elements were determined by inductively coupled plasma spectrometry or atomic adsorption procedures. Organic compounds were analyzed by gas chromatography—mass spectrometry methods. Radioactivity was counted by alpha detectors or beta scintillation techniques. Miscellaneous chemical analyses included alkalinity and inorganic carbon.

The initial uranium content of the bulk waste samples was measured at the Y-12 Plant with a large gamma counter, which is used to analyze truck-size loads of waste. (See evaluation of this counter in Sect. 3.2.7.)

3. RESULTS

3.1 SELECTION OF SYNTHETIC GROUNDWATER COMPOSITION

Because of our need to prepare large volumes (hundreds of liters) of synthetic groundwater for the 30-gal-scale waste leach tests, an approach to the selection of a synthetic groundwater composition was adopted that avoided an extensive laboratory development activity. Experience has shown that the exact duplication of all natural groundwater species in a solution prepared in the laboratory can be time consuming because saturation or near-saturation, with respect to carbonate, silica, or aluminosilicate phases, can be difficult to achieve, or to maintain if achieved. Many of the groundwater components that are important in studying rock/groundwater chemistry, such as Al, Si, Na:K ratio, Fe(II):Fe(III) ratio, or degree of saturation with calcite or dolomite, are probably unimportant (or at least a second- or third-level-of-importance parameter) in the uranium leaching tests. The important water composition parameters involved in uranium solubility are pH, PO_4^{3-}, SO_4^{2-}, F^-, and CO_3^{2-} because these control the U(VI) speciation, and, in consort with the solid phases present, the uranium solubility (see Appendix F). We therefore compared the leaching of uranium into several well waters and a simple synthetic groundwater.

A series of 2-L-size batch leach tests at a 20:1 leachate:waste ratio was undertaken to compare the leaching of uranium from uranium oxide powder from the UCOF. Uranium oxide powder was chosen as the

waste for these tests to ensure use of a reproducible waste material for the replicate tests. This test series was designed to compare the aggressiveness (ability to leach uranium) of various well waters that could be used in the accelerated field lysimeter tests with a synthetic groundwater for the laboratory tests. The synthetic landfill leachate pH 4.9 buffer solution specified in the proposed EPA TCLP[12] was also included as a test leachant for comparison with the groundwaters. The tests were run in triplicate to explore the reproducibility of the laboratory procedure and analytical methods.

The uranium leaching data are presented in Table 3.1. A summary of the artificial shallow groundwater and well water composition data is included in Sect. 7.3. Excellent reproducibility of the uranium concentration values can be seen for the four sets of triplicate leach tests. The standard deviation values are only a small fraction of the uranium concentration values. This reproducibility results from several aspects of these tests: (1) the starting materials – both the uranium

Table 3.1 Comparison of uranium leaching from uranium oxide powder by three groundwaters and synthetic landfill leachate[a]

Leachant[b]	Uranium concentration (mg U/L) (mean ± 1 σ)	Final pH (mean ± 1 σ)
GW-84	77 ± 6	6.38 ± 0.06
GW-376	143 ± 1	6.82 ± 0.12
Syn. Groundwater	56 ± 1	5.74 ± 0.08
Syn. Landfill	1608 ± 23	4.92 ± 0.00

[a]All leach tests were run in triplicate for 24 h at 20:1 leachant: uranium oxide powder from the UCOF.

[b]GW-84 was water from well GW-84 located in the Maryville Formation of the Conasauga Group; GW-376 was water from well GW-376 (50 ft deep) which is located up-grade of the Y-12 lysimeter site in Bear Creek Valley; Syn. groundwater was prepared in the laboratory; Syn. landfill was prepared in the laboratory to the proposed EPA Toxicity Characteristic Leach Procedure formulation.

oxide powder and, of course, the solutions were well mixed – and replicate samples taken for parallel tests were highly reproducible; (2) the 2-L-size test procedure is relatively easy to carry out; and (3) the fluorometric and Davies-Gray analytical methods for uranium are well established methods.

The data in Table 3.1 show that the well waters or synthetic groundwater solubilized much less uranium than did the synthetic landfill leachant. The synthetic groundwater was the least aggressive and leached the smallest amount of uranium. Thus, it was expected that use of the synthetic landfill leachate and synthetic groundwater in the 30-gal-scale leach tests would bracket the ranges of aggressiveness which might be exhibited by potential waste leachants.

Based on the uranium leaching data and the general approach to synthetic groundwater preparation, a decision was reached to prepare synthetic groundwater containing only Na^+, Cl^-, and HCO_3^-, at concentrations equivalent to Conasauga artificial shallow groundwater (see Sect. 7.3), and to adjust the pH to get the equivalent acidity. A composition equivalent to the Conasauga saprolite water was selected. The Conasauga saprolite water composition (see Sect. 7.3) did not contain detectable amounts of F^-, SO_4^{2-}, or PO_4^{3-}. Also, Ca^{2+} was not detected and Mg^{2+} was very low. The synthetic groundwater formulation selected for the leaching tests was: Na^+, 0.10 m$\underline{M}$; Cl^-, 0.02 m$\underline{M}$; HCO_3^-, 0.08 m$\underline{M}$; pH, 7.3.

This synthetic groundwater composition was prepared by dissolving NaCl and $NaHCO_3$ in deionized water and then adjusting the pH to 7.3 ± 0.1 with HCl as needed (see Sect. 7.2.1). This composition is a very dilute, very weakly buffered solution, and exact control of the pH at a predetermined value may be difficult to achieve and also may be unimportant with respect to the waste-leaching tests because the acid/base capacity of the wastes likely will establish the leach test pH. This synthetic groundwater is a stable, easy-to-prepare water that avoids the difficulties often encountered with attempting to poise redox couples such of Fe(II):Fe(III), or in dissolving and keeping silicates and aluminosilicates in solution.

3.2 URANIUM LEACHING

3.2.1 Production Trash

A summary of the uranium data for the four batch leach tests with production trash is given in Table 3.2 and Fig. 3.1. A similar data summary and plot for the two sequential leach tests is given in Table 3.3 and Fig. 3.2.

The batch test protocol results all showed an increasing leach mode. When plotted as either the fraction of the initial uranium released or as the uranium concentration in solution vs time, there was generally a rapid increase by the first time point (day 1) and then a continuing but more gradual increase up to the last time point (day 7). In one case, ~1.6% of the initial uranium was leached, while in the other cases, <0.8% was leached. The release of uranium from the waste did not seem to correlate with the liquid/solid ratio (L/S), the leachant composition, or the leachate pH. The greatest leaching occurred in the test at 2/1 L/S with synthetic groundwater which terminated at a pH of 7.4. If the solution chemistry was controlling the uranium leaching, then the greatest release might have been expected in the test at 20/1 L/S with synthetic landfill leachate, which terminated at pH 5.5. It seems that properties of the production trash and/or the form of uranium in the waste rather then the apparent solution chemistry may be controlling the uranium release rate in these tests.

The two sequential leach tests showed a rapid release of uranium in the early, low L/S ratio contacts, and then smaller releases into the later, high L/S ratio contacts. Surprisingly, more uranium was leached by the synthetic groundwater than by the synthetic landfill leachate. Perhaps the waste sample used in the synthetic groundwater test had a more soluble form of uranium than did the other waste sample. A maximum of ~1% of the uranium was leached from this waste in these tests; little additional uranium was being solubilized in the final contacts with the larger volumes of leachant.

Table 3.2. Summary of batch leach data for production trash

	Test Parameters					Results							
Sample No.	Total Leach (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Total Uranium Leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
4FSA	71.2	TCLP	3.56	425	20.0	25.5	25.5	13.0	0.926	0.22	5.09	4.79	25.1
4FSB	71.2	TCLP	3.56	425	20.0	20.0	45.5	20.0	1.424	0.34	5.04	4.43	24.6
4FSC	71.2	TCLP	3.56	425	20.0	23.0	68.5	28.0	1.994	0.47	5.17	5.01	25.2
4FSD	71.2	TCLP	3.56	425	20.0	23.5	92.0	40.0	2.848	0.67	5.22	4.85	25.4
4FSE	71.2	TCLP	3.56	425	20.0	72.0	164.0	50.0	3.560	0.84	5.50	5.99	26.1
8FSAAA	42.6	SNGW	2.13	354	20.0	18.8	19.0	2.5	0.105	0.03	6.67	0.66	26.1
8FSBBB	42.6	SNGW	2.13	354	20.0	25.1	42.5	4.3	0.185	0.05	6.49	0.78	25.9
8FSCCC	42.6	SNGW	2.13	354	20.0	23.5	66.0	9.5	0.403	0.11	6.73	0.82	26.0
8FSDDD	42.6	SNGW	2.13	354	20.0	23.2	90.0	18.0	0.768	0.22	6.81	0.83	25.8
8FSEEE	42.6	SNGW	2.13	354	20.0	72.2	162.0	47.0	2.004	0.57	6.73	0.79	26.3
3FSA	18.3	TCLP	9.14	1224	2.0	26.5	26.5	210.0	3.839	0.31	6.70	7.23	25.2
3FSB	18.3	TCLP	9.14	1224	2.0	22.0	48.5	249.0	4.552	0.37	6.58	7.86	24.0
3FSC	18.3	TCLP	9.14	1223	2.0	24.0	72.5	377.0	6.892	0.56	6.77	7.21	25.5
3FSD	18.3	TCLP	9.14	1223	2.0	23.3	95.8	467.0	8.537	0.70	6.73	8.36	25.8
3FSE	18.3	TCLP	9.14	1223	2.0	69.0	164.8	458.0	8.372	0.68	6.63	8.02	26.4
7FSAAA	17.3	SNGW	8.62	876	2.0	19.8	19.8	168.0	2.903	0.33	7.09	3.77	25.9
7FSAAB	17.3	SNGW	8.62	876	2.0	24.8	44.58	476.0	8.228	0.94	7.04	4.16	26.0
7FSAAC	17.3	SNGW	8.62	876	2.0	21.5	66.08	592.0	10.562	1.21	7.05	4.36	25.5
7FSAAD	17.3	SNGW	8.62	876	2.0	25.8	91.91	656.0	11.714	1.34	7.15	4.14	25.8
7FSAAE	17.3	SNGW	8.62	876	2.0	72.1	163.99	796.0	14.097	1.61	7.40	3.00	25.9

* TCLP leachant: pH = 4.88 at 25 C; conductivity = 4.24 mmho.
Synthetic Groundwater leachant: pH = 7.34 at 25.9 C; conductivity = 0.013 mmho.

** Corrected for analytical samples that were removed.

ORNL DWG 88-957

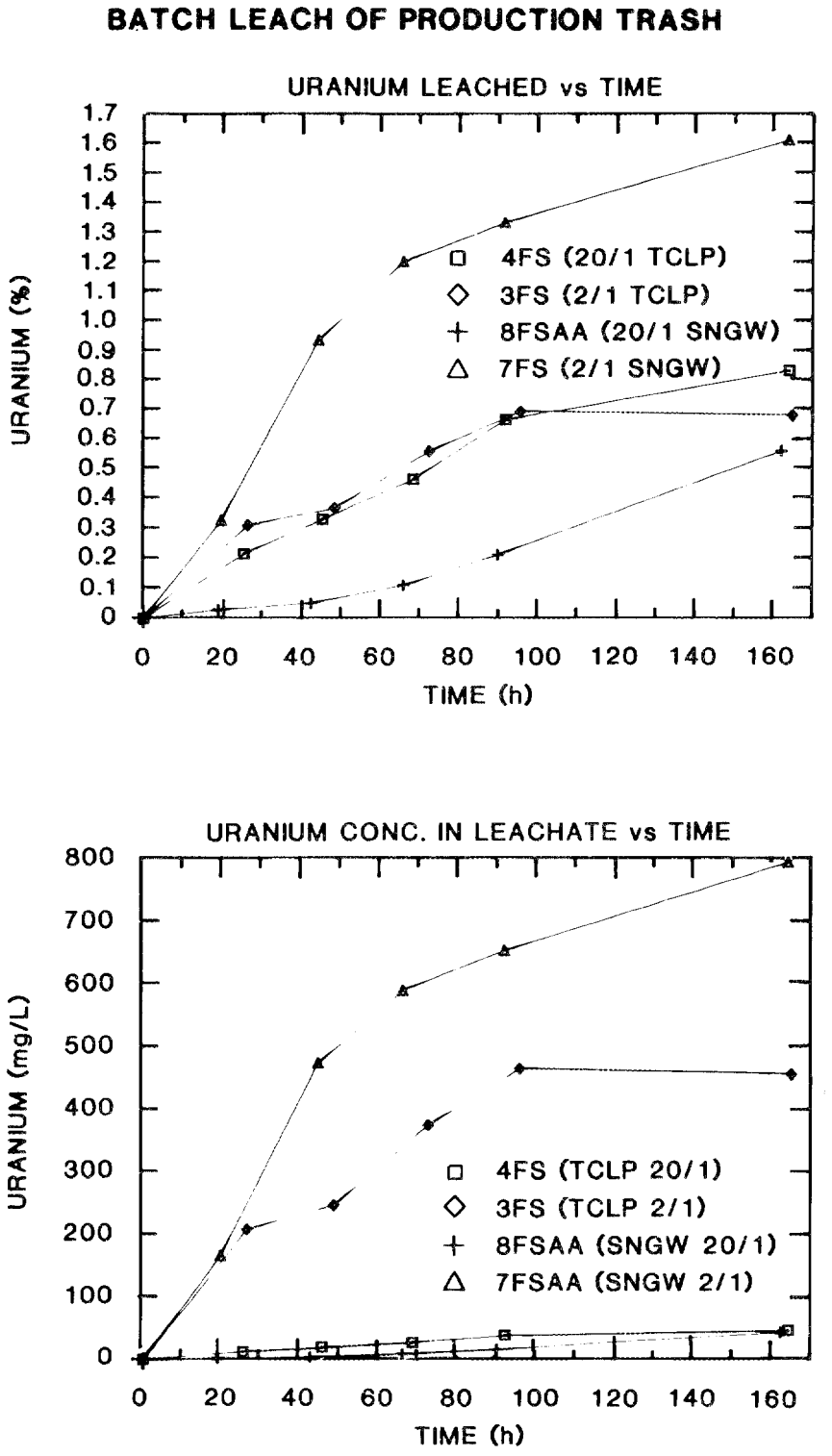

Fig. 3.1. Batch leach of production trash.

Table 3.3. Summary of sequential leach data for production trash

	Test Parameters							Results									
Sample No.	Leach Vol. (L)	Cum. Leach Vol. (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Cum. L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Uranium in Leachate (g)	Leached Uranium (g)**	Cum. Uranium Leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
1FSA	7.2	7.2	TCLP	3.56	710.0	2.0	2.0	21.0	21.0	84.0	0.61	0.61	0.61	0.09	6.53	5.05	25.7
1FSB	15.9	23.1	TCLP	3.56	709.6	4.5	6.5	23.5	44.5	57.0	0.90	0.73	1.33	0.19	5.93	3.92	26.1
1FSC	28.5	51.6	TCLP	3.56	708.8	8.0	14.5	24.1	68.6	61.0	1.74	1.60	2.94	0.41	5.54	3.70	26.7
1FSD	57.0	109.0	TCLP	3.56	707.2	16.0	30.5	23.0	91.6	23.0	1.31	1.19	4.12	0.58	5.18	5.01	26.6
1FSE	99.7	208.2	TCLP	3.56	705.9	28.0	58.5	71.0	162.6	7.7	0.77	0.72	4.85	0.69	5.14	3.81	24.9
5FSA	7.4	7.4	SNGW	3.67	749.0	2.0	2.0	20.8	20.8	369.0	2.71	2.71	2.71	0.36	7.65	3.74	25.0
5FSB	14.7	22.1	SNGW	3.67	747.5	4.0	6.0	23.2	43.9	234.0	3.44	2.21	4.92	0.66	7.15	2.46	25.5
5FSC	29.4	51.4	SNGW	3.67	745.0	8.0	14.0	25.3	69.3	69.0	2.03	1.10	6.02	0.81	7.10	0.35	24.6
5FSD	58.8	110.2	SNGW	3.67	743.3	16.0	30.0	23.1	92.3	16.0	0.94	0.60	6.62	0.89	7.10	1.93	24.1
5FSE	80.8	191.1	SNGW	3.67	742.5	22.0	52.0	72.3	164.7	11.0	0.89	0.81	7.43	1.00	7.03	1.71	24.6

* TCLP Leachant: pH = 4.88 at 25 C; conductivity = 4.24 mmho.
Synthetic Groundwater leachant: pH = 7.34 at 25.9 C; conductivity = 0.013 mmho.

** Values corrected for dissolved uranium in the leachate which was not removed after each leach period.

ORNL DWG 88-953

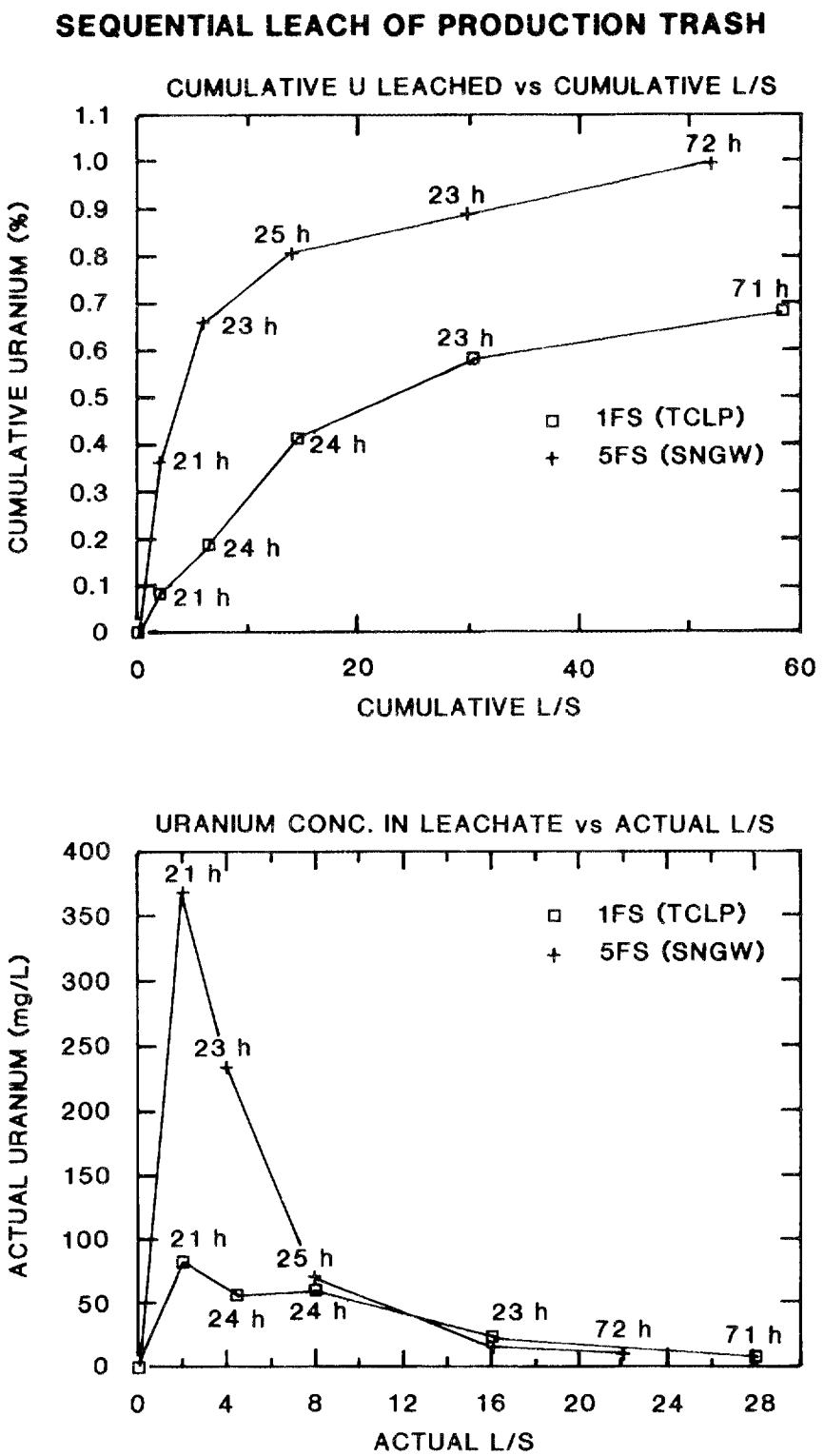

Fig. 3.2. Sequential leach of production trash.

3.2.2 Composite Waste

A summary of the uranium data for the five batch leach tests (four planned tests and one partial duplicate test due to a plastic barrel failure) with composite waste is given in Table 3.4 and in Fig. 3.3. A similar data summary and a plot for the two sequential leach tests are given in Table 3.5 and Fig. 3.4, respectively.

The batch test protocol results showed a more complex uranium release pattern than for production trash. When plotted as either the fraction of the initial uranium released or as the uranium concentration in solution vs time, there was an increase to the first time point (day 1). Subsequently, however, some tests showed a continuing but more gradual increase up to the last time point (day 7), while in other tests, the uranium concentration in solution (and therefore the fraction released) decreased to low values by day 7. The release of uranium from the waste did not seem to correlate with the L/S ratio, the leachant composition, or the leachate pH. The greatest release (~4.6%) occurred in the test at 2:1 L/S with synthetic landfill leachate, while the lowest release (~0.01%) occurred in the parallel synthetic landfill leachate test at 20:1 L/S. This 20:1 L/S test also had the lowest final pH. It seems that properties of the composite waste and/or the form of uranium in the waste, rather than the apparent solution chemistry, may be controlling the uranium release rate in these tests.

The two sequential leach tests with this waste showed markedly different behavior. Much larger amounts of uranium were leached by the synthetic landfill leachant than by synthetic groundwater. Even at the final 34:1 batch L/S ratio contact, appreciable amounts of uranium were being released, and it was clear that the system had not reached steady state. As in the case of the production trash sequential tests, a possible conclusion is that the different samples have uranium present in different forms – at least insofar as leaching is concerned. An alternative explanation could be that other waste components could also be affecting or controlling the uranium leaching.

Table 3.4. Summary of batch leach data for composite waste

	Test Parameters					Results							
Sample No.	Total Leach (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Total Uranium leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
4BALAA	81.5	TCLP	4.08	220	20.0	22.6	22.6	16.0	1.304	0.59	6.28	5.12	25.5
4BALBB	81.5	TCLP	4.08	220	20.0	22.4	45.0	9.4	0.766	0.35	5.88	4.57	25.6
4BALCC	81.5	TCLP	4.08	220	20.0	23.8	68.8	4.0	0.328	0.15	5.73	4.30	25.8
4BALDD	81.5	TCLP	4.08	220	20.0	25.2	94.0	2.2	0.181	0.08	5.46	4.56	26.3
4BALEE	81.5	TCLP	4.08	220	20.0	71.1	165.1	0.3	0.024	0.01	5.47	5.67	25.9
8BALAAA	99.8	SNGW	8.10	194	12.3	20.9	20.9	1.6	0.157	0.08	6.77	0.52	26.1
8BALBBB	99.8	SNGW	8.10	194	12.3	23.7	44.6	14.2	1.418	0.73	6.49	0.78	25.9
8BALCCC	99.8	SNGW	8.10	194	12.3	24.9	69.5	20.2	2.017	1.04	6.47	0.60	26.0
8BALDDD	99.8	SNGW	8.10	194	12.3	23.1	92.6	25.4	2.536	1.31	6.47	0.62	25.8
8BALEEE	99.8	SNGW	8.10	194	12.3	70.7	163.3	27.9	2.785	1.44	6.40	0.64	26.4
3BALA	19.9	TCLP	8.96	317	2.0	19.5	19.5	8.8	0.174	0.06	6.16	5.51	25.2
3BALB	19.9	TCLP	8.96	317	2.0	24.0	43.5	2.7	0.053	0.02	6.56	5.08	25.3
3BALC	19.9	TCLP	8.96	317	2.0	23.0	66.5	1.1	0.022	0.01	6.62	5.49	25.7
3BALAA	21.8	TCLP	10.91	138	2.0	27.3	27.3	63.0	1.375	1.00	5.23	4.36	25.8
3BALBB	21.8	TCLP	10.91	138	2.0	21.4	48.7	73.0	1.593	1.15	5.50	4.43	25.8
3BALCC	21.8	TCLP	10.91	138	2.0	23.3	72.0	86.0	1.876	1.36	5.62	3.97	25.2
3BALDD	21.8	TCLP	10.91	138	2.0	23.4	95.4	143.0	3.120	2.26	5.66	4.18	25.3
3BALEE	21.8	TCLP	10.91	138	2.0	73.3	168.7	290.0	6.327	4.59	6.07	5.99	26.1
7BALAAA	21.9	SNGW	10.93	131	2.0	27.9	27.9	12.6	0.276	0.21	6.90	2.02	26.1
7BALBBB	21.9	SNGW	10.93	131	2.0	22.8	50.8	2.0	0.044	0.03	6.93	1.89	26.2
7BALCCC	21.9	SNGW	10.93	131	2.0	21.8	72.6	1.9	0.040	0.03	6.85	1.68	26.1
7BALDDD	21.9	SNGW	10.93	131	2.0	26.3	98.8	0.8	0.018	0.01	6.99	1.51	26.0
7BALEEE	21.9	SNGW	10.93	131	2.0	70.9	169.7	9.6	0.209	0.16	7.06	1.23	26.3

* TCLP Leachant: pH = 4.88 at 25 C; conductivity = 4.24 mmho.
Synthetic Groundwater leachant: pH = 7.34 at 25.9 C; conductivity = 0.013 mmho.

** Corrected for analytical samples that were removed.

ORNL DWG 88-959

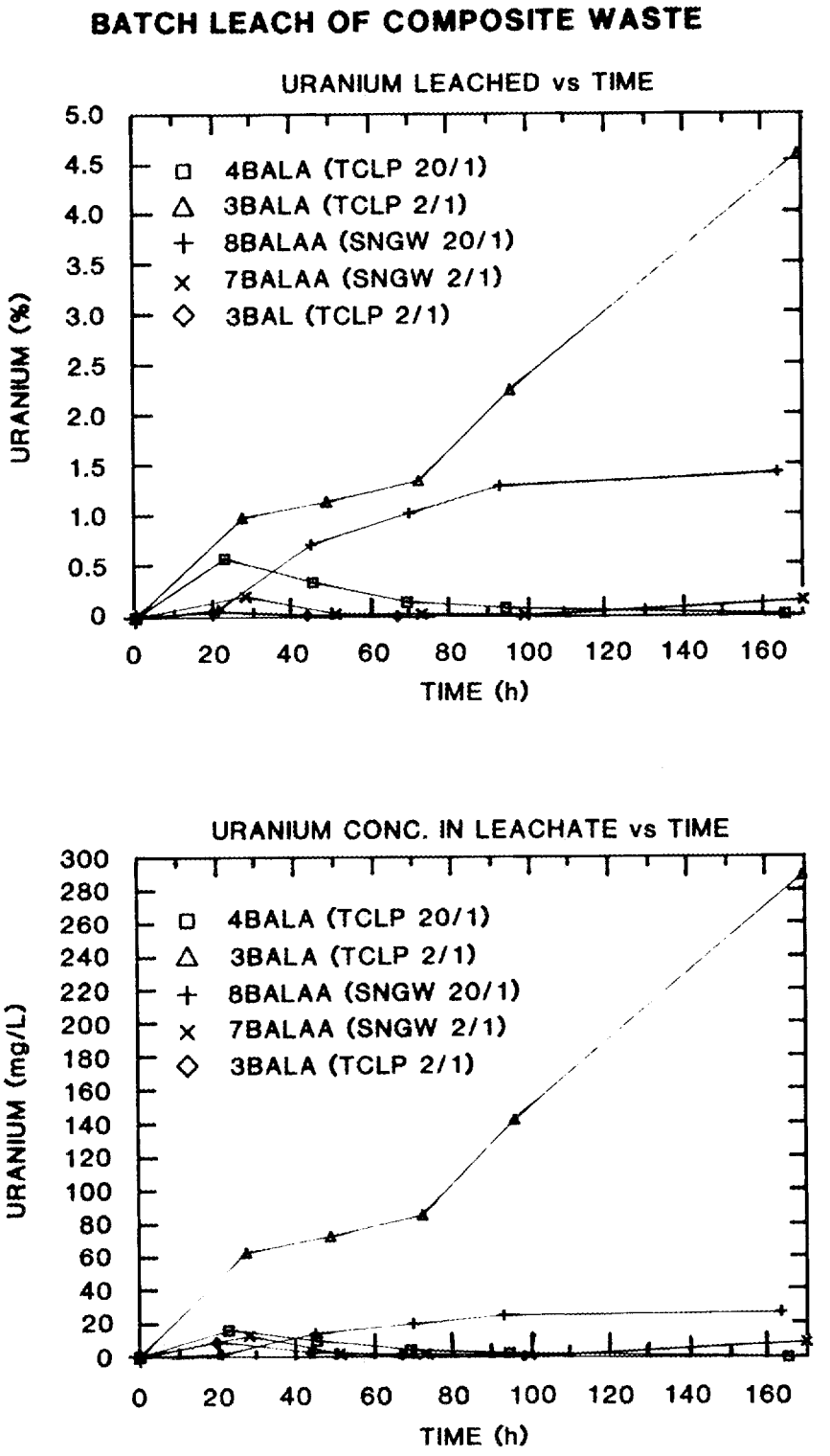

Fig. 3.3. Batch leach of composite waste.

Table 3.5. Summary of sequential leach data for composite waste

	Test Parameters							Results									
Sample No.	Leach Vol. (L)	Cum. Leach Vol. (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Cum. L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Uranium in Leachate (g)	Leached Uranium (g)**	Cum. Uranium Leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
1BALA	7.2	7.2	TCLP	3.38	154.0	2.1	2.1	18.3	18.3	20.0	0.14	0.14	0.14	0.09	6.28	5.12	25.5
1BALB	20.7	27.9	TCLP	3.38	154.0	6.1	8.2	25.0	43.3	19.6	0.41	0.30	0.44	0.29	5.88	4.57	25.6
1BALC	31.0	59.0	TCLP	3.38	153.7	9.2	17.4	23.5	66.8	17.2	0.53	0.46	0.90	0.58	5.73	4.30	25.8
1BALD	58.2	117.1	TCLP	3.38	153.2	17.2	34.6	24.1	90.9	12.1	0.70	0.63	1.53	1.00	5.46	4.56	26.3
1BALE	118.0	235.1	TCLP	3.38	152.6	34.9	69.5	71.0	161.9	5.0	0.59	0.54	2.07	1.36	5.47	5.67	25.9
5BALA	5.9	5.9	SNGW	2.95	110.0	2.0	2.0	22.7	22.7	13.0	0.08	0.08	0.08	0.07	6.44	3.16	25.0
5BALB	11.8	17.7	SNGW	2.95	110.0	4.0	6.0	20.8	43.4	4.3	0.05	0.04	0.12	0.11	6.60	1.14	25.9
5BALC	23.6	41.3	SNGW	2.95	110.0	8.0	14.0	24.3	67.8	0.6	0.01	0.01	0.13	0.12	6.30	0.35	24.6
5BALD	47.2	88.5	SNGW	2.95	110.0	16.0	30.0	24.1	91.8	0.2	0.01	0.01	0.14	0.13	6.42	0.12	24.4
5BALE	64.9	153.4	SNGW	2.95	110.0	22.0	52.0	74.7	166.5	0.5	0.03	0.03	0.17	0.16	6.37	0.16	24.6

* TCLP Leachant: pH = 4.88 at 25 C; conductivity = 4.24 mmho.
Synthetic Groundwater leachant: pH = 7.34 at 25.9 C; conductivity = 0.013 mmho.

** Values corrected for dissolved uranium in the leachate which was not removed after each leach period.

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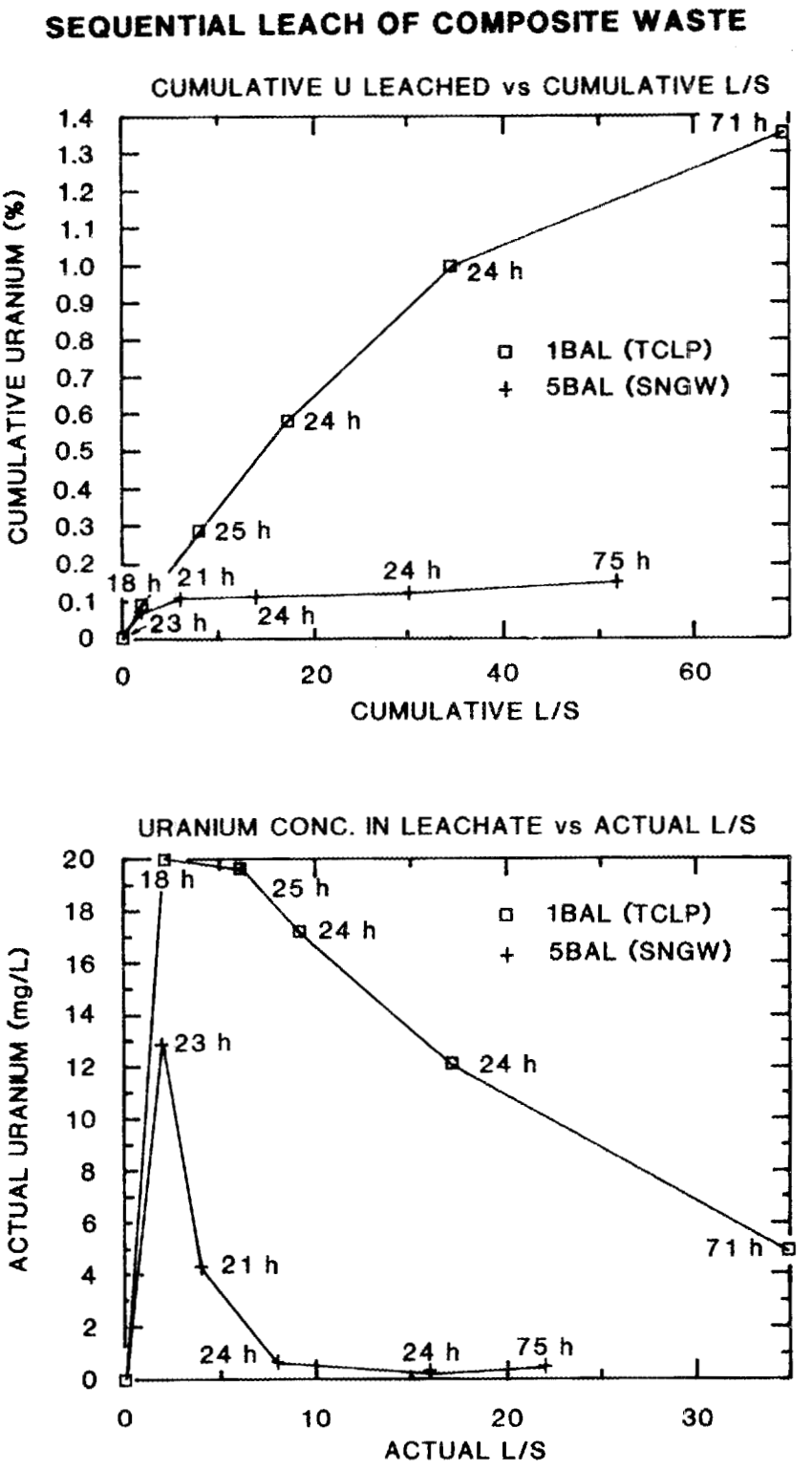

Fig. 3.4. Sequential leach of composite waste.

3.2.3 Mixed Metal Chips

A summary of the uranium data for the four batch leach tests with mixed metal chips is given in Table 3.6 and in Fig. 3.5. A similar data summary and a plot for the two sequential leach tests are given in Table 3.7 and Fig. 3.6, respectively.

All the batch leach tests showed similar decreasing-mode uranium release behavior. The fraction released or the concentration in solution maximized by the first data point (day 1) and decreased at longer times (up to day 7, the last time point) to very low values. The final pH of both the synthetic groundwater and the synthetic landfill leachates were similar throughout the tests and ranged from about pH 5.8 to 6.5. A decreasing release mode can occur only if uranium initially solubilized is subsequently removed from solution during extended waste/leachant contact. Either precipitation or sorption phenomena could produce such uranium behavior. As for the production trash and composite waste tests, the release of uranium appeared to be independent of the L/S ratio or the leachant composition. Again, it seems that properties of the mixed metal chips and/or the form of uranium in the waste rather than the apparent solution chemistry may be controlling the uranium release rate in these tests.

The sequential leach tests showed uranium leaching behavior that was different from the sequential leaches of production trash or combined waste. As with the batch tests, only a small fraction of the total uranium was solubilized; the maximum was ~0.05%. The synthetic landfill leachant was more aggressive than the synthetic groundwater and was continuing to leach small but steady amounts of uranium even at the final, largest L/S ratio contacts. Because the leachate is removed after each contact, it is not possible for the sequential tests to have a decreasing leach mode as was observed for the batch tests with mixed metal chips.

3.2.4 Air Filters

A summary of the uranium data for the four batch leach tests with the media cut from air filters is given in Table 3.8 and in Fig. 3.7. A

Table 3.6. Summary of batch leach data for mixed metal chips

	Test Parameters					Results							
Sample No.	Total Leach (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Total Uranium Leached (mg)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
4CHIPA	73.48	TCLP	3.67	255	20.0	18.6	18.6	0.570	41.88	1.64E-02	6.20	5.61	25.8
4CHIPB	73.48	TCLP	3.67	255	20.0	23.7	42.3	0.180	13.23	5.19E-03	6.31	5.49	25.6
4CHIPC	73.48	TCLP	3.67	255	20.0	25.3	67.5	0.091	6.69	2.62E-03	6.40	5.77	25.5
4CHIPD	73.48	TCLP	3.67	255	20.0	22.9	90.5	0.077	5.66	2.22E-03	6.30	5.93	25.8
4CHIPE	73.48	TCLP	3.67	255	20.0	72.5	163.0	0.022	1.62	6.34E-04	6.45	5.72	25.6
8CHIPA	107.05	SNGW	9.07	236	11.8	17.0	17.0	1.360	145.59	6.17E-02	6.10	0.05	25.8
8CHIPB	107.05	SNGW	9.07	236	11.8	24.6	41.6	0.240	25.69	1.09E-02	6.37	0.06	25.7
8CHIPC	107.05	SNGW	9.07	236	11.8	23.3	64.9	0.091	9.74	4.13E-03	5.84	0.05	25.4
8CHIPD	107.05	SNGW	9.07	236	11.8	25.3	90.2	0.028	3.00	1.27E-03	6.47	0.06	25.8
8CHIPE	107.05	SNGW	9.07	236	11.8	73.2	163.4	0.013	1.39	5.90E-04	6.08	0.07	26.1
3CHIPA	5.67	TCLP	2.84	55	2.0	18.2	18.2	0.680	3.85	7.01E-03	6.09	4.46	25.9
3CHIPB	5.67	TCLP	2.84	55	2.0	24.2	42.3	0.035	0.20	3.61E-04	6.30	4.27	25.8
3CHIPC	5.67	TCLP	2.84	55	2.0	24.0	66.3	0.011	0.06	1.13E-04	6.46	4.18	25.8
3CHIPD	5.67	TCLP	2.84	55	2.0	26.0	92.3	0.006	0.03	6.18E-05	6.47	3.97	26.0
3CHIPE	5.67	TCLP	2.84	55	2.0	69.3	161.7	0.007	0.04	7.22E-05	6.45	3.92	26.1
7CHIPA	7.59	SNGW	3.79	103	2.0	19.0	19.0	0.003	0.02	2.21E-05	5.90	0.19	25.9
7CHIPB	7.59	SNGW	3.79	103	2.0	24.5	43.5	0.007	0.05	5.15E-05	6.15	0.19	25.8
7CHIPC	7.59	SNGW	3.79	103	2.0	23.6	67.1	0.003	0.02	2.21E-05	6.25	0.20	25.6
7CHIPD	7.59	SNGW	3.79	103	2.0	25.8	92.9	0.003	0.02	2.21E-05	6.25	0.20	26.1
7CHIPE	7.59	SNGW	3.79	103	2.0	73.2	166.1	0.003	0.02	2.21E-05	6.03	0.25	26.9

* TCLP Leachant: pH = 4.90 at 25 C; conductivity = 4.25 mmho.
Synthetic Groundwater leachant: pH = 7.05 at 25.8 C; conductivity = 0.012 mmho.

** Corrected for analytical samples that were removed.

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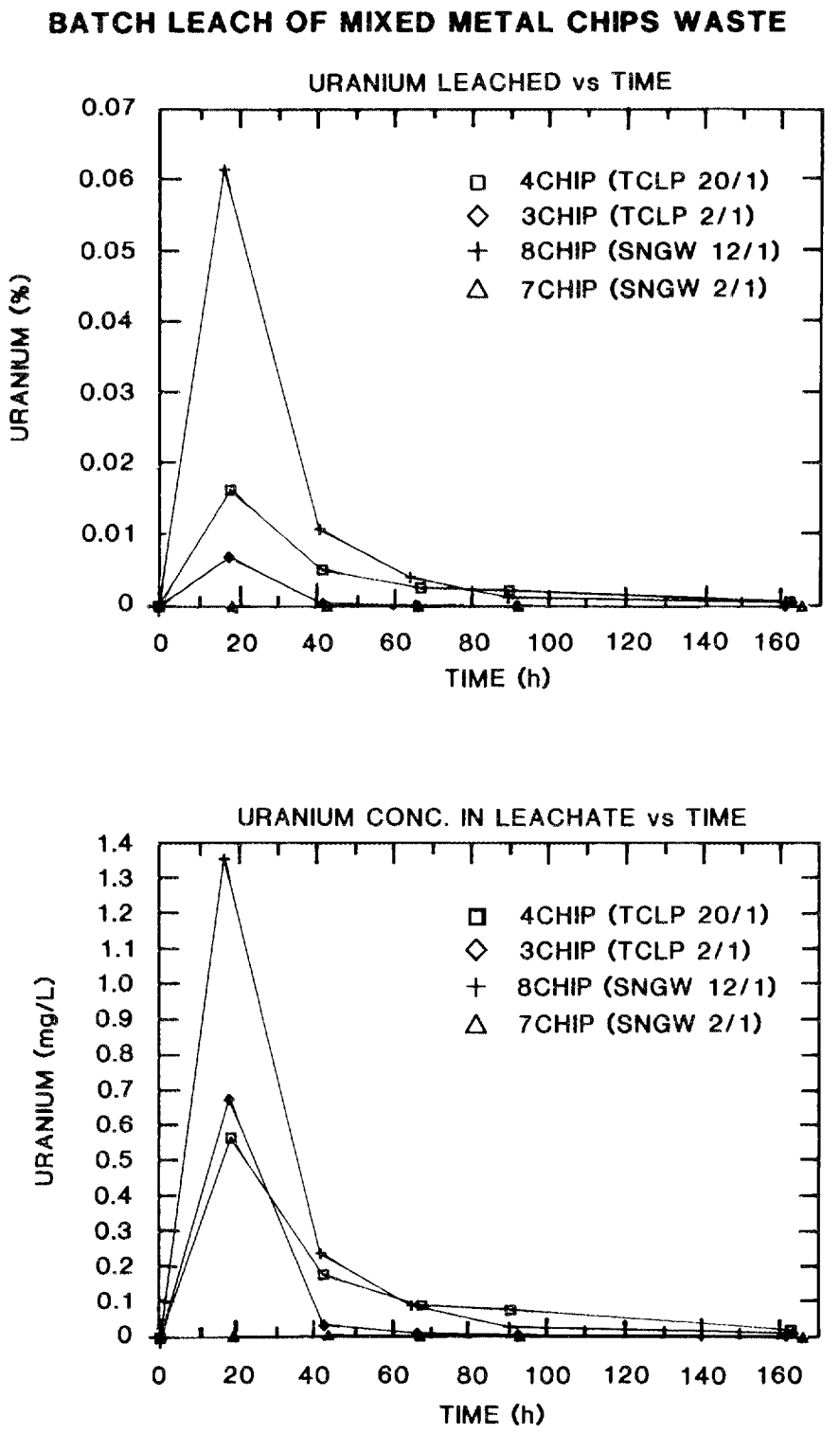

Fig. 3.5. Batch leach of mixed metal chips waste.

Table 3.7. Summary of sequential leach data for mixed metal chips

	Test Parameters							Results									
Sample No.	Leach Vol. (L)	Cum. Leach Vol. (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Cum. L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Uranium in Leachate (g)	Leached Uranium (g)**	Cum. Uranium Leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
1CHIPA	7.6	7.6	TCLP	3.81	119.0	2.0	2.0	22.6	22.6	0.95	0.0072	0.0072	0.0072	0.0061	6.18	5.35	26.1
1CHIPB	15.2	22.9	TCLP	3.81	119.0	4.0	6.0	20.2	42.8	0.48	0.0073	0.0065	0.0137	0.0115	6.09	5.66	26.1
1CHIPC	30.5	53.3	TCLP	3.81	119.0	8.0	14.0	27.5	70.3	0.45	0.0137	0.0133	0.0270	0.0227	6.11	5.61	25.5
1CHIPD	61.0	114.3	TCLP	3.81	119.0	16.0	30.0	24.8	95.0	0.15	0.0091	0.0084	0.0353	0.0297	6.31	5.34	25.9
1CHIPE	121.9	236.2	TCLP	3.81	119.0	32.0	62.0	67.2	162.2	0.18	0.0219	0.0218	0.0572	0.0480	6.17	5.72	25.9
5CHIPA	5.9	5.9	SNGW	2.90	93.0	2.0	2.0	23.1	23.1	0.064	0.0004	0.0004	0.0004	0.0004	6.48	0.24	25.5
5CHIPB	11.6	17.5	SNGW	2.90	93.0	4.0	6.0	23.0	46.1	0.022	0.0003	0.0002	0.0006	0.0006	6.42	0.07	25.8
5CHIPC	23.2	40.7	SNGW	2.90	93.0	8.0	14.0	21.0	67.1	0.035	0.0008	0.0008	0.0014	0.0015	6.60	0.04	25.7
5CHIPD	46.4	87.1	SNGW	2.90	93.0	16.0	30.0	24.0	91.1	0.016	0.0007	0.0007	0.0021	0.0023	6.80	0.03	28.6
5CHIPE	92.8	179.9	SNGW	2.90	93.0	32.0	62.0	71.0	162.1	0.009	0.0008	0.0008	0.0030	0.0032	7.95	0.03	25.7

* TCLP Leachant: pH = 4.88 at 25 C; conductivity = 4.24 mmho.
Synthetic Groundwater leachant: pH = 7.34 at 25.9 C; conductivity = 0.013 mmho.

** Values corrected for dissolved uranium in the leachate which was not removed after each leach period.

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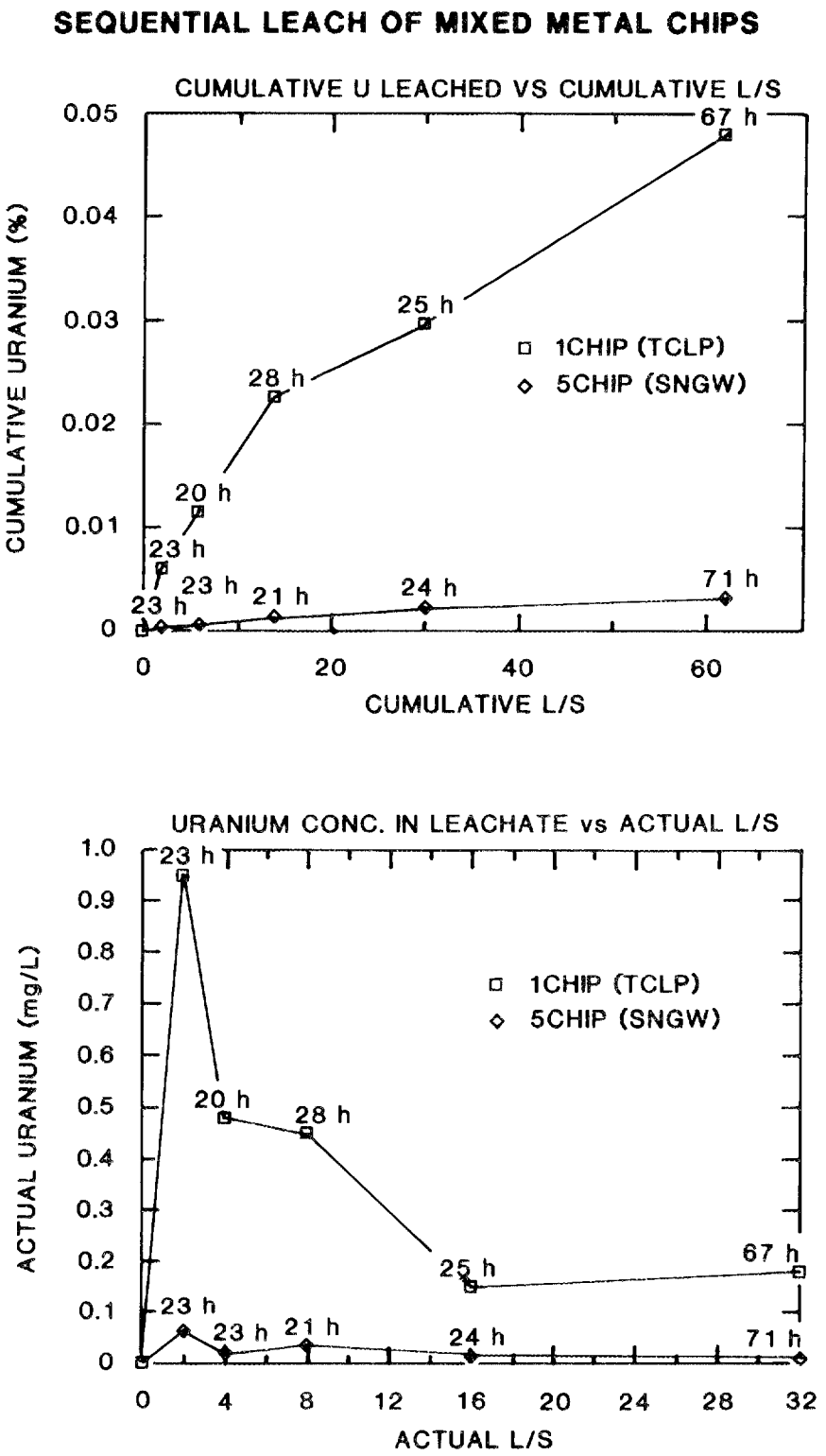

Fig. 3.6. Sequential leach of mixed metal chips waste.

Table 3.8. Summary of batch leach data for air filters

	Test Parameters							Results					
Sample No.	Leach Vol. (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Leach Time (h)	Cum. Leach Time (h)	Leachate Uranium Conc. (mg/L)	Total Uranium Leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
4FILA	47.2	TCLP	2.36	218	20.0	18.4	18.4	3630	171.3	78.6	4.96	3.67	26.6
4FILB	47.2	TCLP	2.36	218	20.0	24.6	43.0	3480	170.3	78.1	4.95	3.70	26.8
4FILC	47.2	TCLP	2.36	218	20.0	23.8	66.8	3430	164.0	75.2	5.05	3.74	27.4
4FILD	47.2	TCLP	2.36	218	20.0	23.8	90.6	3260	155.7	71.4	5.05	3.41	26.0
4FILE	47.2	TCLP	2.36	218	20.0	70.8	161.3	3110	148.5	68.1	5.13	3.38	26.4
8FILA	47.2	SNGW	2.34	200	20.2	22.3	22.3	610	28.8	14.4	4.25	0.14	26.7
8FILB	47.2	SNGW	2.34	200	20.2	24.6	46.9	570	29.9	14.9	3.85	0.16	27.0
8FILC	47.2	SNGW	2.34	200	20.2	22.6	69.5	620	29.6	14.8	4.17	0.16	27.3
8FILD	47.2	SNGW	2.34	200	20.2	24.3	93.7	650	31.0	15.5	4.26	0.16	26.2
8FILE	47.2	SNGW	2.34	200	20.2	70.2	163.9	610	29.1	14.6	4.32	0.15	26.5
3FILA	4.5	TCLP	2.27	231	2.0	20.6	20.6	5760	26.1	11.3	4.92	3.53	26.7
3FILB	4.5	TCLP	2.27	231	2.0	23.0	43.6	3920	22.6	9.8	4.96	3.48	26.8
3FILC	4.5	TCLP	2.27	231	2.0	25.6	69.2	2130	11.8	5.1	5.07	3.48	27.1
3FILD	4.5	TCLP	2.27	231	2.0	23.3	92.4	1700	8.9	3.8	5.00	3.52	26.2
3FILE	4.5	TCLP	2.27	231	2.0	71.7	164.1	560	3.5	1.5	5.48	3.51	26.9
7FILA	5.2	SNGW	2.59	198	2.0	23.8	23.8	1740	9.0	4.5	3.92	0.67	26.8
7FILB	5.2	SNGW	2.59	198	2.0	24.2	48.0	510	4.2	2.1	4.10	0.47	26.9
7FILC	5.2	SNGW	2.59	198	2.0	24.7	72.7	240	1.5	0.8	4.46	0.34	27.0
7FILD	5.2	SNGW	2.59	198	2.0	20.6	93.3	40	0.3	0.2	4.69	0.23	26.0
7FILE	5.2	SNGW	2.59	198	2.0	73.0	166.3	140	0.7	0.4	5.37	0.16	26.9

* TCLP leachant: pH = 4.85 at 25.7 C; conductivity = 4.30 mmho.
Synthetic Groundwater leachant: pH = 6.85 at 25.9 C; conductivity = 0.012 mmho.

** Corrected for analytical samples that were removed.

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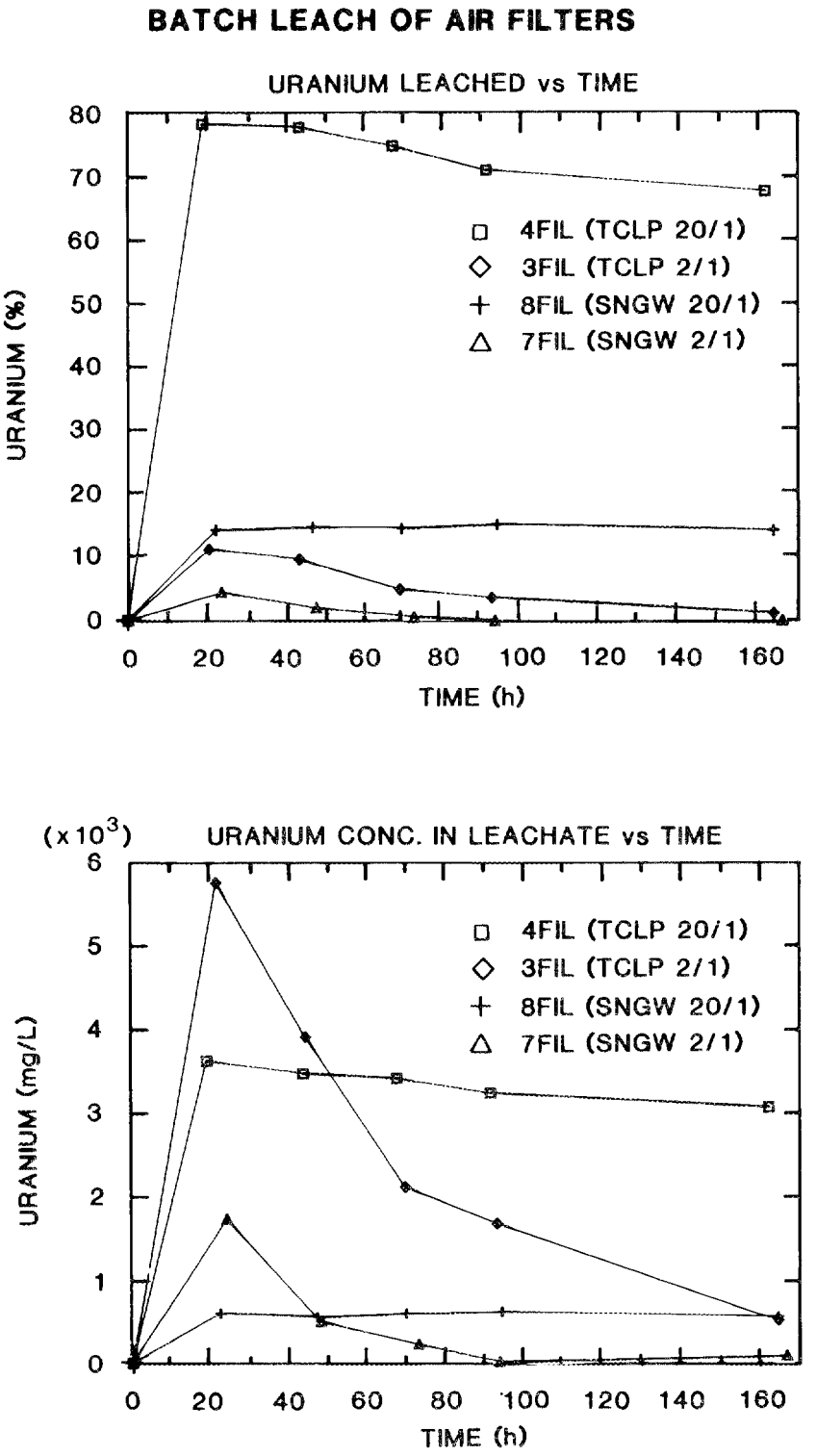

Fig. 3.7. Batch leach of air filters.

similar data summary and a plot for the two sequential leach tests are given in Table 3.9 and Fig. 3.8, respectively.

The uranium leaching data for the air filter samples showed two significant differences from the other wastes. First, and perhaps most important, was the high solubility of the uranium contaminant. The fraction leached by day 7 was as high as 66% in batch test 4FIL; however, in the other three tests, <15% was leached. In sequential test 1FIL, in which synthetic landfill leachant was used, ~51% of the initial uranium was solubilized in 7 d. By comparison, in the parallel test (5FIL) using synthetic groundwater, only 17% was leached. In general, it appeared that the uranium leaching, at least on day 1, may have been constrained only by the solubility limitation of the leachant. High leaching of uranium from the air filters may be rationalized by assuming that only small particles ($\leq$10 μm in diameter) of contaminant reached the filters in the building ventilation systems and that a large fraction of these small particles may be readily oxidized to soluble uranium-containing solids.

A second, and surprising, observation for the batch tests was the appearance of a decreasing leach mode in some cases. (In the sequential tests, the solubilized uranium was removed after each contact leach period and thus was not available for precipitation or sorption reactions.) Particularly in the tests with an L/S ratio of 2, much or nearly all of the uranium was removed from the leachate with extended time. Examination of the contact vessel for the synthetic landfill leachate tests showed a varying degree of bubbling and sludge formation. It appeared that the aluminum filter components were reacting with the leachate; this reaction would generate hydrogen and also a very strongly reducing redox condition. Thus, as in the case of mixed metal chips, uranium removal from solution could be due to reduction of soluble uranium (VI) species to insoluble uranium (IV) solids and/or to sorption on the gelatinous sludge. In batch leach test 8FIL, the drum was resealed and stored for 804 h to allow static leaching. As can be seen in Table 3.8, the concentration of uranium in the leach decreased from 610 to 410 mg/L or 33%. Further drops in uranium concentration resulted after two additional 24-h leaching periods on the drum roller. The

Table 3.9. Summary of sequential leach data for air filters

	Test Parameters									Results							
Sample No.	Leach Volume (L)	Cum. Leach Volume (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Cum. L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Uranium in Leachate (g)	Leached Uranium (g)**	Cum. Uranium Leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
1FILA	5.8	5.8	TCLP	2.68	259.0	2.2	2.0	18.3	18.3	6840	39.74	39.74	39.74	15.3	4.81	2.99	26.9
1FILB	11.0	16.8	TCLP	2.68	259.0	4.1	6.0	24.3	42.6	3050	33.61	13.84	53.58	20.7	4.87	3.76	27.0
1FILC	21.4	38.2	TCLP	2.68	259.0	8.0	14.1	24.0	66.6	2320	49.67	38.20	91.78	35.4	5.09	3.79	26.9
1FILD	42.8	81.1	TCLP	2.68	259.0	16.0	30.6	24.8	91.3	930	39.82	30.08	121.86	47.1	4.82	3.70	27.1
1FILE	85.6	166.7	TCLP	2.68	259.0	32.0	64.1	71.0	162.3	170	14.56	10.55	132.41	51.1	4.90	3.71	26.7
5FILA	3.9	3.9	SNGW	1.91	198.0	2.0	2.0	20.0	20.0	1280	4.97	4.97	4.97	2.5	3.75	0.63	26.8
5FILB	7.6	11.5	SNGW	1.91	198.0	4.0	6.0	24.3	44.3	1130	8.61	4.23	9.20	4.6	3.75	0.37	27.0
5FILC	15.2	26.7	SNGW	1.91	198.0	8.0	14.0	26.1	70.4	430	6.55	2.17	11.37	5.7	4.08	0.14	27.0
5FILD	30.6	57.4	SNGW	1.91	198.0	16.0	30.0	22.7	93.1	230	7.04	5.47	16.84	8.5	4.20	0.05	27.1
5FILE	61.0	118.3	SNGW	1.91	198.0	31.9	62.0	70.5	163.6	290	17.68	16.82	33.66	17.0	5.01	0.02	26.8

* TCLP Leachant: pH = 4.85 at 25.7 C; conductivity = 4.30 mmho.
Synthetic Groundwater leachant: pH = 6.95 at 25.9 C; conductivity = 0.0125 mmho.

** Values corrected for dissolved uranium in the leachate which was not removed after each leach period.

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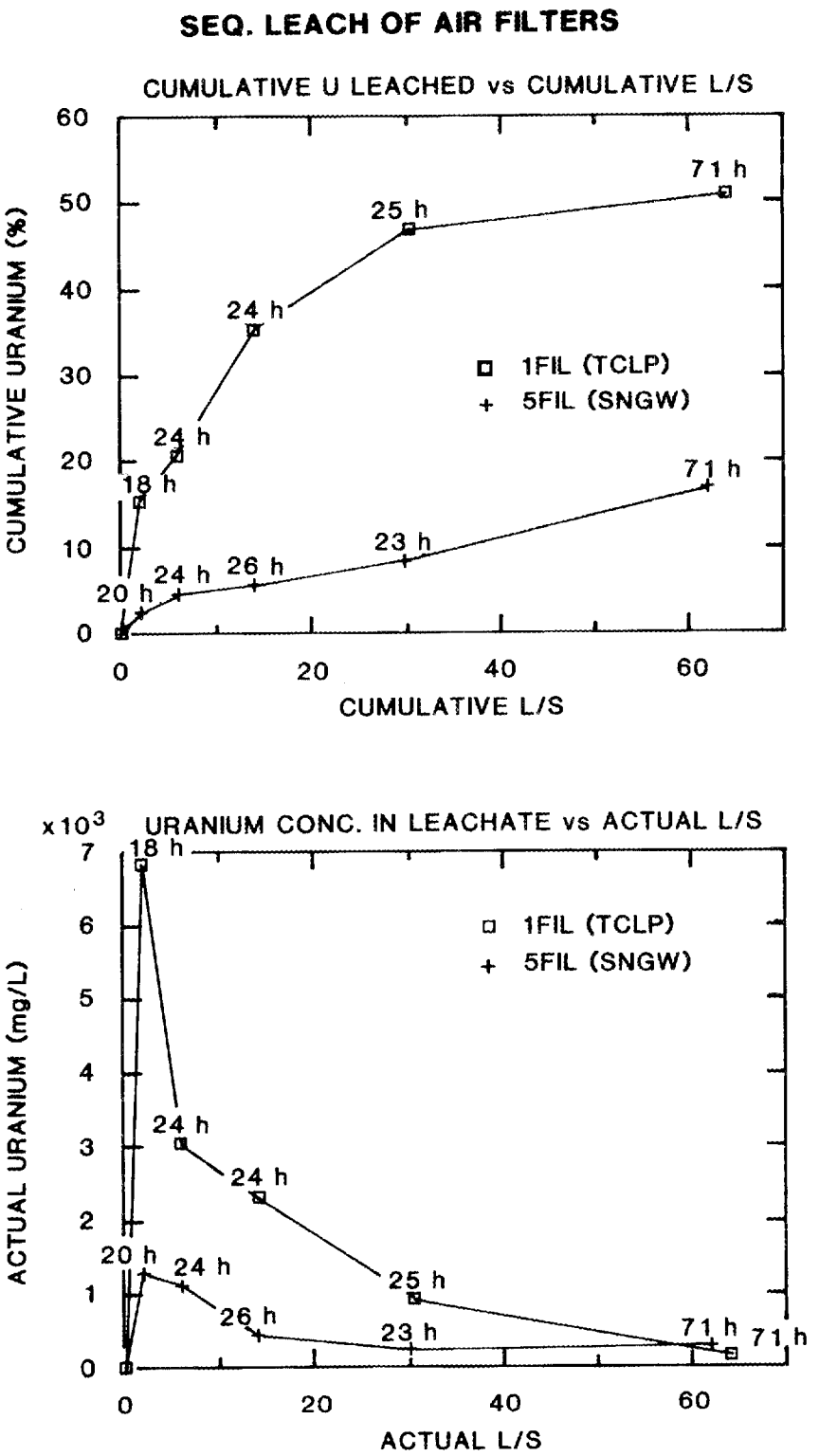

Fig. 3.8. Sequential leach of air filters.

concentration of the last leachate was 280 mg/L (a drop of 54%). A major difference noted in samples 8FILE, 8FILH, and 8FILI was the amount of gelatinous precipitate on the filter papers. There was very little precipitate on the 8FILE filter paper compared to the amounts obtained for the other two samples. Furthermore, the 8FILH and 8FILI filter cakes were considerably radioactive when checked with the beta-gamma monitor. The gelatinous sludge was probably aluminum hydroxide, which would be capable of sorbing precipitated or ionic uranium. After the initial TCLP leaches in the 3FIL and 7FIL tests, the concentration of uranium in the leachates decreased with time; the amounts of gelatinous sludge noticeably increased; the 3FIL leachates were very foamy, while the 7FIL leachates were not. In test 4FIL, the uranium concentration in the leachate was fairly constant, the leachates were not foamy, and there was little gelatinous precipitate on the filter papers.

3.2.5 Uranium Oxide Powder from the UCOF

A summary of the uranium data for the four batch leach tests with uranium oxide powder from the UCOF is given in Table 3.10 and in Fig. 3.9. A similar data summary and a plot for the two sequential leach tests are given in Table 3.11 and Fig. 3.10, respectively.

As in the case of the composite waste batch leaching tests, the batch leach tests of uranium oxide powder showed a somewhat more complex leaching pattern. As was expected, the uranium was more soluble in synthetic landfill than in synthetic groundwater leachant. These data show that a 1-d leach period was sufficient for each leachant to become saturated with uranium when the L/S ratio was 2:1. The apparent saturation uranium concentrations for the synthetic landfill leachate and synthetic groundwater were 3300 ± 300 and 193 ± 3 mg/L, respectively. Six separate 1-d tests at a 2:1 L/S ratio (using synthetic landfill leachant) were also conducted with uranium oxide powder from the UCOF using synthetic landfill leachant (Table 3.12). The uranium concentration in the leachate for those tests was 3300 ± 200 mg/L. The time needed for the leachants to become saturated with uranium for larger L/S ratios was much longer. The average uranium concentration in TCLP

Table 3.10. Summary of batch leach data for uranium oxide powder from UCOF

	Test Parameter					Results							
Sample Run	Total Leach (ml)	* Leachant	Solid Waste (g)	Uranium (g)	L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Total Uranium Leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
31A	1700.2	TCLP	85.9	72.9	19.8	21.8	21.8	1480	2.52	3.45	5.08	3.65	26.2
31B	1700.2	TCLP	85.9	72.9	19.8	21.1	42.9	1640	2.87	3.93	5.09	3.70	26.1
31C	1700.2	TCLP	85.9	72.9	19.8	24.1	67.0	1850	3.21	4.40	4.98	3.59	26.3
31D	1700.2	TCLP	85.9	72.9	19.8	96.2	163.2	2880	4.97	6.81	5.20	3.59	26.3
31E	1700.2	TCLP	85.9	72.9	19.8	192.3	355.5	3050	5.29	7.25	5.10	3.62	25.7
31F	1700.2	TCLP	85.9	72.9	19.8	167.3	522.7	3300	5.76	7.90	5.10	3.85	25.8
31G	1700.2	TCLP	85.9	72.9	19.8	337.2	859.9	3800	5.88	8.07	5.13	3.74	25.4
32A	1701.6	SNGW	85.9	72.9	19.8	22.7	22.7	42.0	0.071	0.098	6.00	0.023	26.3
32B	1701.6	SNGW	85.9	72.9	19.8	21.1	43.8	37.0	0.065	0.090	6.13	0.019	26.1
32C	1701.6	SNGW	85.9	72.9	19.8	24.0	67.8	45.0	0.077	0.106	5.88	0.020	26.1
32D	1701.6	SNGW	85.9	72.9	19.8	96.0	163.8	54.0	0.092	0.127	5.81	0.019	26.3
32E	1701.6	SNGW	85.9	72.9	19.8	195.0	358.8	66.0	0.114	0.157	5.56	0.019	25.8
32F	1701.6	SNGW	85.9	72.9	19.8	167.3	526.1	71.0	0.124	0.171	5.92	0.016	25.8
32G	1701.6	SNGW	85.9	72.9	19.8	334.0	860.1	75.0	0.131	0.179	5.30	0.016	25.0
33A	1604.3	TCLP	799.8	678.8	2.0	22.7	22.7	3490	5.60	0.82	5.25	3.37	26.3
33B	1604.3	TCLP	799.8	678.8	2.0	19.9	42.6	3590	5.95	0.88	5.23	3.16	26.1
33C	1604.3	TCLP	799.8	678.8	2.0	24.3	66.9	3740	6.13	0.90	5.01	3.16	26.1
33D	1604.3	TCLP	799.8	678.8	2.0	96.0	162.9	3210	5.28	0.78	5.03	3.18	26.3
33E	1604.3	TCLP	799.8	678.8	2.0	192.5	355.4	2860	4.70	0.69	4.93	3.08	25.7
33F	1604.3	TCLP	799.8	678.8	2.0	167.5	522.9	3000	4.96	0.73	4.90	3.43	25.9
33G	1604.3	TCLP	799.8	678.8	2.0	337.5	860.5	3200	5.25	0.77	4.83	3.24	25.3
34A	1604.7	SNGW	799.3	678.3	2.0	21.8	22.7	193.0	0.310	0.046	5.17	0.077	26.4
34B	1604.7	SNGW	799.3	678.3	2.0	20.5	43.2	195.0	0.323	0.048	5.25	0.074	26.2
34C	1604.7	SNGW	799.3	678.3	2.0	24.2	67.3	190.0	0.312	0.046	4.90	0.082	26.2
34D	1604.7	SNGW	799.3	678.3	2.0	95.8	163.1	131.0	0.216	0.032	5.01	0.082	26.4
34E	1604.7	SNGW	799.3	678.3	2.0	196.1	359.2	30.0	0.053	0.008	5.00	0.094	26.1
34F	1604.7	SNGW	799.3	678.3	2.0	167.3	526.5	19.0	0.032	0.005	5.20	0.103	25.8
34G	1604.7	SNGW	799.3	678.3	2.0	334.3	860.8	7.0	0.013	0.002	5.30	0.100	24.8

* TCLP leachant: pH = 4.90 at 26 C; concuctivity = 4.25 mmho.
Synthetic Groundwater leachant: pH = 7.00 at 26 C; conductivity = 0.013 mmho.

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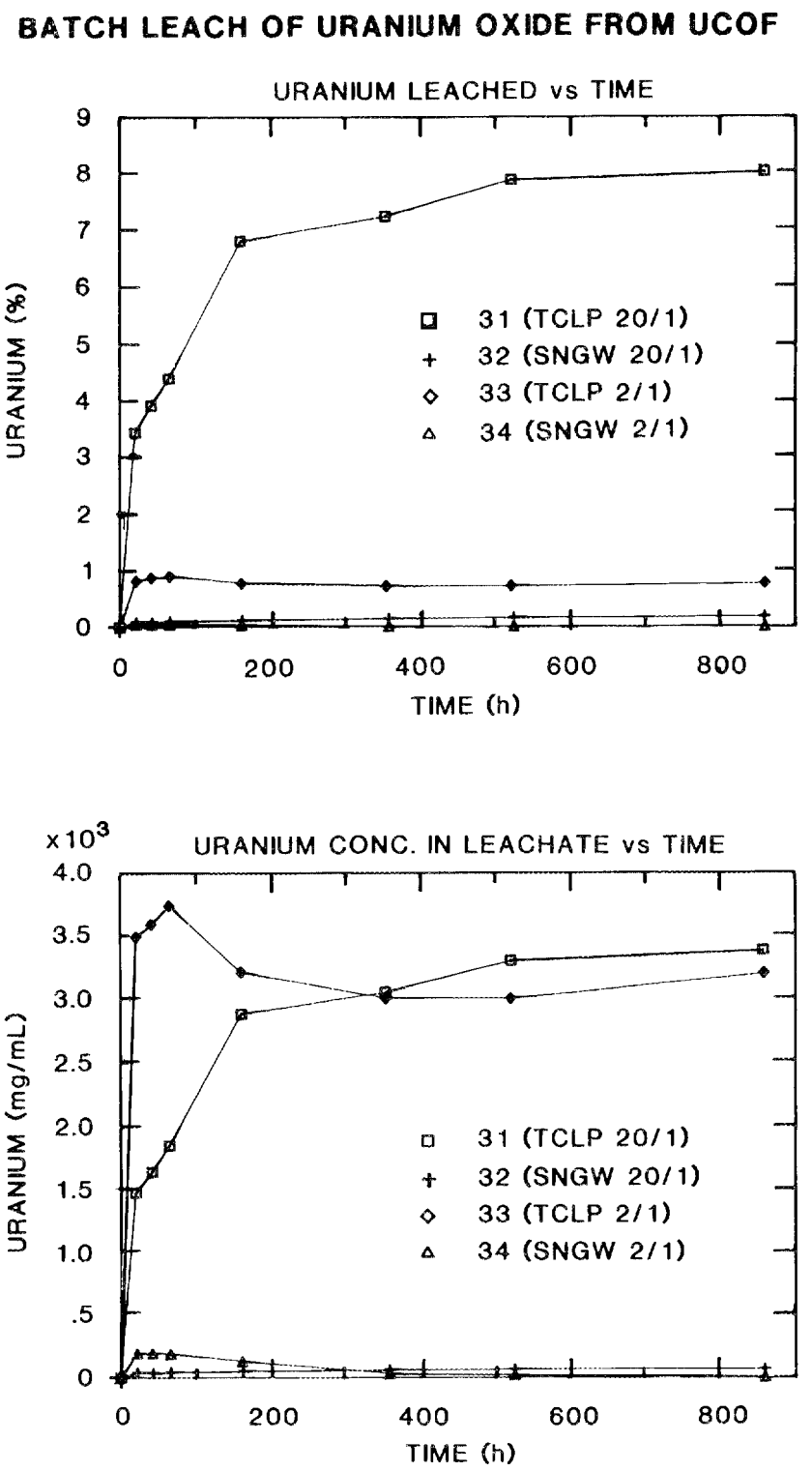

Fig. 3.9. Batch leach of uranium oxide from UCOF.

Table 3.11. Summary of sequential leach data for uranium oxide powder from the UCOF

	Test Parameters							Results									
Sample No.	Leach Volume (L)	Cum. Leach Volume (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Cum. L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Uranium in Leachate (g)	Leached Uranium (g)**	Cum. Uranium Leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
35A	0.113	0.113	TCLP	0.0563	47.78	2.0	2.0	23.1	23.1	3400	0.383	0.383	0.383	0.80	4.85	3.37	26.0
35B	0.225	0.338	TCLP	0.0562	47.66	4.0	6.0	27.2	50.3	3300	0.743	0.481	0.864	1.81	4.96	3.88	25.7
35C	0.451	0.788	TCLP	0.0555	47.02	8.1	14.1	21.0	71.3	2200	0.991	0.885	1.749	3.66	4.75	4.03	25.7
35D	0.901	1.689	TCLP	0.0546	46.08	16.5	30.6	26.8	98.1	930	0.838	0.793	2.542	5.32	4.72	3.69	25.6
35E	1.802	3.491	TCLP	0.0538	45.25	33.5	64.1	71.9	170.0	830	1.495	1.463	4.005	8.38	4.74	3.77	26.1
36A	0.113	0.113	SNGW	0.0563	47.78	2.0	2.0	25.2	25.2	127	0.014	0.014	0.014	0.03	5.40	0.119	26.0
36B	0.225	0.338	SNGW	0.0563	47.77	4.0	6.0	24.0	49.2	64	0.014	0.012	0.026	0.05	5.70	0.033	25.7
36C	0.450	0.788	SNGW	0.0563	47.76	8.0	14.0	26.9	76.1	26	0.012	0.010	0.036	0.07	6.11	0.018	25.7
36D	0.901	1.689	SNGW	0.0563	47.75	16.0	30.0	23.8	100.0	16	0.014	0.013	0.049	0.10	5.72	0.013	25.6
36E	1.802	3.490	SNGW	0.0563	47.73	32.0	62.0	69.0	169.0	26	0.047	0.046	0.095	0.20	5.50	0.013	26.2

* TCLP Leachant: pH = 4.85 at 25.7 C; conductivity = 4.30 mmho.

** Synthetic Groundwater leachant: pH = 6.95 at 25.9 C; conductivity = 0.0125 mmho.

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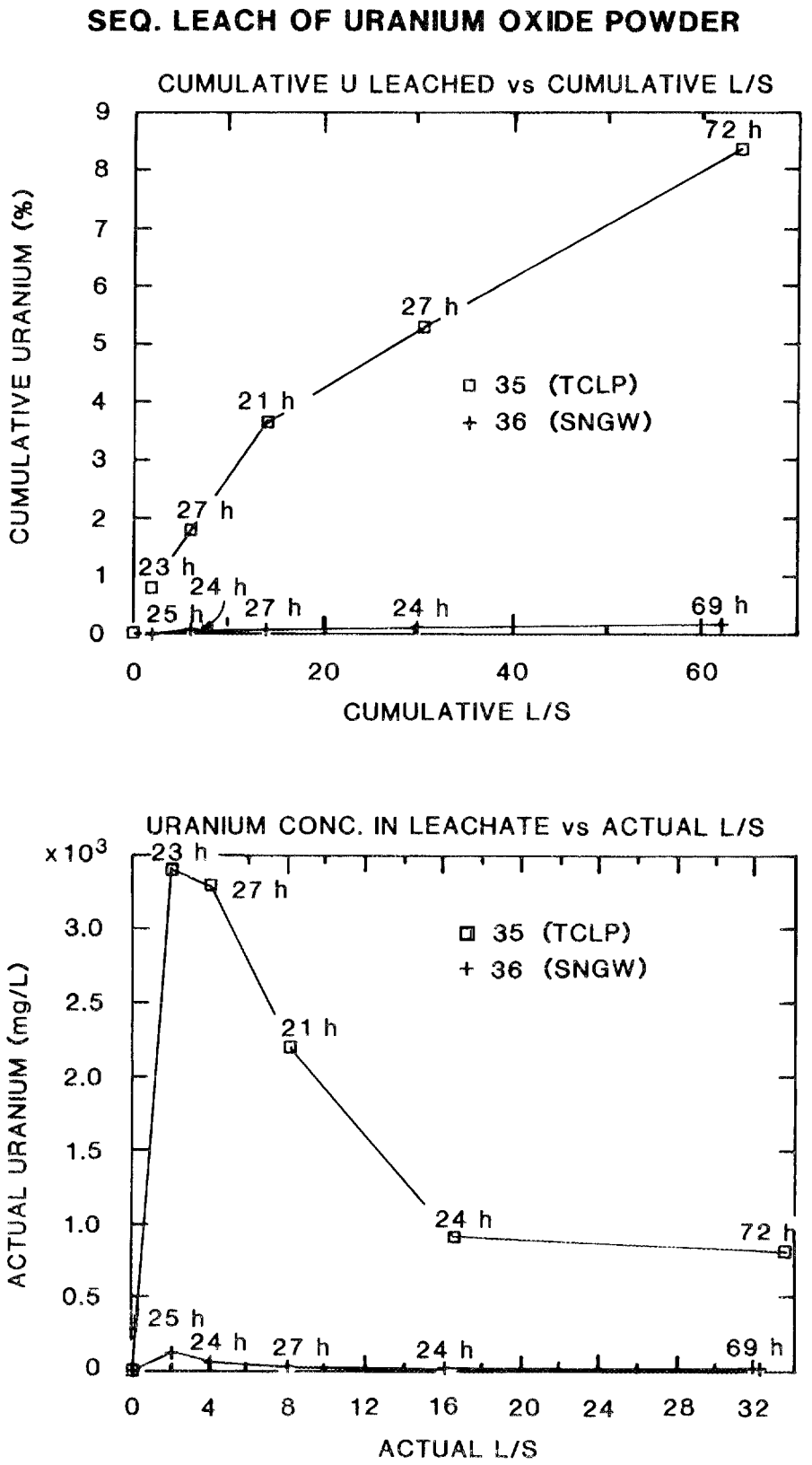

Fig. 3.10. Sequential leach of uranium oxide from UCOF.

Table 3.12. Summary of batch TCLP leach data for uranium oxide powder from UCOF

	Test parameters					Results					
Sample no.	Leachant vol.(a) (ml)	Solid waste (g)	Uranium (g)	Leach time (h)	L/S(b)	Leachate uranium conc. (mg/ml)	Uranium leached (g)	Initial uranium leached (%)	pH	Cond. (mmho)	Temp. (C)
2	2000.1	40.14	34.07	26.6	49.8	0.77	1.54	4.52	4.87	NM(c)	26.2
10	2000.0	40.10	34.04	22.5	49.9	0.74	1.48	4.35	4.87	NM	26.2
12	2000.0	40.16	34.09	24.7	49.8	0.77	1.54	4.52	4.88	NM	26.3
25A	2010.0	40.64	34.50	23.5	49.5	0.79	1.59	4.62	4.83	3.98	26.6
8	2000.0	40.15	34.08	236.4	49.8	1.18	2.36	6.93	5.04	NM	25.6
15	2000.2	40.11	34.05	236.8	49.9	1.37	2.74	8.05	4.86	NM	26.4
18	2000.0	39.92	33.88	236.4	50.1	1.43	2.86	8.44	4.84	NM	26.4
26U1	1700.0	85.47	72.55	24.5	19.9	1.61	2.74	3.78	4.93	3.45	25.1
26U2	1700.2	85.48	72.56	24.5	19.9	1.58	2.68	3.70	4.92	3.47	25.1
26U3	1700.0	85.45	72.53	24.5	19.9	1.63	2.77	3.83	4.92	3.51	25.1
31A	1700.2	85.90	72.90	21.8	19.8	1.48	2.52	3.45	5.08	3.35	26.2
31G	1700.2	85.90	72.90	859.9	19.8	3.80	5.88	8.07	5.13	3.43	25.4
1	2000.0	758.90	644.15	22.0	2.6	2.99	5.98	0.93	5.02	NM	26.2
5A	1500.0	747.90	634.80	22.2	2.0	3.36	5.04	0.79	5.29	NM	23.3
9	1500.0	753.70	639.74	23.6	2.0	3.30	4.95	0.77	5.00	NM	26.3
17	1500.0	749.80	636.43	19.0	2.0	3.33	5.00	0.78	4.67	NM	25.8
21A	1501.0	750.30	636.90	23.0	2.0	3.38	5.07	0.80	5.29	NM	23.3
23A	1501.1	750.70	637.10	23.2	2.0	3.50	5.25	0.82	5.18	NM	23.5
33A	1604.3	799.80	678.80	22.7	2.0	3.49	5.60	0.82	5.25	3.09	26.3
33G	1604.3	799.80	678.80	860.5	2.0	3.20	5.25	0.77	4.83	2.97	25.3

(a)TCLP = synthetic landfill leachate; pH = 4.85 at 26 C; conductivity = 4.24 mmho.
(b)L/S = liquid/solid ratio.
(c)NM = not measured.

leachates for four 20:1 L/S ratio batch leach tests (26U1, 26U2, 26U3, and 31A) was 1580 ± 70 mg/L (48% of saturation) compared with 770 ± 20 mg/L (23% of saturation) for four 50:1 L/S ratio batch leach tests (2, 10, 12, and 25A) for 24-h leaching periods. For a 10-d leach period, the average uranium concentration in the leachate for three other 50:1 L/S ratio tests (8, 15, and 18) was 1330 ± 130 mg/L (40% of saturation). It took ~22 d of leaching for the 20:1 L/S ratio leachate in test 31 to become saturated with uranium. Fig. 3.11 shows the effect of L/S ratio on the concentration of uranium for given leach periods.

The leach time needed for synthetic groundwater leachant to become saturated with uranium was longer than for synthetic landfill leachant. In test 32 (Table 3.10), in which synthetic groundwater leachant (20:1 L/S ratio) was used, the concentration of uranium in the leachate after 36 d was only 75 mg/L (~39% saturated), but the leaching of uranium appeared to be in an increasing mode. As mentioned previously, it took 22 d for synthetic landfill leachant (20:1 L/S ratio) in test 31 to become saturated. Anomalous leach behavior was observed in only one of the uranium oxide powder tests, test 34. In that leach test series, apparent saturation occurred during the first day leaching period. However, after 3 d of leaching, the uranium concentration started to decrease. By the end of the seventh day of leaching, the concentration had fallen to 7 mg/L from 190. We offer no explanation at this time as to why the uranium concentration dropped.

The two sequential tests (Table 3.11 and Fig. 3.11) further demonstrated that the synthetic landfill leachant was more aggressive in dissolving uranium than was the synthetic groundwater leachant. The first two leaches with synthetic landfill leachant (2:1 and 4:1 L/S ratios) yielded leachates that appeared to be saturated with uranium. In the subsequent leaches, the concentration of uranium in the leachates decreased.

Table 3.13 and Figs. 3.12 and 3.13 summarize synthetic landfill sequential leach data for additional experiments that were conducted with uranium oxide powder from the same UCOF source as was used to conduct the above-mentioned sequential leach tests. Tests 23, 21, and 5 were identically conducted tests that gave leach results which were also

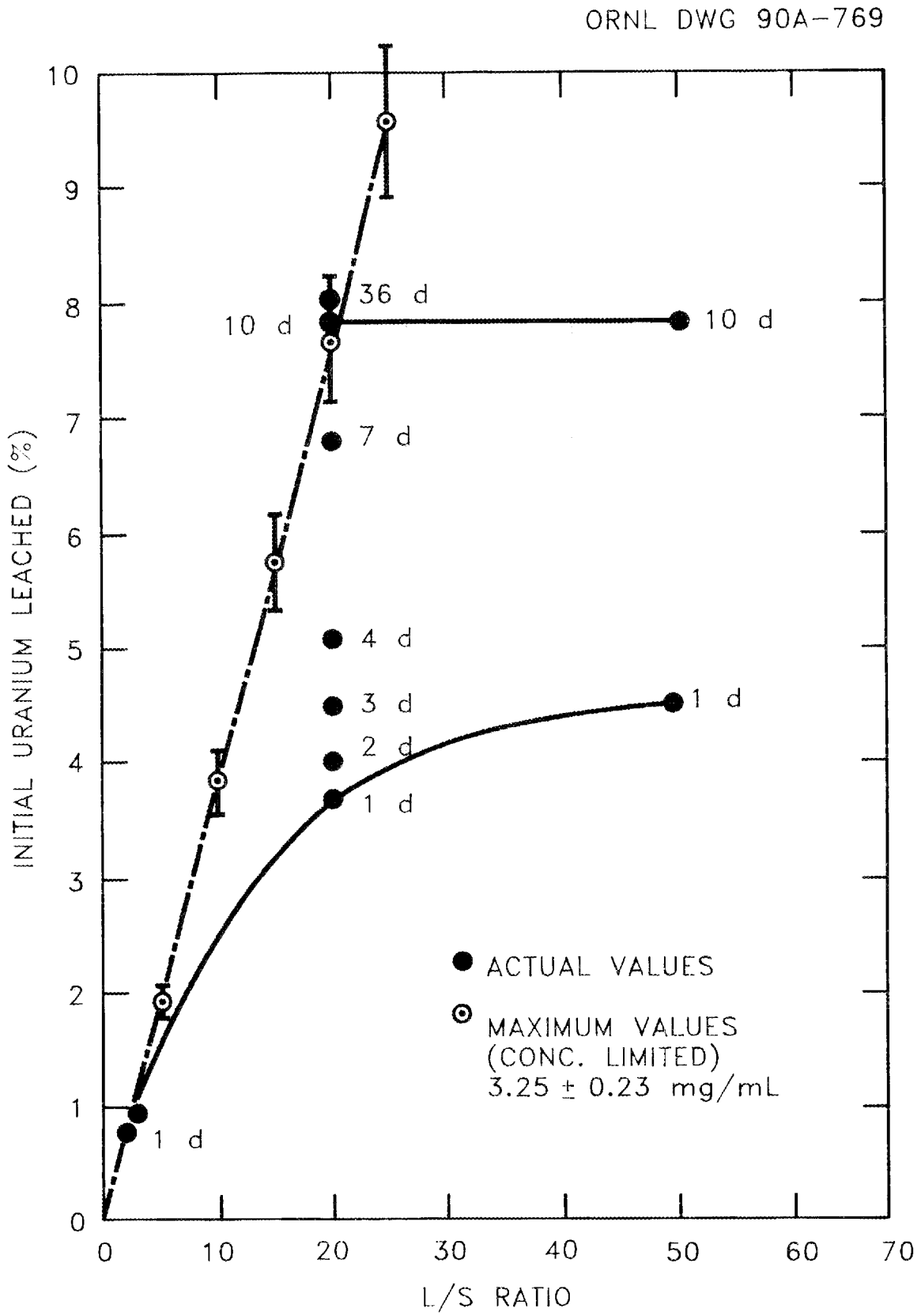

Fig. 3.11. Percentage of initial uranium leached as a function of L/S ratio for certain uranium oxide powder tests which used synthetic landfill leachant.

Table 3.13. Summary of TCLP sequential leach data for uranium powder from UCOF

	Test parameters									Results				
Sample no.	Total leach (L)	Solid waste (kg)	Uranium (g)	L/S	Cum. L/S	Filtered leachate (L)	Leachate in solids (L)	Leach time (h)	Cum. leach time (h)	Leachate uranium conc. (mg/L)	Uranium in leachate (g)	Leached uranium (g)	Total uranium leached (g)	Initial uranium leached (%)
23A	1.501	0.751	637.1	2.0	2.0	1.341	0.160	23.2	23.2	3500	5.25	5.25	5.25	0.82
23B	1.660	0.745	632.4	2.2	4.2	1.482	0.178	21.0	44.2	2990	4.96	4.40	9.66	1.52
23C	1.678	0.740	628.0	2.3	6.5	1.510	0.169	23.4	67.6	2920	4.90	4.37	14.02	2.20
23D	1.669	0.735	623.6	2.3	8.8	1.475	0.193	23.0	90.6	2800	4.67	4.18	18.20	2.86
23E	1.693	0.730	619.4	2.3	11.1	1.465	0.229	23.8	114.4	2590	4.39	3.84	22.05	3.46
23F	1.729	0.725	615.7	2.4	13.5	1.497	0.232	25.3	139.7	2060	3.56	2.97	25.02	3.93
23G	1.732	0.722	612.6	2.4	15.9	1.476	0.256	22.1	161.8	1810	3.14	2.66	27.67	4.34
23H	1.756	0.719	609.9	2.4	18.3	1.596	0.260	22.8	184.6	1630	2.86	2.40	30.07	4.72
23I	1.760	0.716	607.5	2.5	20.8	1.358	0.403	22.3	206.9	1550	2.73	2.30	32.38	5.08
23J	1.903	0.713	605.4	2.7	23.5			24.9	231.8	1650	3.14	2.52	34.89	5.48
21A	1.501	0.750	636.9	2.0	2.0	1.351	0.150	23.0	23.0	3380	5.07	5.07	5.07	0.80
21B	1.650	0.745	632.4	2.2	4.2	1.474	0.176	21.1	44.1	3010	4.97	4.40	9.48	1.49
21C	1.676	0.740	628.0	2.3	6.5	1.484	0.192	22.1	66.2	2970	4.98	4.45	13.92	2.19
21D	1.692	0.735	623.6	2.3	8.8	1.490	0.202	23.7	89.8	2930	4.96	4.39	18.31	2.88
21E	1.702	0.730	619.5	2.3	11.1	1.480	0.222	22.8	112.6	2810	4.78	4.19	22.50	3.53
21F	1.722	0.726	616.0	2.4	13.5	1.482	0.240	22.9	135.5	2350	4.05	3.42	25.92	4.07
21G	1.740	0.722	613.0	2.1	15.6	1.458	0.282	24.2	159.8	2060	3.58	3.02	28.95	4.54
23H	1.782	0.719	610.0	2.5	18.1	1.522	0.260	23.5	183.3	1980	3.53	2.95	31.89	5.01
23I	1.760	0.716	607.2	2.5	20.5	1.476	0.284	24.1	207.4	1860	3.27	2.76	34.65	5.44
21J	1.784	0.712	604.5	2.5	23.0			22.3	229.7	1720	3.07	2.54	37.19	5.84
5A	1.500	0.748	634.8	2.0	2.0	1.350	0.150	22.2	22.2	3360	5.04	5.04	5.04	0.79
5B	1.650	0.743	630.3	2.2	4.2	1.497	0.176	20.0	42.2	3040	5.02	4.51	9.55	1.50
5C	1.653	0.737	625.7	2.2	6.5	1.455	0.192	22.9	65.1	2980	4.93	4.39	13.94	2.20
5D	1.699	0.732	621.4	2.3	8.8	1.503	0.202	23.3	88.3	2930	4.98	4.41	18.35	2.89
5E	1.696	0.727	617.0	2.3	11.1	1.480	0.222	22.9	111.2	2810	4.77	4.17	22.52	3.55
5F*	1.722	0.723	613.5	2.4	13.5									
25A	2.010	0.041	34.50	49.5	49.5	1.928	0.027	23.5	23.5	791	1.59	1.59	1.59	4.62
25B	2.027	0.039	32.90	52.3	101.7	1.926	0.101	22.8	46.3	333	0.68	0.65	2.24	6.52
25C	2.101	0.038	32.26	55.3	157.0	2.032	0.068	24.0	70.3	246	0.52	0.48	2.73	7.93
25D**	2.070	0.037	31.74	55.4	212.4	2.019	0.052	25.3	95.6	256	0.53	0.51	3.24	9.42
25E	2.053	0.037	31.37	55.6	267.9	1.984	0.068	25.5	121.1	189	0.39	0.37	3.61	10.51
25F***	2.071	0.036	30.94	56.8	324.7	1.964	0.107	24.0	145.1	218	0.45	0.44	4.05	11.78
25G	2.107	0.036	30.63	58.4	383.1	2.103		24.8	169.9	149	0.31	0.29	4.34	12.63

* Series terminated because a leak developed in the leach bottle as a result of a crack.
** This leachate also includes dissolved uranium from ~60 h of static leaching.
*** This leachate includes dissolved uranium from ~120 h of static leaching.

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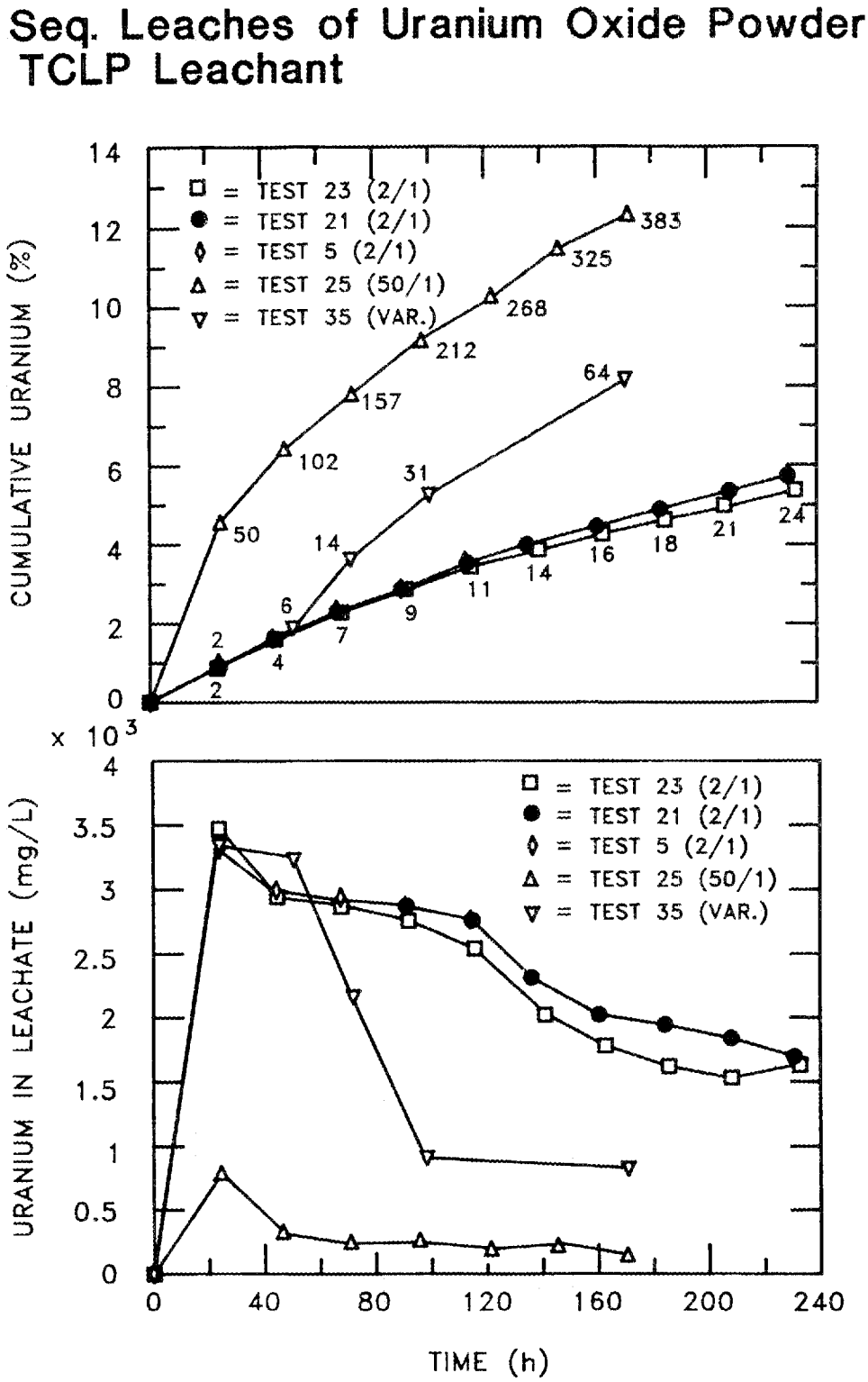

Fig. 3.12. Sequential leaching of uranium oxide powder using TCLP leachant.

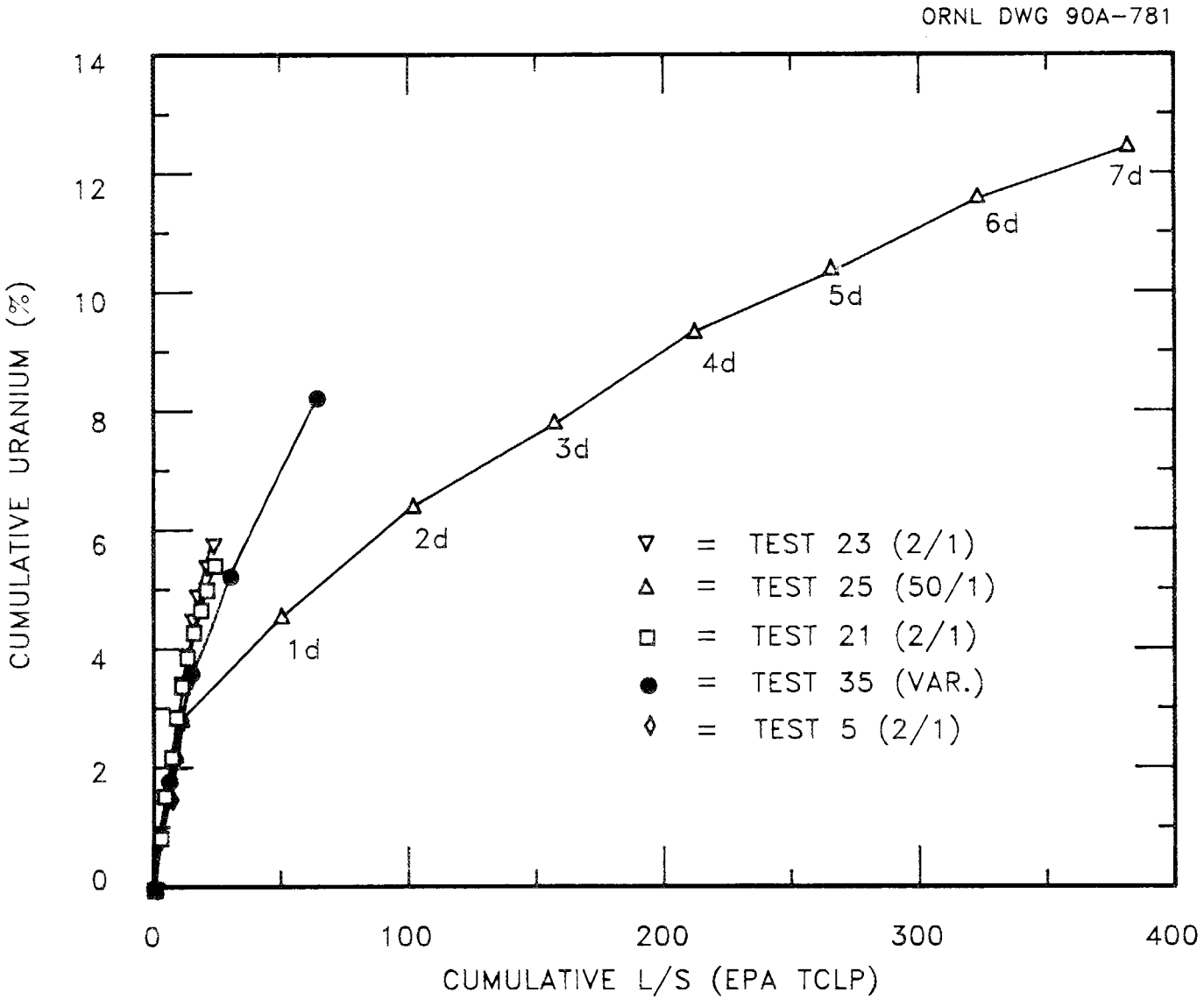

Fig. 3.13. Sequential leaching of uranium oxide powder using TCLP leachant (cumulative U leached vs cumulative L/S ratio).

almost identical, demonstrating good experimental reproducibility. The L/S ratio used in each sequential leach of these tests was ~2.35 ± 0.2. Test 5 was terminated early because a crack developed in the 2-L bottle being used. A L/S ratio of 50:1 was used in test 25. In contrast to the 2:1 ratio tests, the leaches in this test were not concentration limited. About 4.6% of the initial uranium was leached in the first day compared with ~0.8% for the 2:1 leaches which were concentration limited. For the 7-d leach periods, the comparison was 12.6% to 4.5%. These data demonstrate that the uranium oxide supply sample from UCOF was a mixture of soluble and insoluble uranium oxide, with the insoluble fraction being the major component. The curve in Fig. 3.12 for leach test 25 (L/S ratio 50:1) shows that uranium leaching in that test was parabolic, with the leachate concentration decreasing with each subsequent leach period. The uranium concentration in the last sampled leachate was 149 mg/L compared with 790 mg/L for the first leachate. Based on these data, it appears that only ~15% of the oxide was the soluble U_3O_8. Additional leaching would depend on the oxidation rate of the remaining oxide to the soluble form.

3.2.6 Redox Control by Metal Chips

The decrease in uranium solubility mode observed in the mixed metal chips leach tests (described in Sect. 3.2.3) and the air filter tests (described in Sect. 3.2.4) appears to have been caused by the reaction of iron and aluminum components in the waste with the leachant. Reaction was indicated by bubbling and foam formation at the surface of the leachates and by gelatinous sludge formation. In those tests, there were varying degrees of gelatinous sludge formation (hydroxides of iron and aluminum), which was reddish orange when iron chips were present or dirty white when the waste contained aluminum chips or other components in the absence of iron. Either reaction generates hydrogen and a strongly reducing redox condition. The decrease in uranium concentration in the leachate could be caused by the reduction of soluble uranium (VI) species to insoluble uranium (IV) solids which could be sorbed by the gelatinous sludge. Even if reduction did not occur, gelatinous iron

and aluminum hydroxide could act as inorganic ion exchangers to remove uranium and other cations.

To test this theory, noncontaminated iron turnings from one of the Y-12 buildings were added to the leaches that were saved from three of the air filter tests (8FIL, 5FIL, and 1FIL). About 1.8 kg of iron chips was added to each of these leaches (see Table 3.14 and Fig. 3.14). Samples taken from these leaches after 24 h on the drum rollers showed drastic reductions in the uranium concentrations. In tests 8FIL, 5FIL, and 1FIL, the concentrations dropped from 280 mg/L to 1.55, from 13 mg/L to 0.03, and from 210 mg/L to 30, respectively. The uranium concentration dropped to 0.1 mg/L in test 8FIL after an additional 24-h leach period. Additional leaching time on the drum roller gave no change in concentrations in tests 5FIL and 1FIL. After the iron chips were added in each of these tests, there was bubbling and foam formation (more so with the TCLP leachant in test 1FIL) and reddish orange sludge formation.

These data and the air filter data definitely prove that when iron and aluminum chips and components are present in a waste form, they act to severely limit or control the leachability of uranium in synthetic landfill and synthetic groundwater leachants. In fact, these materials could deliberately be added to different waste forms to control uranium leachability. Also, it might be possible to add these chips to settling ponds to remove uranium and other undesirable cations. A period of agitation would be needed to achieve proper mixing and reaction of the chips with the pond water. Afterward, an appropriate time would be needed to allow for sludge settling. If successful, the decontaminated pond water could be removed by decantation. The sludge would then be allowed to dry and eventually be removed in storage containers.

Table 3.14. Effect of adding iron chips to leachates containing dissolved uranium

	Test Parameters							Results					
Sample No.	Total Leach (L)	* Leachant	Solid Waste (kg)	Uranium (g)	L/S	Leach Time (h)	Cum. Leach Time (h)	Uranium Conc. (mg/L)	Total Uranium Leached (g)**	Initial Uranium Leached (%)	pH	Cond. (mmho)	Temp. (C)
8FILA	47.2	SNGW	2.34	200	20.2	22.3	22.3	610	28.79	14.40	4.25	0.14	26.7
8FILB	47.2	SNGW	2.34	200	20.2	24.6	46.9	570	29.85	14.93	3.85	0.16	27.0
8FILC	47.2	SNGW	2.34	200	20.2	22.6	69.5	620	29.62	14.81	4.17	0.16	27.3
8FILD	47.2	SNGW	2.34	200	20.2	24.3	93.7	650	31.00	15.50	4.26	0.16	26.2
8FILE	47.2	SNGW	2.34	200	20.2	70.2	163.9	610	29.13	14.56	4.32	0.15	26.5
8FILG***	47.2	SNGW	2.34	200	20.2	804.0	967.9	410	19.86	9.93	4.38	0.14	29.9
8FILH	47.2	SNGW	2.34	200	20.2	25.5	993.4	340	16.20	8.10	4.63	0.12	26.0
8FILI	47.2	SNGW	2.34	200	20.2	24.5	1017.9	280	13.35	6.67	4.54	0.11	26.5
Added 1.8 kg of noncontaminated iron chips from Y-12 to the 8FILG leachate.													
8FILJ	47.2	SNGW	4.15	200	11.4	23.2	1041.1	1.55	0.073	0.037	5.60	0.07	25.4
8FILK	47.2	SNGW	4.15	200	11.4	26.7	1067.8	0.11	0.005	0.003	5.38	0.06	25.2
5FILE	61.0	SNGW	1.91	182	31.9	70.5	70.5	290	17.68	9.71	5.01	0.02	26.8
5FILF***	61.0	SNGW	1.91	182	31.9	348.0	418.5	20	1.22	0.67	5.45	0.02	26.8
5FILG***	61.0	SNGW	1.91	182	31.9	456.0	874.5	13	0.79	0.43	5.83	0.02	26.9
Added 1.8 kg of noncontaminated iron chips from Y-12 to the 5FILG leachate.													
5FILH	61.0	SNGW	3.72	182	16.4	24.5	899.0	0.03	0.002	0.001	5.65	0.03	26.0
5FILI	61.0	SNGW	3.72	182	16.4	23.2	922.2	0.03	0.002	0.001	6.03	0.03	25.6
5FILJ	61.0	SNGW	3.72	182	16.4	25.4	947.6	0.03	0.002	0.001	6.20	0.03	25.4
5FILK	61.0	SNGW	3.72	182	16.4	25.5	973.1	0.03	0.002	0.001	5.93	0.03	25.2
1FILE	85.6	TCLP	2.56	142	33.5	71.0	71.0	170	14.56	10.25	4.90	3.7	26.7
1FILF***	85.6	TCLP	2.56	142	33.5	348.0	419.0	305	26.11	18.39	5.05	3.4	26.8
1FILG***	85.6	TCLP	2.56	142	33.5	456.0	875.0	210	17.98	12.66	5.56	6.6	27.0
Added 1.8 kg of noncontaminated iron chips from Y-12 to the 1FILG leachate.													
1FILH	85.6	TCLP	4.37	142	19.6	24.0	899.0	30	2.57	1.81	5.66	3.3	26.0
1FILI	85.6	TCLP	4.37	142	19.6	26.0	925.0	40	3.42	2.41	5.63	3.2	25.6
1FILJ	85.6	TCLP	4.37	142	19.6	23.0	948.0	40	3.42	2.41	5.65	3.0	25.4
1FILK	85.6	TCLP	4.37	142	19.6	24.0	972.0	40	3.42	2.41	5.47	3.3	25.1

* TCLP leachant: pH = 4.85 at 25.7 C; conductivity = 4.30 mmho.
Synthetic Groundwater leachant: pH = 6.85 at 25.9 C; conductivity = 0.012 mmho.

** Corrected for analytical samples that were removed.

*** Static leaching only; drum was off drum roller.

ORNL DWG 90A-782

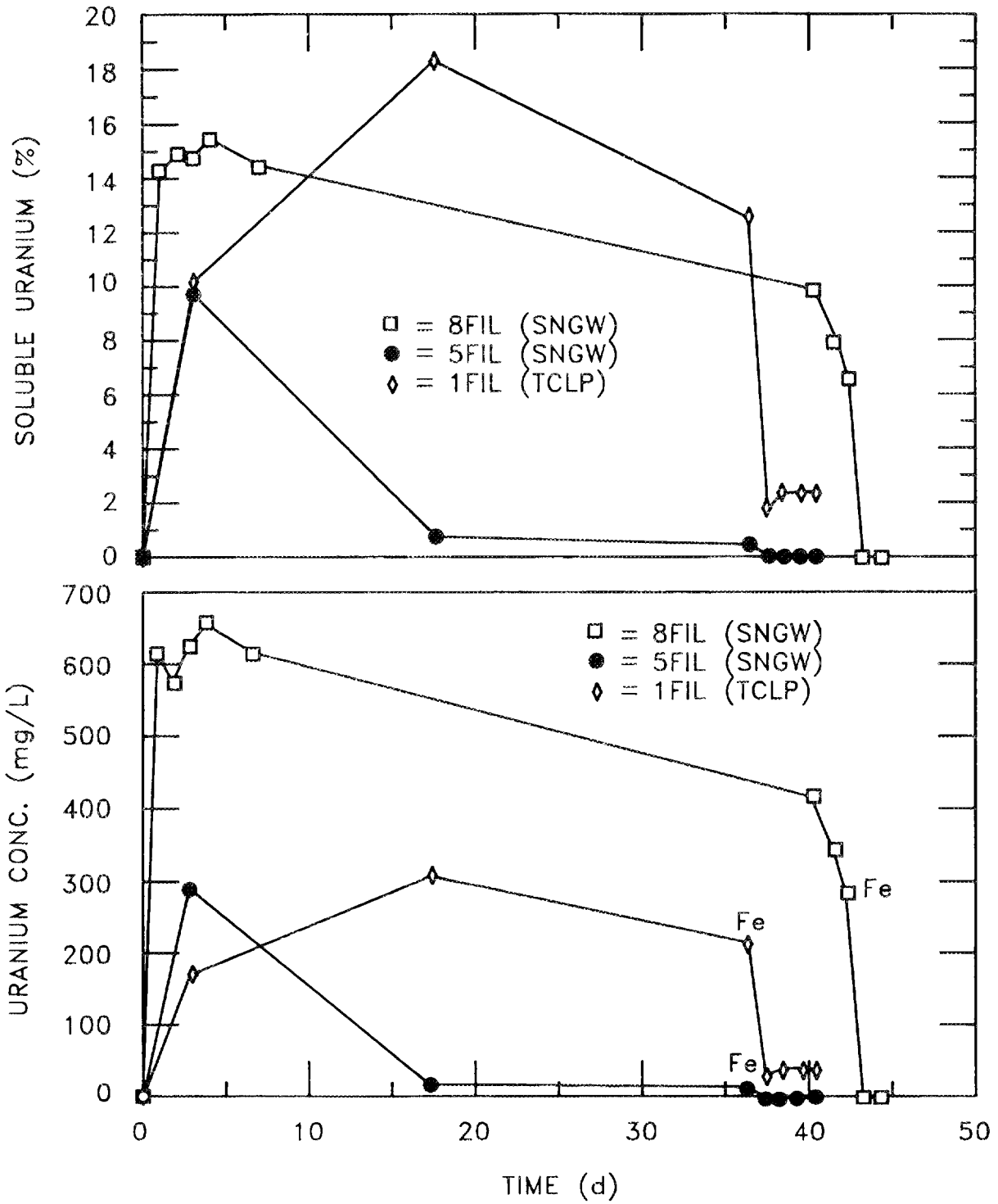

Fig. 3.14. Effect of adding iron chips to leachates containing soluble uranium.

3.3 HAZARDOUS MATERIAL LEACHING

3.3.1 Inorganic Elements

Tables 3.15 through 3.18 show the data for 36 inorganic elements and alkalinity for the first and last leachate samples from each of the batch and sequential leaches for production trash (Table 3.16), composite waste (Table 3.17), and mixed metal chips (Table 3.16). The elemental analyses were performed by ICP, AA, or IC methods, while alkalinity is essentially a titration for bicarbonate. Sodium is high, of course, for the leaches with synthetic landfill leachate and should be discounted.

Sample to sample variation for a given element in the same waste type seems to be nearly as great a difference between various waste types, and generalizations are difficult to draw from the tables.

3.3.2 Organic Compounds

EPA priority pollutant organic compounds were determined by GC-MS methods for a few selected leachate samples, with the results given in Table 3.19. Of the compounds identified, none exceed the proposed regulatory limit.

4. DISCUSSION OF URANIUM LEACHING

In this section, several aspects of the leaching of uranium are discussed in terms of various experimental parameters and conditions. An attempt is made to rationalize the uranium release data to aid in predicting waste performance in the lysimeters and to support analysis of potential disposal options. Because many of the test parameters and conditions interact in their effects on uranium leaching, the following division of the discussion into subsections is somewhat arbitrary and some repetition is unavoidable.

Table 3.15. Concentrations of cations and anions in production trash leach samples (units are mg/L) *

	Sample Nos.											
	Sequential Leaches				Batch Leaches							
	1FSA	1FSE	5FSA	5FSE	3FSA	3FSE	4FSA	4FSE	7FSAAA	7FSAAE	8FSAAA	8FSEEE
Ag	0.096	< 0.036	0.036	0.016	0.64	1.5	0.049	0.16	0.22	< 0.9	< 0.03	0.091
Al	2.3	5.5	--	0.38	3.9	0.3	3.1	0.74	0.98	1.8	0.67	< 0.3
ALKALINITY **	50.0	500.0	125.0	58.8	< 1.0	50.0	< 1.0	< 1.0	62.5	1775.0	2.5	6.3
As	< 0.36	< 0.36	< 0.36	0.071	< 0.15	< 0.15	< 0.15	< 0.15	< 0.36	0.42	< 0.3	< 0.3
B	0.85	< 0.48	1.1	0.08	1.4	1.1	< 0.4	< 0.4	0.96	1.0	< 0.4	< 0.4
Ba	0.25	0.11	0.15	0.04	0.54	0.31	0.2	0.2	0.66	0.47	0.031	0.043
Be	0.022	< 0.014	0.034	0.004	0.015	0.032	0.023	0.004	< 0.002	0.056	< 0.001	0.002
Ca	1300.0	350.0	1100.0	650.0	1200.0	960.0	290.0	370.0	580.0	910.0	36.0	97.0
Cd	0.045	0.018	< 0.012	< 0.002	1.7	0.01	0.14	0.14	0.3	< 0.012	0.024	< 0.01
Cl	150.0	1.8	220.0	2.8	370.0	320.0	60.0	58.0	370.0	300.0	47.0	42.0
Co	1.3	3.0	0.5	0.017	0.53	0.88	0.89	0.50	< 0.18	0.21	< 0.015	0.24
Cr	1.5	0.9	1.2	0.012	3.0	0.092	0.13	< 0.03	< 2.9	2.0	< 0.03	0.041
Cu	0.2	< 0.06	0.97	0.028	0.6	0.74	0.13	0.1	< 0.63	1.1	< 0.05	< 0.05
F	390.0	350.0	38.0	2.2	0.0	290.0	0.0	333.0	32.0	17.0	4.8	1.0
Fe	4.3	240.0	< 20.0	< 0.02	57.0	36.0	87.0	13.0	13.0	3.9	1.2	0.9
Ga	2.3	< 1.8	9.0	0.4	6.1	14.0	< 1.5	1.5	4.5	17.0	< 1.5	< 1.5
Li	1.5	< 1.2	< 1.2	< 0.2	1.8	1.4	< 1.0	< 1.0	1.4	< 1.2	< 1.0	< 1.0
Mg	65.0	69.0	79.0	1.1	152.0	150.0	13.0	15.0	130.0	140.0	6.9	8.4
Mn	3.7	2.0	1.3	0.26	5.5	6.6	1.0	3.1	1.6	2.4	0.15	0.49
Mo	0.49	< 0.24	2.4	< 0.04	2.3	1.5	< 0.2	< 0.2	2.6	2.6	< 0.2	< 0.2
Na	1600.0	1400.0	420.0	4.3	1500.0	1600.0	1400.0	1400.0	330.0	610.0	23.0	20.0
Ni	3.0	5.8	2.8	10.0	2.1	5.8	1.8	9.8	2.4	3.8	0.036	0.56
NO3	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 50.0	< 5.0	< 5.0	< 5.0	< 5.0
P	< 1.8	< 1.8	2.0	< 0.3	2.8	< 1.5	2.8	< 1.5	1.8	< 1.8	1.8	< 1.5
Pb	< 0.3	< 0.3	0.63	< 0.05	0.36	< 0.15	< 0.26	< 0.15	< 0.3	< 0.3	< 0.25	< 0.25
PO4	< 5.0	< 5.0	< 5.0	< 5.0	< 50.0	< 50.0	< 50.0	< 50.0	< 5.0	< 5.0	< 5.0	< 5.0
Sb	< 0.3	< 0.3	< 0.3	< 0.05	< 0.15	< 0.15	< 0.15	< 0.15	< 0.3	< 0.3	< 0.25	< 0.25
Se	< 0.36	< 0.36	< 0.36	< 0.06	< 0.25	< 0.25	< 0.25	< 0.25	< 0.36	< 0.36	< 0.3	< 0.3
Si	4.7	3.0	2.3	0.59	18.0	6.5	3.9	4.4	10.0	6.1	2.6	3.3
Sn	< 0.3	< 0.3	< 0.3	< 0.05	< 0.25	< 0.25	< 0.25	< 0.25	< 0.3	< 0.41	< 0.25	< 0.25
SO4	2100.0	590.0	2600.0	1100.0	1800.0	480.0	450.0	1700.0	1600.0	1700.0	88.0	150.0
Sr	--	--	--	--	1.7	1.4	5.4	0.94	--	--	0.076	0.24
Ti	0.15	< 0.12	0.34	0.021	0.39	0.35	0.1	0.1	0.29	0.53	< 0.1	< 0.1
U	84.0	7.7	369.0	11.0	210.0	458.0	13.0	50.0	168.0	792.0	2.47	47.0
V	0.041	< 0.024	< 0.024	< 0.004	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.024	< 0.02	< 0.02
Zn	16.0	0.89	6.8	0.47	10.0	0.81	4.2	5.8	6.7	0.35	1.2	0.47
Zr	< 0.12	< 0.12	< 0.12	< 0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.12	< 0.12	< 0.1	< 0.1

* Values with " < " indicate that the concentration was below the given analytical detection limit.
** Alkalinity is a measurement of the total concentration of the hydroxide, carbonate, and bicarbonate ions.

Table 3.16. Concentrations of cations and anions in composite waste leach Samples
(units are mg/L) *

	Sample Nos.													
	Sequential Leaches				Batch Leaches									
	1BALA	1BALE	5BALA	5BALE	3BALA	3BALC	3BALAA	3BALEE	4BALAA	4BALEE	7BALAAA	7BALEEE	8ALAAA	8BALEEE
Ag	< 0.059	< 0.03	< 0.87	< 0.006	0.043	0.19	0.047	0.36	0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.054
Al	0.037	0.77	2.0	0.43	0.78	< 0.3	11.0	12.0	0.3	< 0.3	2.1	< 0.3	0.35	3.1
ALKALINITY **	250.0	< 2.5	2975.0	3.75	--	--	250.0	250.0	500.0	250.0	75.0	6.3	5.0	3.8
As	< 0.3	< 0.3	0.54	< 0.06	< 0.15	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
B	< 0.4	< 0.4	0.6	< 0.08	0.62	< 0.4	1.5	1.2	< 0.4	< 0.4	< 0.4	< 0.4	0.57	< 0.4
Ba	0.12	0.18	0.16	0.007	0.30	0.14	0.23	0.15	0.34	0.31	0.076	0.065	0.16	0.08
Be	0.005	< 0.001	0.003	0.002	0.002	0.005	0.005	0.014	0.0015	0.002	< 0.001	< 0.001	< 0.001	< 0.001
Ca	770.0	17.0	68.0	23.0	80.0	16.0	530.0	440.0	120.0	140.0	23.0	140.0	310.0	64.0
Cd	0.073	0.034	< 0.01	0.01	0.46	< 0.01	0.032	< 0.01	0.24	0.75	0.032	< 0.01	0.079	0.028
Cl	120.0	2.0	1000.0	2.6	95.0	1100.0	265.0	230.0	10.0	12.0	42.0	59.0	75.0	37.0
Co	4.9	12.0	0.13	0.02	32.0	0.37	0.064	0.056	2.7	20.0	0.045	0.25	0.41	0.12
Cr	0.14	0.36	0.93	0.1	0.55	< 0.03	0.081	0.31	1.1	0.9	0.14	< 0.03	0.12	0.33
Cu	0.17	< 0.05	1.3	0.02	< 0.05	0.16	0.27	0.29	0.14	< 0.05	0.13	< 0.05	0.062	0.13
F	340.0	330.0	14.0	< 1.0	320.0	7.3	320.0	260.0	320.0	330.0	4.7	8.6	5.2	5.0
Fe	2.9	260.0	2.7	0.93	41.0	61.0	6.4	11.0	23.0	450.0	3.6	0.6	0.49	9.2
Ga	< 1.5	< 1.5	6.9	0.3	< 1.5	1.6	< 1.5	3.1	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5	< 1.5
Li	28.0	< 1.0	19.0	< 0.2	13.0	2.6	2.3	2.0	3.9	3.9	< 1.0	< 1.0	2.7	< 1.0
Mg	57.0	4.7	14.0	0.89	39.0	7.3	48.0	41.0	6.6	8.4	6.7	28.0	25.0	11.0
Mn	12.0	2.0	0.52	0.093	8.3	0.39	4.1	3.6	1.9	6.6	0.3	2.0	2.2	0.68
Mo	< 0.2	< 0.2	9.2	< 0.04	0.02	0.71	0.66	1.3	< 0.2	< 0.2	0.42	0.34	< 0.2	0.45
Na	1700.0	< 1.0	2300.0	2.7	1400.0	2100.0	1500.0	1500.0	1400.0	1500.0	39.0	80.0	92.0	40.0
Ni	13.0	22.0	2.1	0.081	4.8	0.73	0.48	0.44	4.7	33.0	0.2	0.3	1.2	0.36
NO3	110.0	< 5.0	53.0	< 5.0	59.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 5.0	< 5.0	27.0	< 5.0
P	3.0	< 1.5	22.0	< 0.41	< 1.5	< 1.5	< 1.5	2.1	< 1.5	< 1.5	2.8	< 1.5	3.4	2.8
Pb	< 0.25	< 0.25	0.46	< 0.05	< 0.15	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
PO4	< 5.0	< 5.0	< 50.0	< 5.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 5.0	< 5.0	< 5.0	< 5.0
Sb	< 0.25	< 0.25	< 0.25	< 0.05	< 0.15	< 0.15	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
Se	< 0.3	< 0.3	0.72	< 0.06	< 0.25	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
Si	5.4	5.8	3.2	2.2	5.1	3.3	7.44	8.2	4.8	4.3	2.8	2.5	4.2	8.7
Sn	< 0.25	< 0.25	0.32	< 0.05	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
SO4	880.0	0.053	0.19	0.0	1.3	0.057	1.5	1.2	0.38	0.46	44.0	220.0	710.0	48.0
Sr	2.0	6.3	480.0	27.0	1100.0	120.0	260.0	260.0	91.0	110.0	0.076	0.22	0.62	0.16
Ti	< 0.1	< 0.1	0.28	< 0.22	< 0.1	< 0.1	< 0.1	0.16	< 0.1	< 0.1	0.11	< 0.1	< 0.1	0.14
U	20.0	4.98	13.0	0.52	8.76	70.0	63.0	290.0	16.0	0.29	12.6	9.55	1.57	27.9
V	0.02	0.029	< 0.02	0.004	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.027	0.035	< 0.02
Zn	9.4	1.9	0.17	0.47	15.0	0.036	24.0	13.0	8.3	4.7	1.5	< 0.015	0.28	3.6
Zr	< 0.1	< 0.1	< 0.1	< 0.02	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1

* Values with " < " indicate that the concentration was below the given analytical detection limit.
** Alkalinity is a measurement of the total concentration of the hydroxide, carbonate, and bicarconate ions.

Table 3.17. Concentrations of cations and anions in mixed metal chips leach samples (units are mg/L) *

	Sample Nos.											
	Sequential Leaches				Batch Leaches							
	1CHIPA	1CHIPE	5CHIPA	5CHIPE	3CHIPA	3CHIPE	4CHIPA	4CHIPE	7CHIPA	7CHIPE	8CHIPA	8CHIPE
Ag	< 0.036	< 0.036	< 0.006	< 0.006	0.059	0.049	< 0.03	0.035	0.056	0.072	< 0.03	< 0.03
Al	< 0.36	< 0.36	< 0.06	< 0.06	< 0.36	< 0.36	< 0.3	< 0.3	< 0.36	< 0.36	0.32	< 0.3
ALKALINITY **	375.0	375.0	2.5	2.5	37.5	25.0	< 2.5	< 1.0	< 12.5	< 12.5	2.5	3.75
As	< 0.36	< 0.36	< 0.06	< 0.06	< 0.36	< 0.36	< 0.3	< 0.3	< 0.36	< 0.36	< 0.3	< 0.3
B	< 0.48	< 0.48	< 0.08	< 0.08	< 0.48	< 0.48	< 0.4	< 0.4	< 0.48	< 0.48	< 0.4	< 0.4
Ba	0.098	0.082	0.002	< 0.002	0.03	0.063	0.088	0.1	< 0.012	< 0.012	< 0.01	0.012
Be	0.006	0.005	--	--	0.006	0.005	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Ca	23.0	< 6.0	2.7	0.61	23.0	39.0	2.3	5.4	3.9	5.8	< 1.0	< 1.0
Cd	< 0.012	0.014	< 0.002	< 0.002	< 0.012	< 0.012	0.045	0.034	< 0.012	< 0.012	< 0.01	< 0.01
Cl	26.0	1.2	43.0	2.6	13.0	39.0	4.6	7.7	37.0	52.0	6.6	6.2
Co	41.0	19.0	0.56	0.058	150.0	0.94	13.0	19.0	0.71	0.32	0.46	0.31
Cr	< 0.036	< 0.036	< 0.006	< 0.006	< 0.036	< 0.036	< 0.03	< 0.03	< 0.036	< 0.036	< 0.03	< 0.03
Cu	< 0.06	< 0.06	0.015	0.013	< 0.06	< 0.06	< 0.05	< 0.05	< 0.06	< 0.06	< 0.05	< 0.05
F	290.0	380.0	5.2	1.0	340.0	240.0	320.0	320.0	2.6	3.5	< 1.0	1.0
Fe	140.0	460.0	0.11	< 0.02	14.0	2.9	570.0	520.0	0.77	2.7	4.6	9.1
Ga	< 1.8	< 1.8	< 0.3	< 0.3	< 1.8	< 1.8	< 1.5	< 1.5	< 1.8	< 1.8	< 1.5	< 1.5
Li	< 1.2	< 1.2	< 0.2	< 0.2	< 1.2	< 1.2	< 1.0	< 1.0	< 1.2	< 1.2	< 1.0	< 1.0
Mg	4.6	< 0.06	2.3	0.19	3.5	21.0	0.92	1.9	0.73	1.7	0.26	0.95
Mn	30.0	4.7	0.95	0.031	19.0	9.8	9.9	27.0	4.9	3.7	0.34	0.88
Mo	< 0.24	< 0.24	0.15	0.089	< 0.24	< 0.24	< 0.2	< 0.2	< 0.24	< 0.24	0.88	0.77
Na	1400.0	1400.0	37.0	3.9	1600.0	1700.0	< 1.0	< 1.0	17.0	21.0	4.5	5.2
Ni	190.0	46.0	2.6	0.22	420.0	2.6	60.0	75.0	4.6	1.7	5.0	0.62
NO3	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
P	< 1.8	< 1.8	< 0.3	< 0.3	< 1.8	< 1.8	< 1.5	< 1.5	< 1.8	< 1.8	< 1.5	< 1.5
Pb	< 0.3	< 0.3	< 0.05	< 0.05	< 0.3	< 0.3	< 0.25	< 0.25	< 0.3	< 0.3	< 0.25	< 0.25
PO4	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Sb	< 0.3	< 0.3	< 0.05	< 0.05	< 0.3	< 0.3	< 0.25	< 0.25	< 0.3	< 0.3	< 0.25	< 0.25
Se	< 0.36	< 0.36	< 0.06	< 0.06	0.48	< 0.36	< 0.3	< 0.3	< 0.36	< 0.36	< 0.3	< 0.3
Si	< 1.2	< 1.2	2.2	< 0.2	< 1.2	< 1.2	< 1.0	< 1.0	< 1.2	< 1.2	< 1.0	< 1.0
Sn	< 0.3	< 0.3	< 0.05	< 0.05	< 0.3	< 0.3	< 0.25	< 0.25	< 0.3	< 0.3	< 0.25	< 0.25
SO4	10.0	10.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0	< 5.0
Sr	--	--	--	--	0.057	0.1	< 0.025	0.026	< 0.03	< 0.03	< 0.025	< 0.025
Ti	< 0.12	< 0.12	< 0.02	< 0.02	< 0.12	< 0.12	< 0.1	< 0.1	< 0.12	< 0.12	< 0.1	< 0.1
U	0.95	0.18	0.064	0.009	0.68	0.007	0.57	0.022	0.003	0.003	1.36	0.013
V	< 0.024	< 0.024	0.004	< 0.004	< 0.024	< 0.024	0.054	0.024	< 0.024	0.03	< 0.02	< 0.02
Zn	0.52	0.053	< 0.007	< 0.007	0.98	< 0.018	0.23	< 0.015	< 0.018	< 0.018	< 0.015	< 0.015
Zr	< 0.12	< 0.12	< 0.02	< 0.02	< 0.12	< 0.12	< 0.1	< 0.1	< 0.12	< 0.12	< 0.1	< 0.1

* Values with " < " indicate that the concentration was below the given analytical detection limit.
** Alkalinity is a measurement of the total concentration of the hydroxide, carbonate, and bicarbonate ions.

Table 3.18. Concentrations of cations and anions in air filters leach samples (units are mg/L) *

	Sample Nos.											
	Sequential Leaches				Batch Leaches							
	1FILA	1FILE	5FILA	5FILE	3FILA	3FILE	4FILA	4FILE	7FILA	7FILE	8FILA	8FILE
Ag	7.1	0.17	1.1	0.048	5.9	0.41	4.0	3.1	0.78	0.75	0.64	0.3
Al	34.0	190.0	4.2	< 0.36	38.0	27.0	7.8	58.0	< 1.6	< 0.36	< 3.1	< 1.6
ALKALINITY **	5125.0	375.0	300.0	2.5	500.0	375.0	375.0	500.0	531.0	5.0	205.0	190.0
As	< 6.0	< 0.36	< 0.36	< 0.36	< 3.1	< 0.36	< 3.1	< 3.1	< 1.6	< 0.36	< 3.1	< 1.6
B	4.1	< 0.48	4.6	< 0.48	5.9	4.6	< 4.1	< 4.1	2.5	2.5	< 4.1	< 2.1
Ba	< 0.2	0.22	< 0.012	< 0.012	< 0.1	< 0.012	< 0.1	< 0.1	< 0.052	< 0.012	< 0.1	< 0.052
Be	0.4	0.024	0.063	0.005	0.35	0.038	0.25	0.21	0.056	0.47	0.56	0.029
Ca	71.0	1.2	43.0	< 1.2	140.0	100.0	11.0	10.0	28.0	5.2	< 11.0	< 5.2
Cd	< 0.2	< 0.012	< 0.012	< 0.012	< 0.1	0.18	< 0.1	< 0.1	< 0.052	< 0.012	< 0.1	< 0.52
Cl	50.0	< 10.0	57.0	< 10.0	55.0	38.0	< 10.0	< 10.0	49.0	30.0	< 10.0	< 10.0
Co	< 0.3	0.11	< 0.018	< 0.018	< 0.15	0.055	< 0.15	< 0.15	< 0.078	< 0.018	< 0.15	< 0.078
Cr	5.7	0.28	0.8	< 0.036	4.7	0.33	3.3	3.1	0.79	< 0.036	0.53	0.23
Cu	9.3	0.2	1.5	< 0.06	8.3	0.51	5.6	4.4	1.2	< 0.06	0.91	0.41
F	290.0	280.0	< 10.0	< 10.0	280.0	220.0	300.0	400.0	< 10.0	< 10.0	< 10.0	< 10.0
Fe	5.1	4.7	9.9	< 0.12	1.9	0.29	< 1.0	2.3	< 0.52	< 0.12	< 1.0	< 0.52
Ga	110.0	2.5	18.0	< 1.8	98.0	6.3	67.0	55.0	15.0	< 1.8	< 15.0	< 7.8
Li	< 20.0	< 1.2	< 1.2	< 1.2	< 10.0	< 1.2	< 10.0	< 0.1	< 5.2	< 1.2	< 10.0	< 5.2
Mg	8.7	0.26	10.0	< 0.06	18.0	12.0	1.1	1.1	6.2	5.2	0.7	0.45
Mn	4.4	0.086	2.8	< 0.03	4.2	2.0	1.4	1.3	1.3	0.2	0.33	0.22
Mo	< 4.0	< 0.24	< 0.24	< 0.24	< 2.0	< 0.24	< 2.0	2.0	< 1.0	< 0.24	< 2.0	< 1.0
Na	2200.0	1500.0	7.0	< 1.2	2000.0	1300.0	2100.0	1900.0	< 5.2	5.6	< 10.0	< 5.2
Ni	4.8	0.17	3.7	0.044	4.2	2.2	1.2	1.7	1.7	0.37	0.47	0.36
NO3	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0
P	< 30.0	< 1.8	< 1.8	< 1.8	< 15.0	< 1.8	< 15.0	< 15.0	< 7.8	< 1.8	< 15.0	< 7.8
Pb	< 0.25	< 0.3	< 0.3	< 0.3	< 2.6	< 0.3	< 2.6	< 2.6	< 1.3	< 0.3	< 2.6	< 1.3
PO4	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0	< 50.0
Sb	< 5.0	< 0.3	< 0.3	< 0.3	< 2.6	< 0.3	< 2.6	< 2.6	< 1.3	< 0.3	< 2.6	< 1.3
Se	< 6.0	< 0.36	< 0.36	< 0.36	< 3.1	< 0.36	< 3.1	< 3.1	< 1.6	< 0.36	< 3.1	< 1.6
Si	< 20.0	2.2	9.6	< 1.2	< 10.0	3.9	< 10.0	< 11.0	< 5.2	2.8	< 10.0	< 5.2
Sn	2.6	< 0.3	0.46	< 0.3	< 2.6	< 0.3	< 2.6	< 2.6	< 1.3	< 0.3	< 2.6	< 1.3
SO4	740.0	< 50.0	300.0	< 50.0	720.0	< 50.0	58.0	< 50.0	380.0	< 50.0	< 50.0	59.0
Sr	0.68	< 0.03	0.1	< 0.03	0.5	0.055	0.35	0.28	< 0.13	0.03	< 0.26	< 0.13
Ti	3.7	< 0.16	0.59	< 0.12	3.4	0.26	2.3	1.8	< 0.52	< 0.12	< 1.0	< 0.52
U	6840.0	170.0	1280.0	290.0	5760.0	560.0	3630.0	3110.0	1740.0	140.0	610.0	570.0
V	< 0.4	< 0.024	< 0.024	< 0.024	< 0.2	< 0.24	< 0.2	< 0.2	< 0.1	0.024	< 0.2	< 0.1
Zn	19.0	0.41	15.0	0.13	27.0	13.0	2.3	3.0	10.0	0.97	0.74	0.87
Zr	< 2.0	< 0.12	< 0.12	< 0.12	< 0.1	< 0.12	< 0.1	< 1.0	< 0.52	< 0.12	< 1.0	< 0.52

* Values with " < " indicate that the concentration was below the given analytical detection limit.
** Alkalinity is a measurement of the total concentration of the hydroxide, carbonate, and bicarbonate ions.

Table 3.19. Comparison of 24 h TCLP leach data of different wastes with EPA proposed toxicity characteristic levels

Contaminant	EPA Proposal Regulatory Level (mg/L)	Air Filters (L/S Ratio) (2/1):(a)	Air Filters Sample No.** (20/1):(b)	Production Trash (L/S Ratio) (2/1):(c)	Production Trash Sample No.** (20/1):(d)	Composite Waste (L/S Ratio) (2/1):(e)	Composite Waste Sample No.** (20/1):(f)	Mixed Metal Chips (L/S Ratio) (2/1):(g)	Mixed Metal Chips Sample No.** (20/1):(h)
acrylonitrile	5.0E+00	NA	NA	NA	NA	NA	NA	NA	NA
benzene	7.0E-02	NA	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03
bis(2-chloroethyl)ether	5.0E-02	NA	2.2E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	NA
carbon disulfide	1.4E+01	NA	<5.0E-03	<8.0E-03	<1.8E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03
carbon tetrachloride	7.0E-02	NA	<3.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03
chlordane	3.0E-02	NA	NA	NA	NA	NA	NA	NA	NA
chlorobenzene	1.4E+00	NA	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03
chloroform	7.0E-02	NA	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03
o-cresol	1.0E+01	NA	2.0E-03	NA	NA	NA	NA	NA	NA
m-cresol	1.0E+01	NA	NA	NA	NA	NA	NA	NA	NA
p-cresol	1.0E+01	NA	NA	NA	NA	NA	NA	NA	NA
2,4-D	1.4E+00	NA	NA	NA	NA	NA	NA	NA	NA
1,2-dichlorobenzene	4.3E+00	NA	2.0E-03	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
1,4-diclhorobenzene	1.1E+01	NA	2.2E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
1,2-dichloroethane	4.0E-01	NA	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	1.0E-02
1,1-dichloroethylene	1.0E-01	NA	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03
2,4-dinitrotoluene	1.3E-01	NA	2.2E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
endrin	3.0E-03	NA	NA	NA	NA	NA	NA	NA	NA
heptachlor (as hydroxide)	1.0E-03	NA	NA	NA	NA	NA	NA	NA	NA
hexachlorobenzene	1.3E-01	NA	2.2E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
hexachlorobutadiene	7.2E-01	NA	2.2E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
hexachloroethane	4.3E+00	NA	2.2E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
isobutanol	3.6E+01	NA	NA	NA	NA	NA	NA	NA	NA
lindane	6.0E-01	NA	NA	NA	NA	NA	NA	NA	NA
methoxychlor	1.4E+00	NA	NA	NA	NA	NA	NA	NA	NA
methylene chloride	8.6E+00	NA	<3.0E-03	<5.0E-03	<5.0E-03	<7.0E-03	<9.0E-03	<5.0E-03	<5.0E-03
methylethylketone	7.2E+00	NA	NA	NA	NA	NA	NA	NA	NA
nitrobenzene	1.3E-01	NA	2.2E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
pentachlorophenol	3.6E+00	NA	1.1E-01	<5.0E-02	<5.0E-02	<5.0E-02	<5.0E-02	<5.0E-02	<1.0E-02
phenol	1.4E+01	NA	7.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
pyridine	5.0E+00	NA	NA	NA	NA	NA	NA	NA	NA
1,1,1,2-tetrachloroethane	1.0E+01	NA	NA	NA	NA	NA	NA	NA	NA
1,1,2,2-tetrachloroethane	1.3E+00	NA	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03
tetrachloroethylene	1.0E-01	NA	NA	NA	NA	NA	NA	NA	NA
2,3,4,6-tetrachlorophenol	1.5E+00	NA	NA	NA	NA	NA	NA	NA	NA
toluene	1.4E+01	NA	1.4E-02	2.0E-02	2.9E-02	1.7E-02	5.0E-03	1.4E-02	7.0E-03
toxaphene	7.0E-02	NA	NA	NA	NA	NA	NA	NA	NA
1,1,1-trichloroethane	3.0E+01	NA	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03
1,1,2-trichloroethane	1.2E+00	NA	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03	<5.0E-03
trichloroethylene	7.0E-02	NA	NA	NA	NA	NA	NA	NA	NA
2,4,5-trichlorophenol	5.8E+00	NA	1.1E-01	<5.0E-02	<5.0E-02	<5.0E-02	<5.0E-02	<5.0E-02	<5.0E-02
2,4,6-trichlorophenol	1.0E-01	NA	2.2E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02
2,4,5-TP (silvex)	1.4E-01	NA	<1.0E-02	NA	NA	NA	NA	NA	NA
vinyl chloride	5.0E-02	NA	NA	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02	<1.0E-02

* Federal Register, Vol. 51, No.114, June 13, 1986, Table 1, p. 21652

** Sample Nos. (a) = 3FILA, (b) = 4FILA, (c) = 3FSA, (d) = 4FSA, (e) = 3BALAAA, (f) = 4BALAAA, (g) = 1CHIPA, (h) = 4CHIPA

4.1 EFFECT OF WASTE TYPE

The first question addressed is identification of the differences (or similarities) in uranium leaching for the various Y-12 Plant wastes tested. The wastes studied in this work can be divided into two broad categories, or classes: (1) large-volume trash-type wastes from Y-12 Plant production areas that are contaminated with relatively small proportions of depleted uranium, probably primarily present as uranium metal; and (2) small-volume wastes from specific Y-12 Plant sources that are composed of larger proportions of depleted uranium, primarily present as uranium oxides. The production trash, mixed metal chips, and composite waste fall into the first category, while the air filters and uranium oxide powder fall into the second category. Based on a general understanding of uranium chemistry, it might be anticipated that uranium leaching from these two different waste categories would be significantly different. This expectation was, at best, only partially confirmed by the results of the leach tests.

A comparison of the data for the fraction of the uranium leached by day 7 (the longest experimental time point) for the various wastes is shown in Table 4.1. The data for the longest experimental time were selected for comparison because the longest time might be expected to produce the greatest uranium release. Many tests had not reached steady state after 7 d, and, therefore, the fraction of uranium leached by day 7 does not represent a final or maximum value for these wastes. Also, in a number of tests the fraction of uranium leached actually <u>decreased</u> over time from day 1 to day 7; clearly, the day 7 data for these tests do not represent a maximum uranium release but might represent an environmentally meaningful number.

Substantial data scatter can be seen in Table 4.1 for the fraction of uranium leached as a function of test parameters and conditions, and only very general observations or conclusions can be reached. Only a trivial portion (a tiny fraction of a percent) of the uranium was leached from mixed metal chips in any of the tests. In the case of the production trash, between ~0.6% and 1.6% of the uranium was leached in various tests. Composite waste, which is 1/3 production trash, 1/3

Table 4.1. Uranium leached by day 7 for different waste

Waste	Leachant	Protocol	Liquid/ solid	Uranium leached (%)
Production trash	TCLP	Batch	2.0	0.68
		Batch	20.0	0.84
		Sequential	58.5	0.69
	SNGW	Batch	2.0	1.61
		Batch	20.0	0.57
		Sequential	52.0	1.00
Mixed metal chips	TCLP	Batch	2.0	7.01E-03
		Batch	20.0	6.34E-04
		Sequential	62.0	4.80E-02
	SNGW	Batch	2.0	2.21E-05
		Batch	11.8	5.90E-04
		Sequential	62.0	3.20E-03
Composite waste	TCLP	Batch	2.0	4.59
		Batch	20.0	0.01
		Sequential	69.5	1.36
	SNGW	Batch	2.0	0.16
		Batch	12.3	1.44
		Sequential	52.0	0.16
Air filters	TCLP	Batch	2.0	1.5
		Batch	20.0	68.1
		Sequential	62.0	51.1
	SNGW	Batch	2.0	0.4
		Batch	20.0	14.6
		Sequential	62.0	17.0
Uranium oxide	TCLP	Batch	2.0	0.69
		Batch	19.8	7.25
		Sequential	64.1	8.38
	SNGW	Batch	2.0	0.005
		Batch	19.8	0.17
		Sequential	62.0	0.20

mixed metal chips, and 1/3 other wastes from contaminated areas, showed much more variable uranium leaching, with the fraction leached varying from 0.01 to 4.59%. Perhaps, in some tests, the composite waste performed like mixed metal chips, in other cases, like production trash, and in still other cases, possibly like uranium oxide. Such variable performance might be consistent with the possible heterogeneity of physical/chemical forms of the uranium contaminant in different composite waste samples.

The air filters and the uranium oxide powder gave greater releases (up to ~68% at day 7 in one test) which, at least in part, seemed to correlate primarily with the chemistry of the leachant used but not with the volume of the leachant. In some cases with the air filters and uranium oxide powder, it appeared that the leachate might be saturated with uranium.

The air filters were unique in that essentially most of the uranium was readily leachable. The release of uranium from the filter media seemed to be constrained only by the solubility limit. Such a relatively high leachability is consistent with the composition of the uranium powder in the air filters. An analysis of one sample of the powder by X-ray diffraction showed that it was $\geq$75% U_3O_8 and $\leq$25% UO_2. Several of the air filter tests suggested that a decreasing leach mode was being expressed. Thus, on extended time in the field lysimeters or other disposal modes, the uranium leached might be less than in these short-term laboratory tests.

The range and variability of the uranium leach data obtained with the trash-type wastes suggest that predictions of waste performance based solely on these waste-type classifications may be subject to some uncertainty. The uranium leaching likely reflects the chemical and physical properties of the uranium contaminant in the waste, rather than an arbitrary classification of waste based on Y-12 Plant waste collection categories. Also, the chemistry of other waste components, which are present in much greater quantities than uranium in the trash-type wastes, may also play a dominant role in determining uranium leaching. For example, the presence of oil in some samples could coat metal particles and inhibit oxidation and leaching, while in other cases, the

presence of larger amounts of paper or plastics could adsorb oil which then could allow for acceleration of (or at least no longer inhibition of) oxidation and leaching reactions. Other adsorbents, such as the Hot Hogs, could also adsorb uranium which had been initially solubilized from the waste. It is well known (see Appendix F) that uranium solubility is pH dependent, and any waste components that alter the leachate pH could have a significant impact on the uranium leaching from the waste. Because few of the uranium leaching tests seemed to have reached steady-state conditions after 7 d, uranium leaching was continuing (or, in some cases, decreasing), and the fraction released was still increasing (or decreasing) for many tests. Thus, uranium leach data and a comparison of waste behavior taken at some time period other than 7-d might yield a somewhat different waste-type comparison.

4.2 EFFECT OF LEACHANT USED

In the tests, two different leachants were used which were chosen to bracket the expected acidity of environmental disposal situations: (1) a synthetic groundwater that was a very dilute $NaCl-NaHCO_3$ solution at near-neutral pH, and (2) a synthetic landfill leachate that was a 0.1 M acetic acid-sodium acetate buffer at pH 4.9. Because the dissolution of U_3O_8 (the uranium oxide which might be present in oxidized uranium oxide-containing wastes) consumes acid (see Appendix F) and because the solubility of U(VI) species is highly pH dependent and increases at lower pHs (see Appendix F), it often is assumed that more acidic solutions are more aggressive leachants for the dissolution of uranium oxides. Based on that assumption, the Y-12 Plant waste tests were expected to show much higher uranium leaching with synthetic landfill leachate than with the synthetic groundwater.

Examination of the fraction-uranium-leached values in Table 4.1 shows that this expectation was met only for the tests with uranium oxide powder and air filters. For production trash, the synthetic groundwater actually was a slightly more aggressive leachant than was the synthetic landfill leachate. The values for uranium leached from mixed metal chips were too low to allow a meaningful comparison, and in

the case of composite waste, the values were too scattered to reach any conclusion as to the relative aggressiveness of the two leachants.

In Fig. 4.1, the uranium concentrations in the leach solutions for all wastes are compared as a function of leachate used. In the cases with uranium oxide powder and air filters, both leachants dissolved appreciable amounts of uranium and the uranium release may be solubility limited. In the cases with trash-type wastes, high concentrations of uranium in solution were observed only for synthetic landfill leachate tests where the final sample pH was close to the initial pH of 4.9. The lower plot in Fig. 4.1 clearly shows no correlation with leachate type for samples where the final pH was >5. (The question of pH control of leaching is examined further in Sect. 4.3.3.) The lack of correlation of uranium leaching for the trash-type wastes with the type of leachant used was unanticipated, based on the expected aggressiveness of the two leachants, and suggests that other waste components may be controlling the leaching chemistry.

The test results indicate that the initial acidity (pH) or acid capacity (buffering) of the leachant did not seem to be important in controlling the leaching of uranium from most of these Y-12 Plant wastes, with the exception of the uranium oxide powder and air filters. This is a surprising conclusion and suggests that simple dissolution reactions involving uranium may not be controlling the release of uranium from these wastes. By default, then, reactions such as oxidation of uranium metal or insoluble UO_2 to soluble U(VI) species or reactions involving other waste components (e.g., complex formation to increase uranium solubility or sorption/precipitation reactions which could decrease solubility) may be release-rate controlling in some situations.

4.3 EFFECT OF LEACH TEST PROTOCOL

4.3.1 Batch vs Sequential Methodology

Two leaching experimental protocols were followed in these tests: (1) batch contact methodology at two L/S ratios (~2 and ~20) to measure the uranium leaching as a function of time over a 7-d contact period;

ORNL DWG 88-948

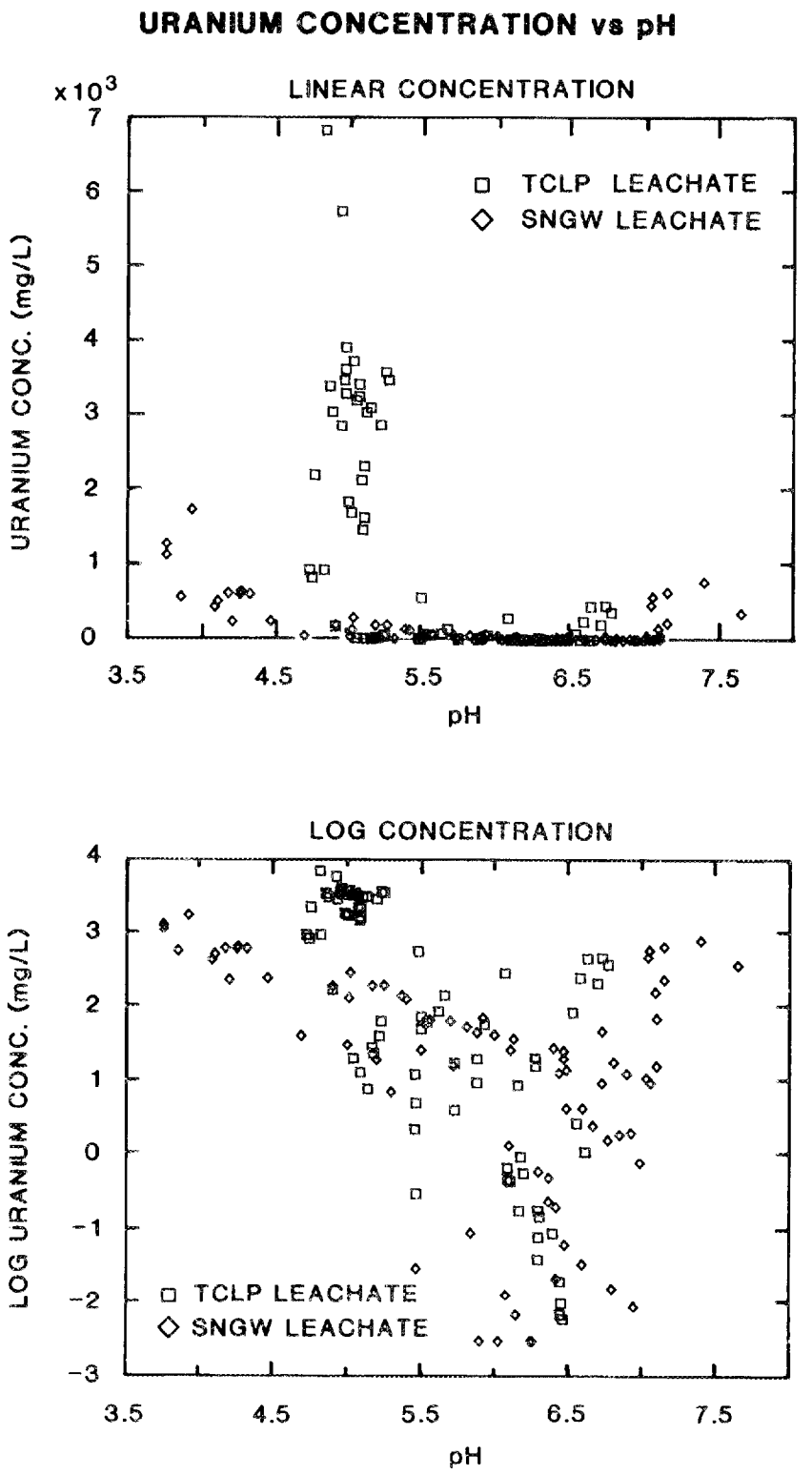

Fig. 4.1. Log plots of the uranium leachate concentration vs pH for all five waste forms.

and (2) sequential contact methodology to measure uranium leaching as a function of the cumulative L/S ratio (~62), also over a cumulative 7-d leaching period. Examination of the data from these tests could reveal several important aspects of uranium leaching and could help identify the release-rate-limiting reaction or process.

The batch contact data showed two important observations: (1) most of the tests had not reached steady state during the 7-d period, and the uranium concentration in solution (or fraction released) had not achieved a constant value; and (2) uranium leaching exhibited bimodal nonsteady-state behavior over time – in some tests the concentration (or fraction released) increased rapidly at first and then continued to increase more slowly with time, while in others, the concentration (or fraction released) maximized on day 1 and then decreased to very low values by day 7. Bimodal leaching behavior may make it difficult to extrapolate these 1-week batch contact laboratory test results to predict uranium behavior over years or decades in the lysimeters or disposal options. A possible explanation of this bimodal behavior is discussed in Sect. 4.6.1.

The data for the sequential leach tests could only show an increasing total amount of leaching because the leachate and the uranium in the leachate were removed after each contact and, thus, the removed uranium was not available to be precipitated or be sorbed in subsequent contacts. Depending on the kinetics of the reactions involved in uranium leaching and then removal-from-solution and the time the leachate may contact the waste in the field lysimeters or various disposal options, sequential test results might more realistically model uranium leaching in a lysimeter or leachant flowthrough situation than would batch contact tests. None of the curves of fraction released vs time for the sequential tests with trash-type wastes had leveled off by day 7 (L/S ratio of 62), and the question at issue is how to extrapolate these curves to times of years or decades. (Some of the curves for the air filter waste appeared to have leveled off because all of the uranium had been leached.) If the curves are assumed (or modeled) to level off at only slightly greater liquid/solid ratios, say at a value of perhaps 2% uranium released, then 98% of the uranium will be modeled as

insoluble or never released at any time. If, on the other hand, the final slope of these curves is extended over time at some finite rate, say 0.1%/d, then 100% of the uranium will be leached after ~3 years. Conversely, the curves could be extended over time as a function of the L/S ratio and the uranium release predicted as a function of the groundwater flux in the lysimeters or other disposal options. In any case, if the rate is modeled as non-zero, then 100% of the uranium will be calculated to be released at some future time. It is not clear that the data obtained from the tests described in this report are adequate to resolve this issue.

4.3.2 Liquid/Solid (L/S) Ratio

The L/S ratio in both the batch contact and sequential leach tests is an important experimental parameter that could have a major impact on the uranium leaching data. If uranium solubility (saturated solution concentration) is the release-rate-controlling parameter, then the uranium leaching would be proportional to the L/S ratio as long as sufficient uranium solids were present to achieve solution saturation. Such a situation might exist for wastes that contain appreciable amounts of higher-valence uranium oxides, such as U_3O_8. The air filters and uranium oxide powder from the UCOF are possible examples of such wastes. A solubility-limited release situation is relatively easy to model because the uranium releases can be equated with the predicted groundwater flux. However, for many of the trash-type wastes it seems more likely that the uranium contaminant will be primarily present as chips of uranium metal. Uranium metal or lower valence oxides such as UO_2 are very insoluble in groundwater, and wastes containing uranium in these forms likely would not yield appreciable uranium release values unless (or until) the metal or UO_2 is oxidized. For such wastes (production trash, mixed metal chips, and composite waste), it seems less likely that solubility would be the release-rate-limiting process and more likely that the rate of oxidation could be the limiting reaction. For

such wastes, it seemed doubtful that the uranium leaching would be proportional to the L/S ratio in the experiments. The experimental results are briefly examined below with respect to this question.

Both the total fraction (%) of uranium leached by day 7, and the uranium concentration in the day 7 leachate are shown in Table 4.2 for all the tests. With the exception of the uranium oxide powder and air filters, no clear trends exist related solely to the experimental L/S ratio. Many of the uranium oxide powder and air filter leachates may be saturated, or near saturation, for U(VI) species at the leachate pH (see Sect. 4.3.3). For the other wastes, the waste type seemed to be the dominant variable in controlling the fraction of uranium leached and/or the leachate concentration of uranium. Little uranium was leached from mixed metal chips in any test, while production trash and composite waste gave more variable results (see Sect. 4.1).

In the absence of additional information, it appears that the L/S ratio for a given waste-leaching test may not be a useful indication or guide to the amount of uranium to be released in that test. Thus, it would seem that predictions of future waste performance in the field lysimeters or other disposal options, which are based solely on knowledge of the cumulative L/S ratio, may not be reliable or defensible.

4.3.3 Leachate pH

Because the solubility (saturated solution concentration) of U(VI) species is highly pH dependent (see Appendix F), it might be anticipated that the uranium concentration in solution for a given sample would correlate with the final sample pH if sufficient soluble uranium were present in the sample to achieve saturation. This hypothesis is explored in Fig. 4.2, where the log of the uranium concentration for all analytical samples (day 1 through day 7) is plotted vs sample pH for the two leachants used (synthetic landfill and synthetic groundwater) for each of the five waste types tested. Surprisingly, the figure revealed clusters of data points for the different waste types, but, as discussed in Sect. 4.2, showed that the initial leachant employed had only a minor

Table 4.2. Fraction uranium leached and uranium concentration in the leachate as a function of liquid/solid ratio

Liquid/solid[c]	Leachant	Waste type	Leached[a] (%)	Concentration[b] (mg/L)
2 (batch)	TCLP	Production trash	0.68	458
		Mixed metal Chips	7E-05	0.007
		Composite waste	4.59	290
		Air Filters	1.5	560
		Uranium oxide powder	0.69	2860
	SNGW	Production trash	1.61	796
		Mixed metal chips	2E-05	0.003
		Composite waste	0.16	9.6
		Air filters	0.4	140
		Uranium oxide powder	2E-03	7.0
20 (batch)	TCLP	Production trash	0.84	50
		Mixed metal chips	6E-04	0.022
		Composite waste	0.01	0.3
		Air filters	68.1	3110
		Uranium oxide powder	7.25	3050
	SNGW	Production trash	0.57	47
		Mixed metal chips	6E-04	0.013
		Composite waste	1.44	27.9
		Air filters	14.6	610
		Uranium oxide powder	0.18	75
62 (sequential)	TCLP	Production trash	0.69	7.7
		Mixed metal chips	5E-02	0.18
		Composite waste	1.36	5.0
		Air filters	51.1	170
		Uranium oxide powder	8.38	830
	SNGW	Production trash	1.00	11
		Mixed metal chips	3E-03	0.009
		Composite waste	0.16	0.5
		Air filters	17.0	290
		Uranium oxide powder	0.20	26

[a]The fraction of the initial uranium in the sample that was leached by day 7; total liquid/solid ratio of 2 or 20 for the batch contact tests and a ratio of 62 for the sequential tests.

[b]The uranium concentration in the final (day 7) sample for the batch tests and the day 7 sample at an actual liquid/solid ratio of 22 for the sequential contact tests.

[c]Nominal liquid/solid ratio; the value was slightly different in a few tests.

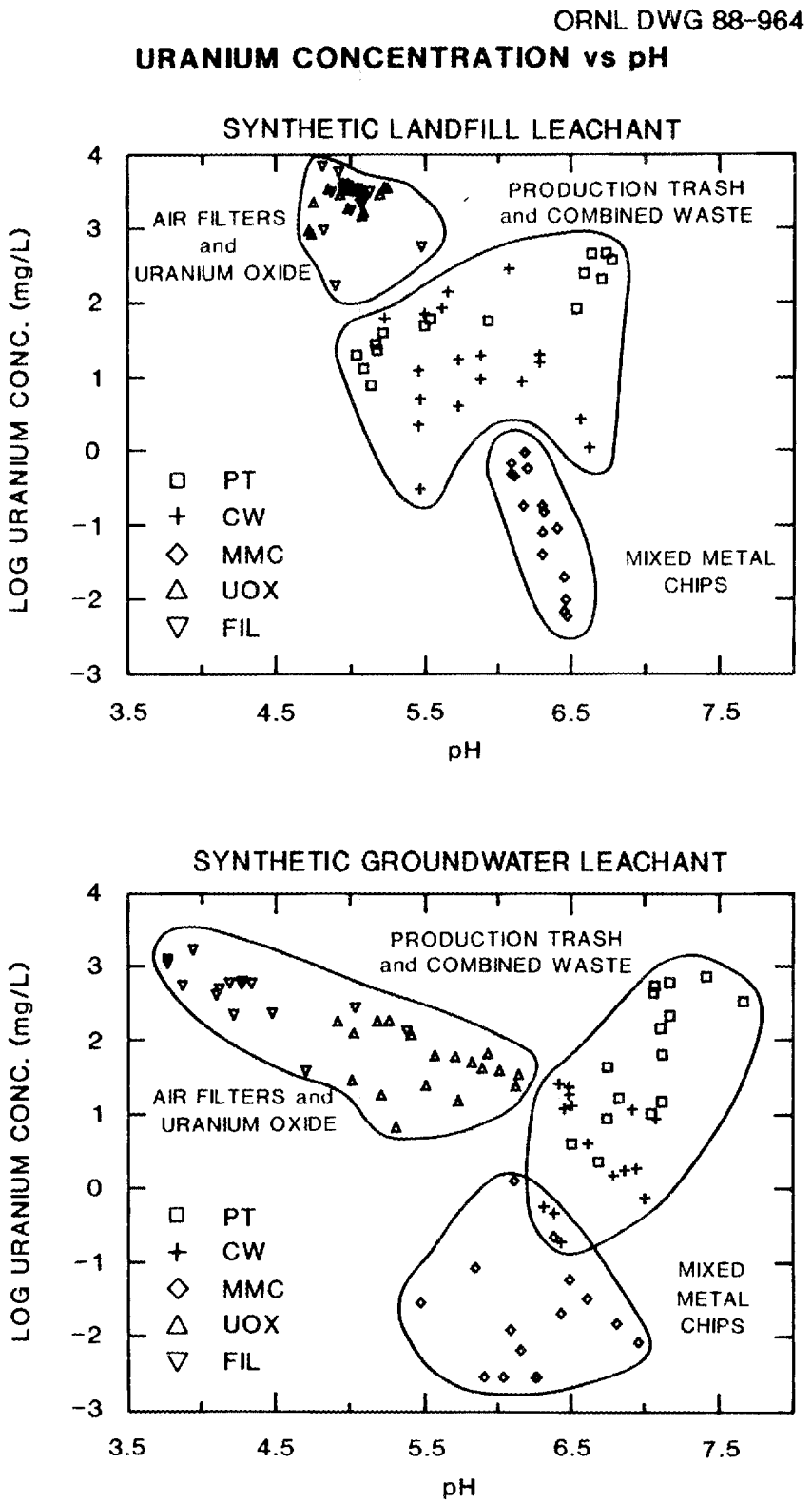

Fig. 4.2. Linear and log plots of the uranium concentration vs pH for all leachate samples.

or second-level effect on the uranium concentration. It is not clear why the sample pH values for the buffered synthetic landfill solution cover essentially as wide a range as the unbuffered synthetic groundwater samples. The chemistry involved here warrants further investigation.

Uranium oxide powder and air filter wastes gave the highest uranium concentrations, and the data points are clustered in the more acidic pH range. This is a logical result for leaching into the buffered landfill leachate, but, because the dissolution reactions consume acid (see Appendix F), unbuffered solutions such as the synthetic groundwater were expected to become more basic, not more acidic, during the test. The mixed metal chip data occupy a region in the plot at very low uranium concentrations. The data points for production trash and combined waste overlap to a considerable degree and generally show more scatter.

A possible conclusion that can be drawn from this plot (this conclusion has been reached several times previously in earlier sections of this report based on other data considerations) is that waste components other than the uranium contaminant or the leachant employed control the chemistry of the leaching system and, in turn, the fraction of uranium leached or the uranium concentration in the leachate.

4.4 EFFECT OF TIME

Although these laboratory leaching data have been collected over 1 to 7 d, extrapolation of the laboratory data over time will be an important lysimeter or disposal option performance modeling aspect, because predictions of waste performance will be needed for periods of decades for the field lysimeters and for centuries or millennia for final disposal options. Data for all leachate samples and waste types for both batch and sequential leach tests in both synthetic landfill leachate and synthetic groundwater are presented in Fig. 4.3 as a function of contact time. The data show very substantial divergence for different tests (i.e., both increasing and decreasing leach modes). In the absence of additional information, it seems that uranium leaching

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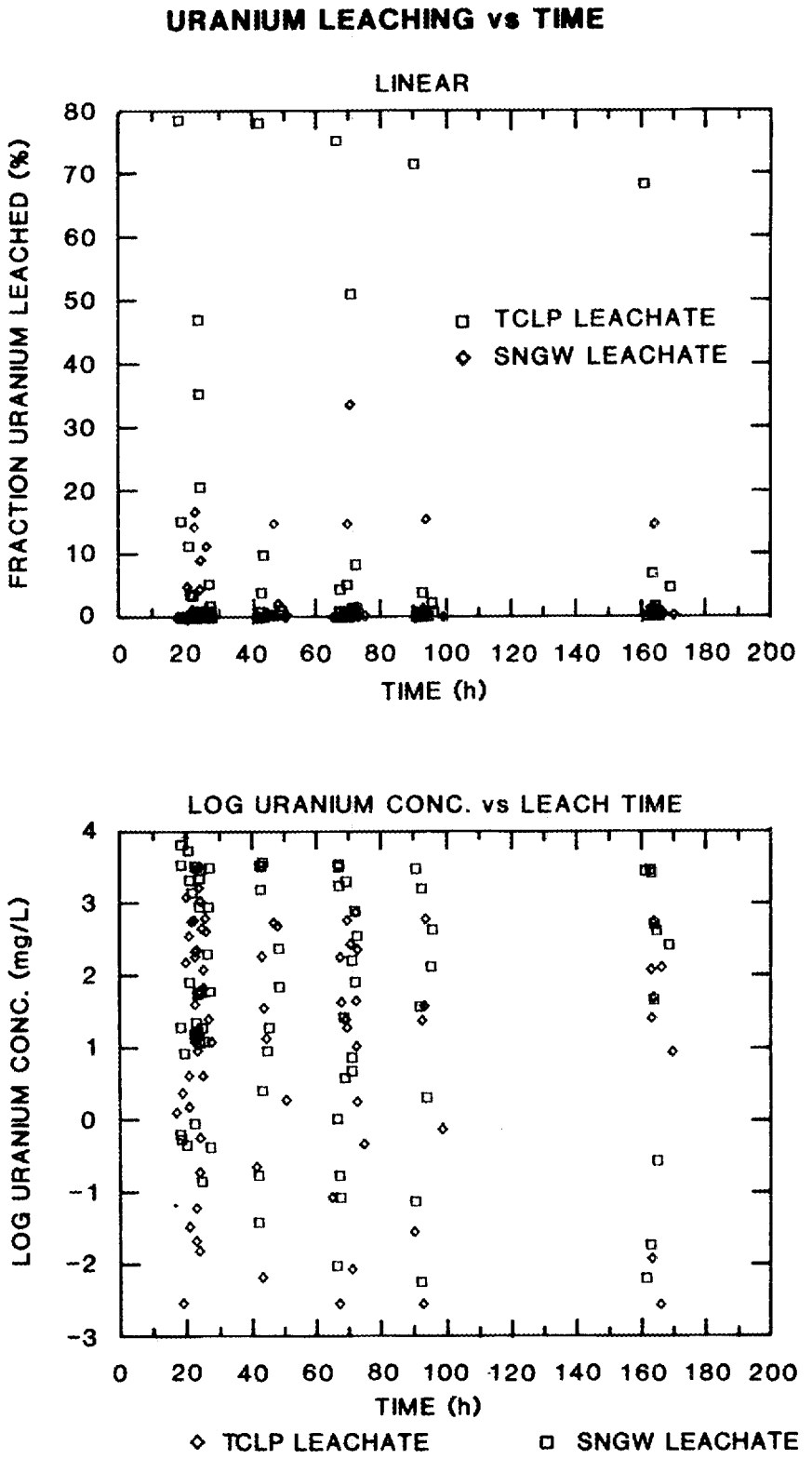

Fig. 4.3. Plots of the fraction of uranium leached and the log uranium concentration of the leachates vs contact time for all the waste type experiments.

cannot be predicted over time. An understanding of the release-rate-limiting reactions and processes and expression of these reactions and processes as a function of time may be necessary for useful or defensible predictions. An additional research program would be required to develop such information.

4.5 LEACHATE SAMPLE STABILITY

Many of the synthetic landfill leachates and the synthetic landfill leachate analytical and archive samples from tests with combined waste, production trash, or mixed metal chips, other than from tests with uranium oxide powder, proved to be unstable (precipitates and sludges formed) on storage.

The analytical samples for uranium and inorganic elements for these samples were stabilized by acidification with HNO_3 to dissolve or prevent precipitation of the sludge. No precipitates or sludges formed in any of the synthetic groundwater leachates, and these were not acidified on storage.

The samples for analysis were filtered when they were prepared and were free of particulates or immiscible liquids/solids at that time. Excess leachate solutions were stored in drums in the laboratory until they could be properly disposed. Analytical samples and replicate archive samples were stored in a refrigerator until they were transferred to the Analytical Chemistry Division for analysis. After either refrigerated or room-temperature storage for ~2 weeks to a month, many, but not all, of the synthetic landfill leachate samples from production trash, mixed metal chips, or combined waste tests released a water-immiscible red oil that both floated to the top of the sample and/or adsorbed into the plastic sample bottles. In addition, some synthetic landfill leachate samples also formed a flocculent red-brown sludge, which settled to the bottom of the samples. In parallel synthetic groundwater tests, a thin film of oil was observed on the surface of some leachates in the 30-gal drum. Sample instability would represent a serious analytical problem because in the resulting heterogeneous samples, the uranium and other elements could be sequestered by the oils or sludges and be incorrectly analyzed. It is likely, but unproven,

that the sludge is a ferric hydroxide precipitate resulting from the dissolution of soluble Fe(II) species during the leaching tests with synthetic landfill leachate and the subsequent precipitation of insoluble Fe(III) hydroxide due to oxidation on sample storage. Ferric hydroxide is known to be a powerful adsorbent for uranium solution species.[13] The source or chemical identify of the oil is unknown at this time.* It is likely that some small amount of immiscible oil was present in many of the trash-type waste-leach tests because oily material was observed in many of the as-received samples (see Appendix A), but the immiscible oil may have been readily observable only when a fine ferric hydroxide precipitate was also present to color the oil red. The problem of precipitate or sludge formation and analytical problems was alleviated by acidification of the appropriate samples to prevent or reverse the formation. The red oil, once it had been adsorbed into plastic, could not be redistributed into the sample.

Instability of the synthetic landfill leachate may have important implications for both the design and operation of the field lysimeters because the biodegradable material in some waste streams might be expected to generate a leach solution on extended contact in the field lysimeters that would be similar to the synthetic landfill leachate. Depending on whether the red oil and the sludge adsorb uranium, and whether the red oil is in turn absorbed by plastic components of the lysimeters or passes out of the lysimeters with the leachate, uranium retention by the lysimeters could be artificially accelerated or diminished, relative to various potential waste disposal options.

The air filter samples showed a different reactivity or instability with the synthetic landfill leachant. The mixture was bubbling after contact, and a fine precipitate had formed. A plausible explanation was that the aluminum filter separators were reacting with the leachant to release hydrogen, forming aluminum hydroxide. The analytical and archive samples appeared to be stable on storage; this

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*Dr. Normal J. Williams, Y-12 Plant, analyzed a sample of the red oil and found aliphatic oils present.

seems reasonable because after filtration, no aluminum metal remains to allow continued reaction and all aluminum hydroxide formed would also be removed because aluminum hydroxide is very insoluble near neutral pH.

4.6 OVERVIEW OF URANIUM LEACHING FROM Y-12 PLANT WASTES

Three of the more significant observations or findings that resulted from this laboratory leaching task are briefly highlighted in the following sections.

4.6.1 Bimodal Uranium Release

Perhaps the single most significant observation to come out of this laboratory investigation is the discovery of bimodal uranium release curves as a function of time for the batch contact tests. In some tests, the uranium concentration in the leachate or the fraction of the initial uranium leached increased over time and did not reach a steady-state limit or constant value in 7 d (the last time point). Such behavior could be consistent with slow leaching kinetics: for example, reactions such as slow oxidation of uranium metal or reduced uranium oxides. In the other tests, the uranium concentration or fraction released maximized on the first day (the first data point) and then decreased steadily to very low values by day 7. Such behavior could be consistent with adsorption or precipitation of initially solubilized uranium. It is possible that the redox state of the system controls the leaching mode observed (see Sect. 4.6.2) and is responsible for the different leaching modes.

Bimodal uranium leaching behavior has been reported previously in tests to study uranium solubilization from wastes at the Portsmouth Gaseous Diffusion Plant.[14] Bimodality may complicate both interpretation of laboratory data and extrapolation of laboratory data to larger-scale, longer-time applications, such as field lysimeters or other disposal options.

4.6.2 Possible Redox Control of Uranium Release Rate

The concept of leaching uranium from Y-12 Plant wastes presented in this section was developed to explain both the bimodal leaching characteristic and several experimental observations. A referenced discussion of the supporting uranium chemistry is given in Appendix F.

Important observations from batch leach tests were:

1. A negative pressure (partial vacuum) developed in the leaching vessel for many, but not all, of the tests with trash-type wastes, but never with uranium oxide or air filter wastes.

2. A brown sludge or precipitate formed upon storage of the synthetic landfill leachate or leachate samples for many, but not all, of the tests with trash-type wastes, but never with uranium oxide or air filter wastes. No sludges or precipitates formed in any synthetic groundwater leachates.

3. The decreasing uranium leach mode was always observed for tests with mixed metal chips, sometimes for tests with composite waste, but never for production trash, uranium oxide powder, or air filters.

These observations are consistent with the development of reducing redox conditions in the leaching vessel. The most likely reductant for these tests is the reactive metal chips (e.g., aluminum, brass, iron) in the various wastes, as well as any uranium metal chips or turnings. These metals can react with water to form strongly reducing conditions. Under such reducing conditions, any solubilized uranium would be reduced to the 4+ valence state, and it is well known that the corresponding U(IV) oxide, UO_2, has a very low solubility in aqueous solutions. Therefore, if strongly reducing redox conditions developed during the leach test, any uranium initially solubilized as U(VI) species would be precipitated (decreasing leach mode); of course, any undissolved uranium, either as uranium metal or lower-valence oxides, could not be solubilized (not leached) because no oxidant remains in the mixture to oxidize the uranium to the soluble 6+ valence. Anaerobic biological activity involving biodegradable carbon-containing components of the

trash-type wastes could also lead to reducing redox conditions, if not in these short-time laboratory leaching tests, then probably in longer-time lysimeter studies or other disposal options. Sanitary landfills form reducing redox conditions due to anaerobic digestion, and similar performance could be anticipated for some of the Y-12 Plant wastes containing significant amounts of paper, cloth, wood, etc., after disposal.

The negative pressure observation supports this reducing redox theory because consumption of the strongest oxidant in the leaching vessel, the O_2 in the air, would produce a partial vacuum. Also, the sludge formation observation is consistent with this theory because under strongly reducing conditions, iron could be leached as soluble Fe(II) species in the acidic synthetic landfill leachate tests [but not in the synthetic groundwater tests because Fe(II) species are less soluble near neutral pH]. Then, oxidation of the dissolved Fe(II) species to very insoluble Fe(III) hydroxide precipitate would be expected to occur in the leachate samples after separation from the leach solids containing the reductant and storage or exposure to air.

A good example of this suggested mechanism can be seen by comparing two tests with production trash (see Table 4.2 and Fig. 4.1). The waste in test 3BALA had no iron turnings; a negative pressure did not develop, no brown sludge was formed, and an increasing leach mode was observed. The waste for test 4BAL contained a large amount of iron turnings, and in this case, the drum developed a negative pressure during leaching, the brown sludge formed, and a decreasing leach mode was observed. Further confirmation is seen in the fact that mixed metal chip wastes always gave a reducing leach mode, while combined waste sample (which had variable amounts of metal chips) sometimes gave the reducing mode. Production trash samples contained much smaller amounts of metal chips, and none of the samples tested exhibited a reducing mode. The uranium oxide and air filter samples contained no metal chips from machining operations, and these leach tests never showed a decreasing mode.

Thus, a reasonable working hypothesis may be that the redox state of the leaching test or waste disposal situation may be the single most

important variable in controlling the leaching or release of uranium from the waste. Wastes containing uranium metal (0 valence) or 4+ valence uranium oxide (lower uranium valences are not stable in the presence of water) could release significant quantities of uranium to groundwater or landfill leachate-type aqueous solutions only after oxidation of the uranium to the 6+ valence and formation of U(VI) solution species. Thus, the rate or time of oxidation and depletion of the reductant in the waste (metal chip and/or biodegradable material) could be the uranium release-rate-controlling process. For wastes that initially contain soluble 6+ valence uranium compounds, if the rate of U(VI) reaction with the reductant exceeds the rate of groundwater movement through the waste, then little uranium may be released until the reductant is exhausted. It seems worthwhile to test this hypothesis in a series of controlled leach experiments with deliberate additions or deletions of specific waste components.

4.6.3 Air Filters

The air filters were unique among the wastes tested. The uranium contaminant was highly soluble, and release seemed to be constrained only by the solubility limit in the leachate sample. The potential for rapid release of uranium from this waste form may have important implications for disposal options.

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APPENDIXES

APPENDIX A
DESCRIPTION OF WASTE SAMPLES

A detailed description of each of the waste samples received from the Y-12 Plant is included in this appendix. This description is based on a careful visual examination of each waste sample before it was placed in the 30-gal leaching drum. The as-collected waste samples for each waste stream were removed from the collection plastic bags and partially remixed and repackaged at the Y-12 Plant to attempt to minimize compositional differences between the same waste-stream-type samples used in the leach tests.

A.1 PRODUCTION TRASH

The Y-12 Plant definition[a] of production trash is any waste generated by the cleaners (job classification) in cleaning and protecting the floors, resulting from efforts to minimize the spread of contamination, and/or general trash found on the floor. A visual description of the trash samples used in each leach test is given below by leach test number (see also Table A.1). A typical sample is shown in Fig. A.1.

A.1.1 Test 3FS (bags A, F, and G from drums 1 and 5)

The following items were identified: cotton rags, several kinds of plastic sheet, screws, Styrofoam®-type drinking cups, candy bar wrappers, aluminum soda cans, chewing gum wrappers, facial tissues, industrial wipes, tubing, small amount of metal turnings (brass and stainless steel), copper electrical wire, dirt, large amount of oily floor sweepings compound, cigarette butts, section of newspaper, nylon mesh, sandpaper mesh screen, "Hot Hogs" (an adsorbent in a cloth tube), blotter paper, memo correspondence, nails, nuts and bolts (brass and stainless steel), paraffin-coated milk cartons, peanuts and peanut

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[a]Personal communication from B. T. Butcher, Y-12 Plant, to J. L. Collins (November 1987).

Table A.1. Production trash

Drum No.	Bag ID	Weight (kg)	Uranium (g)	Test No.
1[a]	A[b]	2.13	342 ± 11	8FSAA
	B[c]	2.68	333	
	C	2.09	232	8FS
	D	2.79	319	
5[a]	E	1.92	253	4FS
	F	1.73	149	8FS
	G	3.05	452	7FSAA
	H	1.65	171	4FS
2[a]	A	3.80	368	3FS
	B	3.03	237	7FSAA
	C	2.42	399	7FS
	D[b]	3.01	616 ± 16	7FS
3[a]	E	2.55	197	7FSAA
	F	1.80	480	3FS
	G	3.47	132	7FS
	H	3.55	376	3FS
16[d]	A	3.56	710	1FS
	B		528	
	C		458	
	D	3.67	832	5FS
	E		749	
17[d]	A		152	
	B		156	
	C		144	
	D		109	
	E		69	

[a]Received from Y-12 Plant on January 15, 1988.
[b]Mean ±1 standard deviation for triplicate counts.
[c]Bags not assigned a Test No. were not used.
[d]Received from Y-12 Plant on April 15, 1988.

ORNL PHOTO-0440-88

Fig. A.1. Typical sample of production trash.

shells, aluminum foil, a telephone directory, a can of rubbing compound, lens cleaning tissue, paper bag of sugar, and gloves (rubber, cloth, and leather).

A.1.2 Test 4FS (bags E and H from drums 1 and 5)

The following items were identified: cotton rags, several kinds of plastic sheet, oily rope, Styrofoam-type drinking cups, candy bar wrappers, aluminum soda cans, chewing gum wrappers, facial tissues, industrial wipes, tubing, small amount of metal turnings (brass and stainless steel), copper electrical wire, dirt, large amount of oily floor sweepings compound, cigarette butts, section of newspaper, nylon mesh, sandpaper mesh screen, Hot Hogs, blotter paper, memo correspondence, nails, screws, nuts and bolts (brass and stainless steel), paraffin-coated milk cartons, and gloves (rubber, cloth, and leather).

A.1.3 Test 7FSAA (bags B and E from drums 2 and 3 and bag G from drums 1 and 5)

The following items were identified: cotton rags, several kinds of plastic sheet, Styrofoam-type and plastic drinking cups, candy bar wrappers, aluminum soda cans, chewing gum wrappers, empty facial tissue box, industrial wipes, tubing, small amount of aluminum metal turnings, copper electrical wire, dirt, large amount of oily floor sweepings compound, cigarette butts, section of newspaper, nylon mesh, oily sandpaper, Hot Hogs, blotter paper, memo correspondence, nails, screws, nuts and bolts (brass and stainless steel), paraffin-coated milk cartons, peanuts and peanut shells, gloves (rubber, cloth, and leather), lint, brown paper lunch bags, rubber "O" rings, and small piece of wood.

A.1.4 Test 8FSAA (bags A from drums 1 and 5)

The following items were identified: cotton rags, several kinds of plastic sheet, Styrofoam-type and plastic drinking cups, aluminum soda cans, industrial wipes, tubing, small amount of iron metal turnings, large amount of oily floor sweepings compound, cigarette butts, oily

sandpaper, "Hot Hogs," blotter paper, a few nails, screws, nuts and bolts (brass and stainless steel), paraffin-coated milk cartons, peanuts and peanut shells, and gloves (rubber, cloth, and leather).

A.1.5 Test 1FS (bag A from drum 16)

The following items were identified: several kinds of plastic sheet, Styrofoam-type and plastic drinking cups, aluminum soda cans, oily industrial wipes, large amount of aluminum metal turnings, small amount of oily floor sweepings compound, cigarette butts, oily sandpaper, "Hot Hogs," blotter paper, memo correspondence, paraffin-coated milk cartons, gloves (rubber, cloth, and leather), brown paper lunch bags, and wooden pencil.

A.1.6 Test 5FS (bag D from drum 16)

The following items were identified: several kinds of plastic sheet, Styrofoam-type and plastic drinking cups, aluminum soda cans, oily industrial wipes, large amount of aluminum, iron, and brass metal turnings, small amount of oily floor sweepings compound, cigarette butts, oily sandpaper, "Hot Hogs," blotter paper, memo correspondence, paraffin-coated milk cartons, gloves (rubber, cloth, and leather), used steel-wool pad, and a small piece of copper wire.

A.2 COMPOSITE WASTE

The Y-12 Plant definition[b] of composite waste is an assortment of trash that contains 1/3 floor sweepings (production trash), 1/3 mixed metal chips, and 1/3 general trash from highly contaminated areas. A visual description of the trash samples used in each leach test is given below by leach test number (see Table A.2). A typical composite waste sample is shown in Fig. A.2.

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[b]Personal communication from B. T. Butcher, Y-12 Plant, to J. L. Collins (November 1987).

A.2.1 3BAL (bags A and L from drums 12, 13, and 15)

The following items were identified: several kinds of plastic sheet, Styrofoam and plastic cups, blotter paper, wipes, dirty and oily leather gloves, rubber gloves, loose liquid pipe-joint compound, cigarette butts, floor sweepings, medium amount of iron and brass tunings, steel wool scouring pad, sandpaper, pieces of insulated copper and aluminum wire, oily cloth, yellow plastic tape, small piece of rubber tubing, oil-soaked paper towels, and a can of pipe-joint compound.

A.2.2 3BALA (bags A, D, and G from drums 11 and 14)

The following items were identified: moldy cotton rags, several kinds of plastic sheet, Styrofoam-type and plastic drinking cups, candy bar wrappers, aluminum soda cans, chewing gum wrappers, facial tissues and box, industrial wipes, tubing, small amount of large metal turnings (aluminum), large copper cable with PVC insulation, long piece of bare copper wire, medium amount of oily floor sweepings compound, cigarette butts, section of newspaper, large ball of aluminum foil with lunch trash inside, lunch bag with rotten sandwich, sandpaper, "Hot Hogs," blotter paper, memo correspondence, screws, nuts and bolts (stainless steel), gloves (rubber, cloth, and leather), yellow plastic tape, pasteboard box, paper fiber "egg carton type," and a folded blue print.

A.2.3 4BALA (bag K from drums 12, 13, and 15)

The following items were identified: several kinds of plastic sheet, Styrofoam-type and plastic drinking cups, aluminum soda cans, industrial wipes, tubing, small amount of oily large metal turnings (iron), medium amount of oily floor sweepings compound, cigarette butts, rubber gloves, oily leather gloves, pasteboard box, red plastic tape, and sheets of newspaper. A good bit of red oil was smeared on the surfaces of items in this bag of waste.

Table A.2. Composite waste

Drum No.	Bag ID	Weight (kg)	Uranium (g)	Test No.
11 and 14[a]	A	2.19	40	3BALA
	B[b]		46	
	C		38	
	D	4.05	48	3BALA
	E		47	
	F	2.06	69	8BALAA
	G	4.66	50	3BALA
	H	2.99	35	8BALAA
12, 13 and 15[a]	A	9.75	184	3BAL
	B		117	
	C	3.38	154	1BAL
	D[c]	3.70	40 ± 6	7BALAA
	E		151	
	F	3.15	55	7BALAA
	G	3.06	90	8BALAA
	H	3.26	34	7BALAA
	I		195	
	J[c]		254 ± 20	
	K	4.08	220	4BALA
	L	10.00	133	3BAL
18[d]	A	2.95	110	5BALA
	B		39	
	C		24	
	D		32	
	E		29	
19[d]	A		65	
	B		45	
	C		70	
	D		76	
	E		32	

[a]Received from Y-12 Plant on February 4, 1988.
[b]Bags not assigned a Test No. were not used.
[c]Mean ± 1 standard deviation for triplicate counts.
[d]Received from Y-12 Plant on April 22, 1988.

ORNL PHOTO-4295-88

Fig. A.2. Typical sample of composite waste.

A.2.4 7BALAA (bags D, F, and H from drums 12, 13, and 15)

The following items were identified: plastic bags, PVC plastic, rubber gloves, oil-soaked paper, iron turnings, Styrofoam-type and plastic cups, floor sweepings, aluminum turnings, cotton rags, oily leather gloves, paper coveralls, blotter paper, cigarette package and butts, tissue papers, cotton gloves, cotton short sleeve shirt, and a time card insert.

A.2.5 8BALAA (bag F from drums 12, 13, and 15 and bags F and H from drums 11 and 14)

The following items were identified: several kinds of plastic sheet, Styrofoam-type and plastic drinking cups, aluminum soda cans, industrial wipes, small amount of oily large metal turnings (iron and aluminum), medium amount of oily floor sweepings compound, cigarette butts, rubber gloves, oily leather gloves, pasteboard box, sheets of newspaper, cardboard packaging material, light bulb carton, broken light bulb, paraffin-coated milk carton, "Hot Hog," empty plastic Joy® and 409® bottles, cloth rags, and red plastic tape.

A.2.6 1BAL (bag C from drums 12, 13, and 15)

The following items were identified: several kinds of plastic sheet, Styrofoam-type and plastic drinking cups, aluminum soda cans, industrial wipes, large amount of oily metal turnings (iron and aluminum) that varied in size from large to fine, medium amount of oily floor sweepings compound, cigarette butts, rubber gloves, oily leather gloves, paper coveralls heavily stained with red ink, small piece of wood, meter-long piece of plastic insulated copper wire, and ~2 m^2 of nylon cloth and ~2 m^2 of cloth rags.

A.2.7 5BAL (bag A from drum 18)

The following items were identified: several kinds of plastic sheet, Styrofoam-type and plastic drinking cups, aluminum soda cans, industrial wipes, large amount of oily metal turnings (iron and aluminum) that varied in size from large to fine, medium amount of oily

floor sweepings compound, cigarette butts, rubber gloves, oily leather gloves, and paper coveralls heavily stained with red ink.

A.3 MIXED METAL CHIPS

The Y-12 Plant definition[c] of mixed metal chips is a mixture composed of metal turnings of aluminum, iron, stainless steel, copper, and/or brass. A visual description of the trash samples used in each leach test is given below by leach test number (see Table A.3). A typical sample of mixed metal chips is shown in Fig. A.3.

Table A.3. Mixed metal chips

Drum No.	Bag ID	Weight (kg)	Uraniun (g)	Test No.
8[a]	A	2.84	55	3CHIP
	B[b]	3.67	255 ± 5	4CHIP
	C	3.79	108	7CHIP
	D	5.35	217	8CHIP
6[c]	A[d]		34	
	B	3.81	119	1CHIP
	C		70	
	D		72	
	E	2.90	93	5CHIP

[a]Received from Y-12 Plant on February 22, 1988.
[b]Mean ± 1 standard deviation for triplicate counts.
[c]Received from Y-12 Plant on April 1, 1988.
[d]Bags not assigned a Test No. were not used.

[c]Personal communication from B. T. Butcher, Y-12 Plant, to J. L. Collins (November 1987).

ORNL PHOTO-4296-88

Fig. A.3. Typical sample of mixed metal chips waste.

A.3.1 Test 3CHIP (bag A from drum 8)

The plastic bag contained fine metal turnings of brass and iron. A heavy coating of rust appeared on the surface of the bag, and the turnings were damp.

A.3.2 Test 7CHIP (bag C from drum 8)

The contents of this bag were similar in appearance to those in Test 3CHIP; however, these turnings were greasier.

A.3.3 Test 4CHIP (bag B from drum 8)

The contents appeared to be fine turnings of copper and iron which were greasy.

A.3.4 Test 8CHIP (bag D from drum 8)

The contents of this waste were like that for Test 4CHIP.

A.3.5 Test 1CHIP (bag B from drum 6)

A large fraction of this waste was large-sized turnings of stainless steel; the remainder was fine, rusty iron turnings. Also, a great deal of oil was found on the surface of the bag and on larger-sized turnings.

A.3.6 Test 5CHIP (bag E from drum 6)

Similar to waste in Test 1CHIP.

A.4 AIR FILTERS

The air filters were standard High Efficiency Particulate Absorber (HEPA) filters from building ventilation systems in Y-12 Plant areas working with depleted uranium. The filters are constructed of a fiberglass filter medium with aluminum separators and are supported by galvanized steel wire face guards on both sides. The filtering medium is sealed with gaskets on both sides into steel frames which measure

24 × 24 × 11.5 in. Appreciable amounts of an easily dispersed yellow-green powder were observed on all filters. The filter medium was cut from the steel frames and used in the leaching tests. The frames were discarded because they were too large to fit into the 30-gal leaching drums. A listing of the air filter medium samples used in each leach test is given in Table A.4. An air filter is shown in Fig. A.4.

Table A.4. Air filters

Filter[a] No.	Bag ID	Weighty (kg)	Uranium (g)	Test No.
1	06-03-01	2.45	144	UFIL[b]
1	06-03-02[c]		131	
2	06-03-03[d]		409 ± 15	
3	06-03-04	2.27	231	3FIL
3	06-03-05	2.59	198	7FIL
4	06-03-06		132	
4	06-03-07		122	
5	06-03-08		370	
6	06-03-09	2.34	200	8FIL
6	06-03-10	2.36	218	4FIL
7	06-03-11	2.67	259	1FIL
7	06-03-12	1.91	198	5FIL

[a]Received from the Y-12 Plant on June 6, 1988.

[b]Four sequential leaches (3 M HNO_3, 1.5 M HNO_3, H_2O, H_2O) were made on this bag of filter media to remove all the uranium. The total leachate volume was 108 L.

[c]Bags not assigned a test number were not used.

[d]Mean ± 1 standard deviation for quadruple counts.

ORNL PHOTO-4294-88

Fig. A.4. Typical air filter.

A.5 URANIUM OXIDE POWDER

An ~13-kg sample of uranium oxide from the Y-12 UCOF was received from J. E. Cline (Y-12 Plant) and chemically and physically characterized. The sample was a mixture of black powder and intact larger hulls or residual chips and turnings (see Fig. A.5). Representative samples of the powder and hulls were examined (Analytical Chemistry Division) by energy-dispersive X-ray analysis in the scanning electron microscope (EDX-SEM) and by X-ray diffraction (XRD). The EDX-SEM analysis detected only uranium; no other elements were identified. The EDX-SEM method is sensitive to elements with atomic number greater than 11 and has a detection limit of ~1%. The XRD analysis showed that the powder was a mixture of U_3O_8 and UO_2. The hulls were primarily $UO_{2.25}$ and contained some UO_2 that contained a trace amount of niobium. No XRD lines for uranium metal were observed. The uranium oxide mixture was thoroughly blended to prepare working samples for the leach tests. After blending, analytical samples were taken from the top, middle, and bottom of the bottle containing the blended sample. These analyzed at 85.4, 84.5, and 84.6% U, respectively. Surface area measurements on portions of the blended sample showed a relatively low value for a powder; three separate samples gave a surface area of 0.87 ± 0.10 m^2/g.

Fig. A.5. Example of uranium oxide powder from the UCOF.

APPENDIX B
METHODS FOR PREPARATION OF LEACH SOLUTIONS

Large volumes of synthetic groundwater and synthetic landfill leachate were needed. Stock solutions were prepared in cleaned, 30-gal polyethylene tanks which were equipped with polyethylene faucets.

Deionized water was used in the preparation of all leachants. The deionized water was prepared by passing building distilled water through a Milli-Q® Water System,[d] which consisted of one activated carbon cartridge, two ion-exchange cartridges, one Organex-Q® cartridge, and one Milli-Pak® filter. Before use, the purity of the water was checked by measuring its conductivity.[e] Typically, the conductivity values were near or less than 0.2 μmho.

B.1 SYNTHETIC GROUNDWATER

The synthetic groundwater composition selected was 0.10 m$\underline{M}$ Na^+, 0.02 m$\underline{M}$ Cl^-, and 0.08 m$\underline{M}$ HCO_3^-, adjusted with HCl to pH 7.3. Thirty-gallon batches of synthetic groundwater were prepared by adding 0.763 g $NaHCO_3$ (ACS grade) and 0.113 g NaCL (ACS grade) to 113.65 L of deionized water and mixing well by mechanical stirring. The pH was adjusted by adding 4 mL of 1.0 $\underline{N}$ HCL (NBS[g] certified) and 6 mL 0.1 $\underline{N}$ NaOH (NBS certified) and mixing well. Conductivity, pH, and temperature measurements were made for each batch and recorded in addition to the quantities of chemicals used. After standing overnight, the pH nominally was 7.15 ± 0.15 at 25 ± 1°C, and the conductivity was 11.5 ± 0.5 μmho.

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[d]Millipore Corp.

[e]Yellow Springs Instrument Co., Model 32 conductance meter equipped with a Radiometric America type PP1042 immersion conductivity cell.

[f]American Chemical Society.

[g]National Bureau of Standards.

B.2 SYNTHETIC LANDFILL LEACHATE

The recipe for the preparation of synthetic landfill leachate is given in the TCLP[1] as follows: "This fluid is made by adding 5.7 mL glacial acetic acid to 500 mL of the appropriate water, adding 64.3 mL of 1.0 N NaOH, and diluting to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05."

Thirty gallons of synthetic landfill leachate were prepared by adding 0.640 L (0.676 kg, 1.49 lb, or 0.169 gal) glacial acetic acid (ACS grade) to 50 L (110.23 lb or 13.21 gal) deionized water. These components were well stirred and then followed by the addition of 0.372 L (0.569 kg, 1.25 lb, or 0.098 gal) of 19.3 M NaOH (50.5 w/w % NBS-certified NaOH) and 62.55 L (137.8 lb or 16.52 gal) of deionized water. The mixture was again well mixed. Subsequently, pH, conductivity, and temperature measurements were made. The pH and conductivity values were 4.89 ± 0.03 and 3.95 ± 0.05 μmho, respectively, at 25 ± 1°C.

APPENDIX C
ANALYTICAL DATA FOR WELL WATER SAMPLES AND SOIL SAMPLE LEACHATES

Soil samples were acquired from locations in Bear Creek Valley where soil for the lysimeter cap might be excavated, and these soil samples were leached to generate artificial shallow groundwaters for chemical analysis. Because groundwater composition is dependent on the soil composition in communication with the water, several different soils were leached. Four samples of Conasauga colluvium and three samples of Conasauga saprolite were received from R. B. Clapp (ESD), and a 55-gal barrel of Knox residuum was received from L. S. Jones (Y-12 Plant). (Details of the location of these soil samples are given in footnotes to Table C.1.) Samples of well water from wells GW-84 and GW-376 were also received from L. S. Jones. These soils were prepared and leached as described below to generate the artificial shallow groundwater samples for chemical analysis.

The following procedure was used to prepare analytical samples of artificial groundwaters representative of shallow groundwater at various Bear Creek Valley or Chestnut Ridge locations which may be considered for the disposal of Y-12 Plant low-level wastes:

1. The soil was air dried at room temperature to remove excess moisture. (Some samples were muddy or moist as received.) The operator wore rubber gloves during this and all subsequent steps to avoid possible contamination of the soil. The soil was spread in a thin layer on polyethylene sheeting in a large hood. (The hood had an appreciable air flow.) An infrared heat lamp in the hood was used to help accelerate the evaporation of water from the soil surface. (The temperature of the soil was not significantly increased by the heat lamp.) The soil was allowed to air dry for several days, or until dry and friable enough to permit mild disaggregation and screening.

2. The air-dried soil was placed in 4-mil polyethylene bags and disaggregated by mild contact with a fiber-head hammer. The hammer head also was wrapped in polyethylene. Only readily friable soil lumps were disaggregated. No attempt was made to crush rock fragments.

3. The soil was screened through a 6 mesh (Tyler equivalent; 3.36-mm openings) brass screen to remove and discard >6 mesh-size rock fragments, roots, etc.

4. After screening, all the screened portions (<6 mesh material) were combined and the soil was mixed for 5 min in a large Hobart mixer to yield a well-blended soil sample.

5. Portions of the soil were leached with a minimum volume of demineralized water (Millipore MILLI-Q water system). Two different leaching steps (6A and 6B below) were followed for each soil.

6A. 500 g of soil and 700 mL of demineralized water were placed in an EPA TCLP 2-L glass jar. The jar was capped and rotated for ~60 h.

6B. 500 g of soil and 700 mL of demineralized water were placed in an EPA TCLP 2-L glass jar. The jar was capped and rotated. The rotation was periodically stopped, a sample of the leachate removed, and the leachate conductivity measured (Yellow Springs Instrument model 32 conductance meter) and recorded. The leachate was returned to the jar, and rotation was continued. The conductivity was periodically measured in this manner (every 2 h during the first day, two or three times during the second day, and after filtration on the third day after ~60 h of leaching). A constant conductivity value was assumed to indicate solution saturation or steady-state leaching conditions.

7. After completion of the soil leach (step 6A or 6B), the mixture was poured into an EPA TCLP stainless steel Millipore pressure filtration apparatus and filtered through a 0.6- to 0.8-μm glass fiber filter (filter medium specified in the EPA TCLP proposed procedure). The first volume of filtrate often was cloudy, and this was returned to the apparatus and refiltered. The air pressure on the filter was slowly increased from ~20 to 50 psi. Filtration was terminated after ~250 to 300 mL of clear filtrate were obtained.

8. The pH, conductivity, and temperature were measured immediately after filtration and recorded.

9. Samples of the filtrate were submitted to Analytical Chemistry Division for the following analyses: (1) elements by Inductively Coupled Plasma Spectrometry (ICP), (2) anions by ion chromatography, (3) alkalinity by wet chemical titration, and (4) inorganic and organic carbon with the International Carbon Analyzer.

The chemical analyses of the artificial groundwaters and well waters are given in Table C.1.

Table C.1. Artificial shallow groundwater and well water data

	Conasauga Colluvium[a] A	Conasauga Colluvium[a] B	Conasauga Saprolite[b]	Knox Residuum[c]	Well GW-84[d]	Well GW-376[e]
Elements by ICP[f] (mg/L)						
Al	0.55 ± 0.37	0.82 ± 0.85	0.23 ± 0.04	<0.21	<0.21	<0.03
Ba	0.07 ± 0.08	0.07 ± 0.03	<0.02	0.02	0.15	0.32
Ca	0.89 ± 0.78	3.30 ± 0.36	<0.10	80.00	60.00	56.00
Fe	0.47 ± 0.44	0.48 ± 0.34	0.13 ± 0.05	0.03	0.04	<0.01
Mg	0.64 ± 0.29	1.78 ± 0.13	0.06 ± 0.02	13.00	4.80	13.00
Mn	0.08 ± 0.08	0.23 ± 0.09	0.01 ± 0.004	0.08	0.01	0.10
Na	5.23 ± 3.57	2.83 ± 0.63	2.77 ± 0.74	12.00	6.60	21.00
Si	10.33 ± 0.81	11.50 ± 1.00	24.00 ± 5.57	2.00	10.00	9.80
Elements by AA (mg/L)						
K	1.07 ± 0.22	5.63 ± 0.35	1.10 ± 0.56	1.20	0.70	3.00
Anions by Ion Chromatography[g] (mg/L)						
Cl^-	1.45 ± 0.44	1.93 ± 0.31	1.20 ± 0.35	16.00	1.00	2.20
SO_4^{2-}	5.35 ± 0.47	18.00 ± 1.15	<5.00	57.00	6.50	14.00
Wet Chemical Methods[h] (mg/L)						
Alka.	2.81 ± 4.48	2.38 ± 2.56	0.92 ± 0.52	175.00	158.00	222.50
TIC	1.73 ± 1.45	1.58 ± 0.42	1.20 ± 0.26	0.30	35.90	50.00
TOC	1.30 ± 0.41	6.28 ± 0.33	0.83 ± 0.15	1.80	0.50	0.60
Other						
pH	6.5 ± 0.5	6.1 ± 0.3	7.3 ± 0.3	7.8	8.0	7.8
Cond.[h]	31.2 ± 7.8	69.9 ± 4.5	16.0 ± 5.7	506.0	321.0	438.0

[a]These data are the mean ± 1 std dev of four separate soil leach tests (two leach tests each on two different soil samples). These two soil samples were from the C-horizon at the Y-12 lysimeter site in Bear Creek Valley. Samples A were taken at a depth of 78 to 120 cm below the surface, and samples B were taken at 25 to 45 cm below the surface. These soils reportedly are not typical of the shaley soils in the Conasauga Group.

[b]These data are the mean ± 1 std dev of three separate soil leach tests (one leach test each on three different soil samples). These three soil samples were from the Packing Disposal Demonstration site in Bear Creek Valley. This soil reportedly [R. B. Clapp (ESD)] is typical Conasauga Group soil.

[c]These data are from a single leach test of a single soil sample. This 55-gal barrel of soil was from the Y-12 sanitary landfill on Chestnut Ridge. The sample was from a depth of 20 ft below original grade at the north end of trench 3. The soil reportedly [R. B. Clapp (ESD)] is Knox residuum.

[d]This sample was water from well GW-84. The well is in the Maryville Formation of the Conasauga Group.

[e]This sample was water from well GW-376 (50 ft deep) which is located slightly upgrade of the Y-12 lysimeter site.

[f]Most other elements were below the detection limit.

[g]NO_3^- and PO_4^{3-} were <5 mg/L in all samples.

[h]Alkalinity is $CaCO_3$ in mg/L.

[i]Conductivity (μmho) measured at 25°C and corrected for the cell constant (1.089/cm).

APPENDIX D
LABORATORY FACILITY AND PROCEDURE FOR 30-GAL-SIZE LEACH TESTS

D.1 DESCRIPTION OF LABORATORY FACILITY

The Waste Characterization Facility (laboratory BG-74 in Building 4501, ORNL) consists of an ~30 × 60 ft radiochemical laboratory with two large walk-in radiochemical hoods, one large double-sided radiochemical hood, and one smaller radiochemical hood. Equipment installed in the hoods and laboratory permits physical disaggregation and blending of bulk waste samples, allows waste leaching tests in both 2-L-size (Fig. D.1) and 30-gal-size apparatus (Fig. D.2), is equipped for recovery of the leachates and preparation of analytical and archive samples, and provides for preparation of both liquids and solids for disposal as radioactive solid or liquid waste. A rotary-tine mill[a] for shredding paper-like or friable wastes and a 12-qt stainless steel food mixer[b] for blending soils or powdered wastes are installed in one of the walk-in hoods. The large hood is used to house the filtering apparatus (four 1.5-L Teflon®-lined filters[c]) for preparation of the analytical and archive leachate samples (see Fig. D.3). The small radiochemical hood is used as a general-purpose laboratory hood. The facility also contains two refrigerators for storing samples at ~4°C.

A calibrated electronic scale[d] with a capacity of 500 lb is used for large-scale weighing (Fig. D.4). Two small-scale calibrated balances[e] are used for weighing chemical reagents, etc.

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[a]Laboratory Mill Model 4, Thomas Scientific Co.

[b]Holbart Corp., Model A120.

[c]Catalog No. YT30142HW, Millipore Corp.

[d]Weightmeter model DR-525, Electroscale Corp.

[e]Sybron model 36DK with a capacity of 3600 g made by the Digimetric Sybron Corp., and an Ohaus model 400D with a capacity of 400 g made by the Ohas Scale Corp.

ORNL PHOTO-9788-87

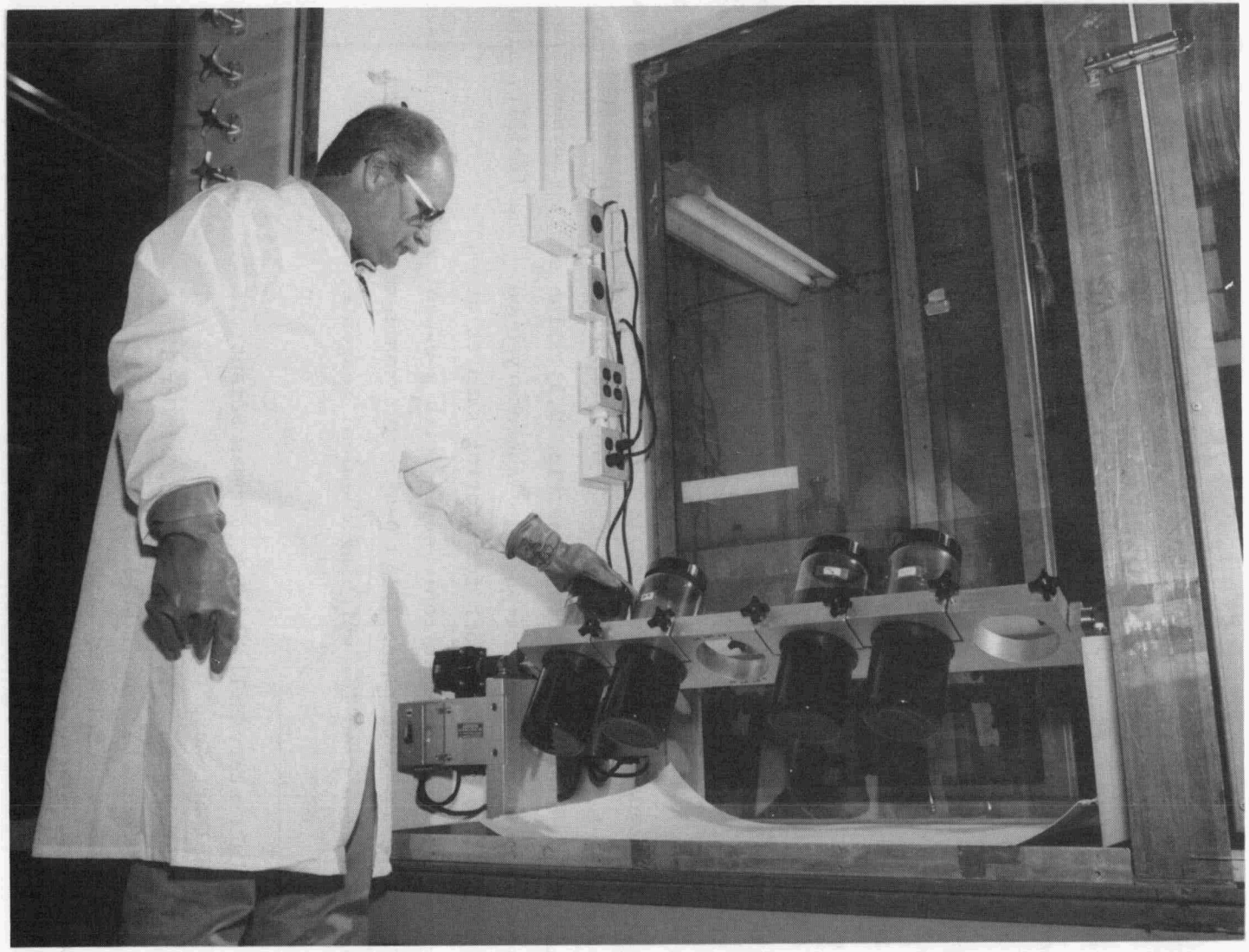

Fig. D.1. Mixing rotator used in the 2-L size leach tests.

ORNL PHOTO-9796-87

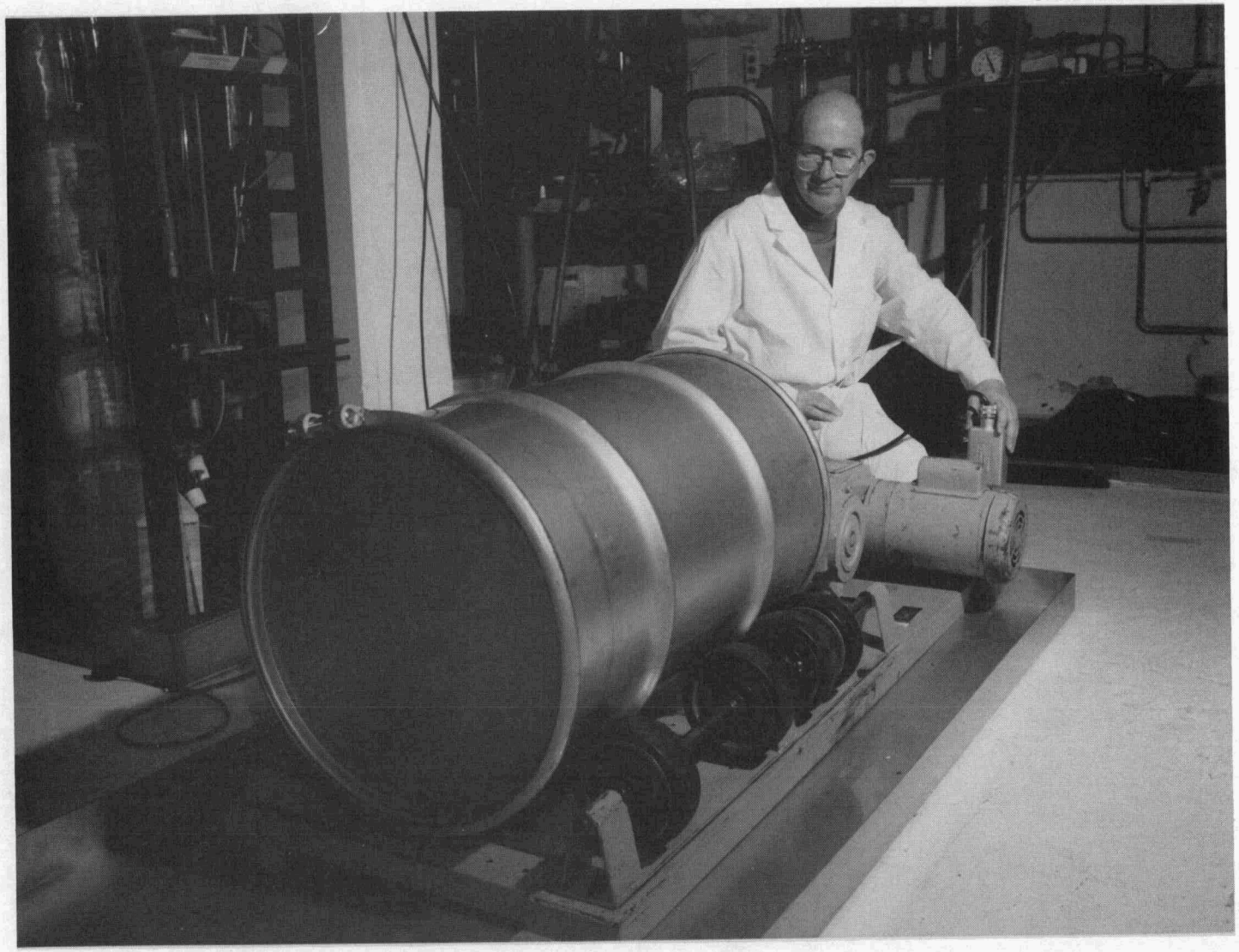

Fig. D.2. Thirty-gallon-drum roller apparatus.

ORNL PHOTO-9789-87

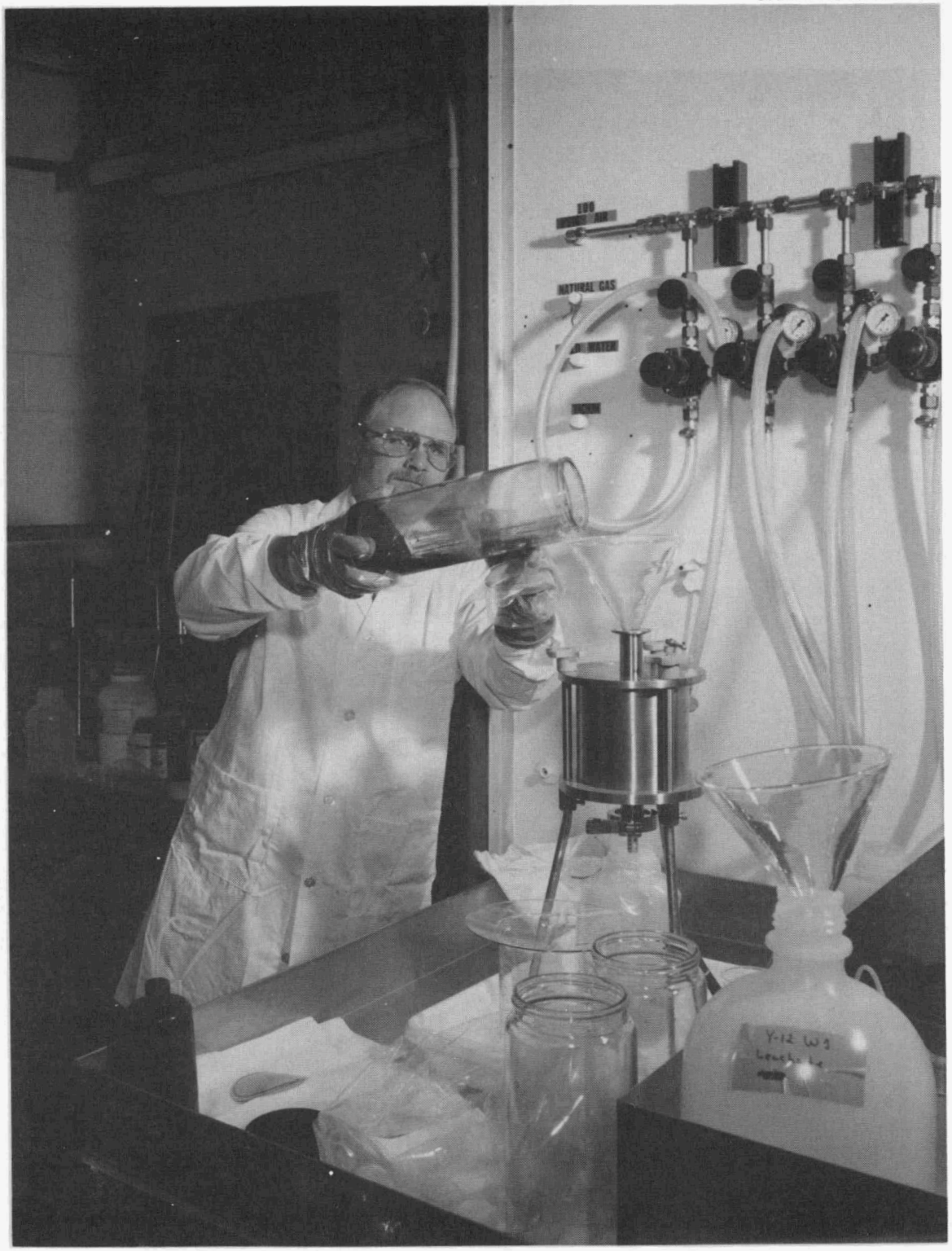

Fig. D.3. Filtering apparatus used to filter samples of leachate for analytical analysis.

ORNL PHOTO-0442-88

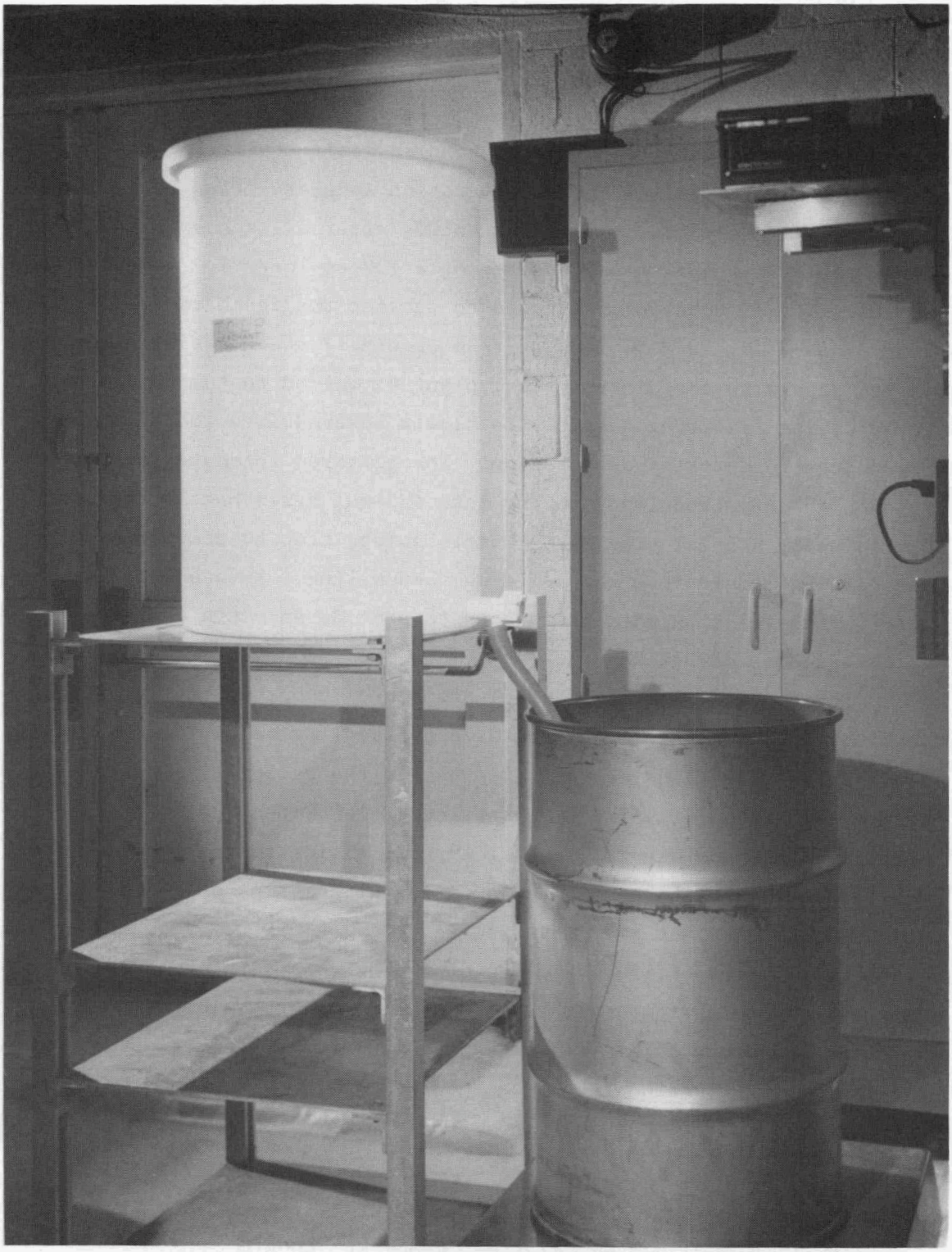

Fig. D.4. Electronic scale used for large-scale weighing.

Three stationary drum rotators[f] are used to agitate the 30-gal drums employed as the leaching apparatus. A drum handler[g] is available for moving both 30-gal- and 55-gal-sized drums. The drum handler has a manual pump to hydraulically raise and lower the drums and a pull-chain crank which allows the drums to be handled horizontally and to be tilted for pouring purposes. A vacuum filtration apparatus (see Fig. D.5) is used to separate leachate from the solids after a leach step has been completed. This apparatus consists of a 122-cm long, 1.27-cm-diam stainless steel tube which is used to suction the leachate from a 91-cm-long, 5-cm-diam, 50 × 50 mesh (297-μm openings) stainless steel screen-walled tube with a stainless steel planchet welded to the bottom end. For use, the filtering assembly is slowly lowered into the drum to remove the leachate by decantation. The filtered leachate is vacuumed through thick-walled Tygon tubing into a 5-gal Pyrex bottle that is backed up by a 5-gal-size Pyrex bottle safety trap to prevent sucking radioactive liquid into the building vacuum line. Both bottles are placed in 5-gal-size metal lard cans to provide an extra degree of safety in case of breakage.

Three 55-gal stainless steel drums are in one of the large radiochemical hoods. These drums are used as settling tanks for the liquid leachate wastes. Liquids that are sent to the radioactive waste tank farm must be free of solids. The filtered leachates are stored in the settling tanks for several weeks. Any oil rising to the surface from the leachate is daily removed by skimming with strips of blotter paper (Fig. D.6). Once the oily material (if present) is removed, the stored leachate is vacuum-filtered to one of two 90-gal stainless steel holding tanks which are designed to allow liquids to be steam-jetted to the building hot drain. This liquid waste discharge system is used because the facility is located in the basement of Building 4501 and below the

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[f]Morse Manufacturing Co., Inc. model No. 1-5154-1. which rotated the drums at a rate of 39 rpm.

[g]Morse Manufacturing Co., Inc. model No. 400ALO.

ORNL PHOTO-2396-88

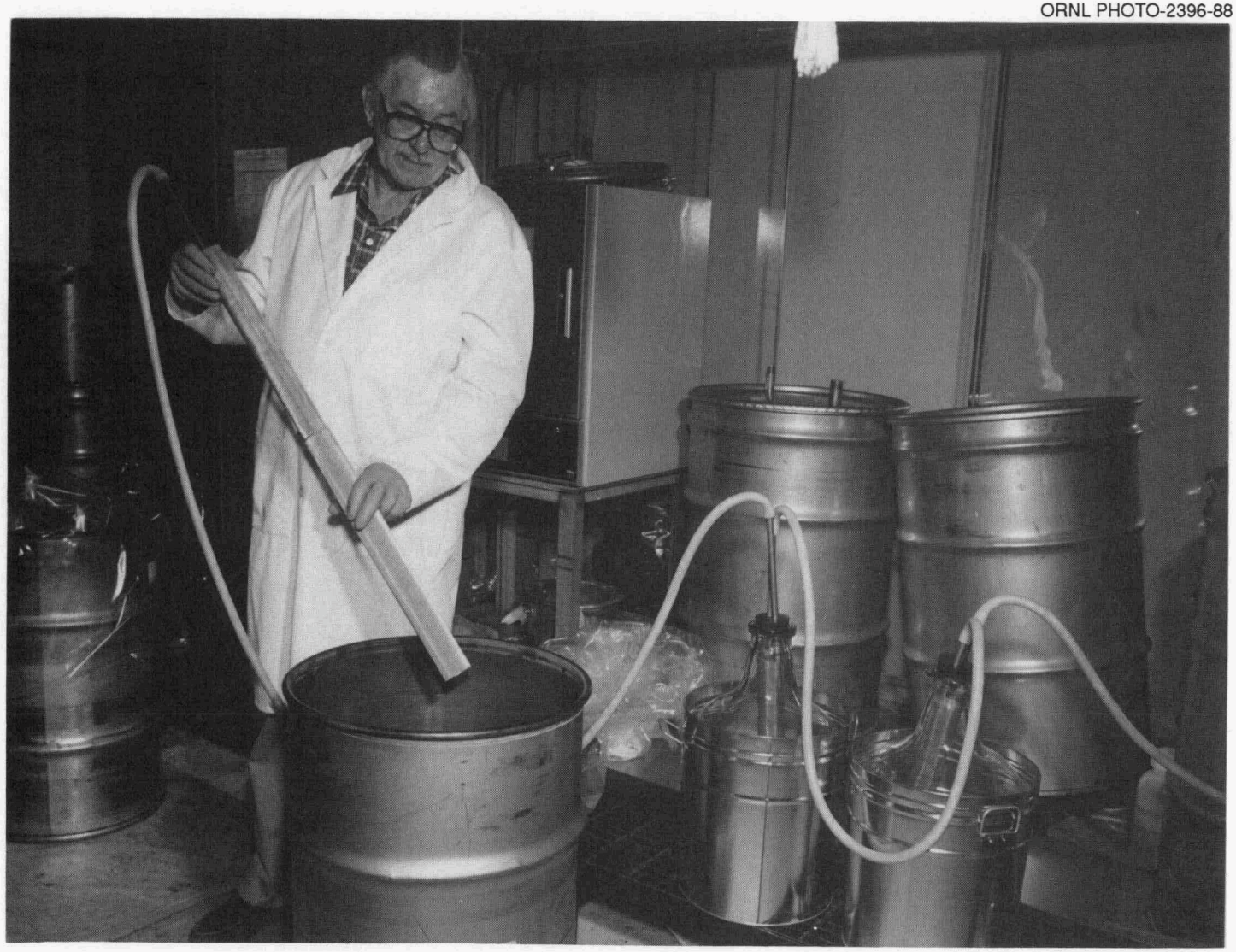

Fig. D.5. Vacuum filtration apparatus used to separate leachate from solids after leaching tests.

ORNL PHOTO-2398-88

Fig. D.6. Method for removing oily material from leachate to prepare leachate for disposal.

level of the main hot drain line from Building 4501 to the WC-10 Tank Farm.

In the other walk-in hood, there is a drying oven[h] for drying small volumes of laboratory-generated wastes after leaching. Drying is used to prepare wastes for disposal because solid wastes must contain no free liquid when sent to the SWSA-6 burial grounds. After oven and/or air-drying, solids from several 30-gal-scale leach tests are mixed with bentonite or clay[i] in 55-gal-size disposal drums. Either of these adsorbents will remove any residual free liquid. A nearby laboratory is used as a temporary storage area for the drums of solid waste generated before shipment to SWSA-6. While in storage, the drums are left open, but covered with cheesecloth, to allow as much water as possible to vaporize (Fig. D.7). This is fairly effective because the temperature in that room typically is 29 ± 2°C.

D.2 PROCEDURE FOR 30-GAL-SIZE LEACH TESTS

Waste-stream samples for the leaching tests were prepackaged in plastic bags in 55-gal-size drums at the Y-12 Plant. Each package contained from 2.3 to 5.4 kg waste. The packages were gamma counted to determine the amount of depleted uranium present. Counting was done in a large-scale analytical facility[j] at the Y-12 Plant used to assay truckloads of waste. The counter contains a pair of NaI(Tl) detectors. Each package was placed midway between the detectors (detectors are positioned ~4.6 m apart). A few of the bags were counted three separate times after the contents were physically rearranged and oriented differently in relation to the detectors. Replicate counts showed good agreement. The uranium content for each bag was determined by comparing the gamma count with a curve based on counting known depleted uranium standards. The standards were counted in a geometry similar to the

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[h]GCA Corp precision model 27, capacity 0.14 m^3.

[i]Wyoming Bentonite or AGGUGEL-150 clay.

[j]Personal communication from J. T. Foust, Y-12 Plant, to J. L. Collins (November 1987).

ORNL PHOTO-2400-88

Fig. D.7. Method of drying experimental solid waste.

waste packages. Only waste packages with ≥50 g uranium were used in the leach tests. For the packages that contained 50 to 100 g uranium and were recounted as described above, the triplicate uranium values (gamma counts) had a standard deviation of ± 8%; for packages that contained >200 g uranium, the triplicate standard deviation was ± 3%. However, there were large differences in counts for packages containing as little as 15 g uranium.

The stainless steel drums (and drum lids) (see Fig. D.8) employed in the leaching tests were coated on the inside surfaces with Halar.[k] The Halar coating was applied at the Rubber Shop at the Y-12 Plant after the stainless steel surfaces were cleaned and sandblasted at ORNL. Before being used in leach tests, the drums and lids were cleaned as follows: (1) they were brushed several times with solutions of Mr. Clean® all-purpose cleaner; (2) they were hosed several times with building distilled water and then deionized water; (3) after hosing, the drums were partially filled with deionized water and shaken vigorously, with this being repeated several times; (4) rinsing was continued until there was little change in the conductivity of the deionized water after washing; and (5) finally, the drums were air-dried for several days and covered with clean plastic bags until used. The gasket[l] used in the drum-lid seal was made of 0.95-cm neoprene tubing joined at the ends with Zip Grip® glue. The gasket was attached to the lid with Plybond® glue in a way that allowed no contact with the leachate during a test.

At the start of a leaching test, the 55-gal shipping drum containing the waste packages selected for a given leach test was opened. The waste components were closely examined as to content and composition and photographed. This examination was done in one of the walk-in radiochemical hoods, and the waste was placed into a weighed, cleaned, Halar-coated stainless steel 30-gal drum. Larger items, such as sheets of paper or plastic, gloves, beverage cups, aluminum cans, etc., were cut into smaller pieces. Afterwards, the gross weight of the

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[k]Halar is a fluoropolymer resin, Ausimont, Inc.

[l]These gaskets were specially made by the Green Door Shop, ORNL.

ORNL PHOTO-0443-88

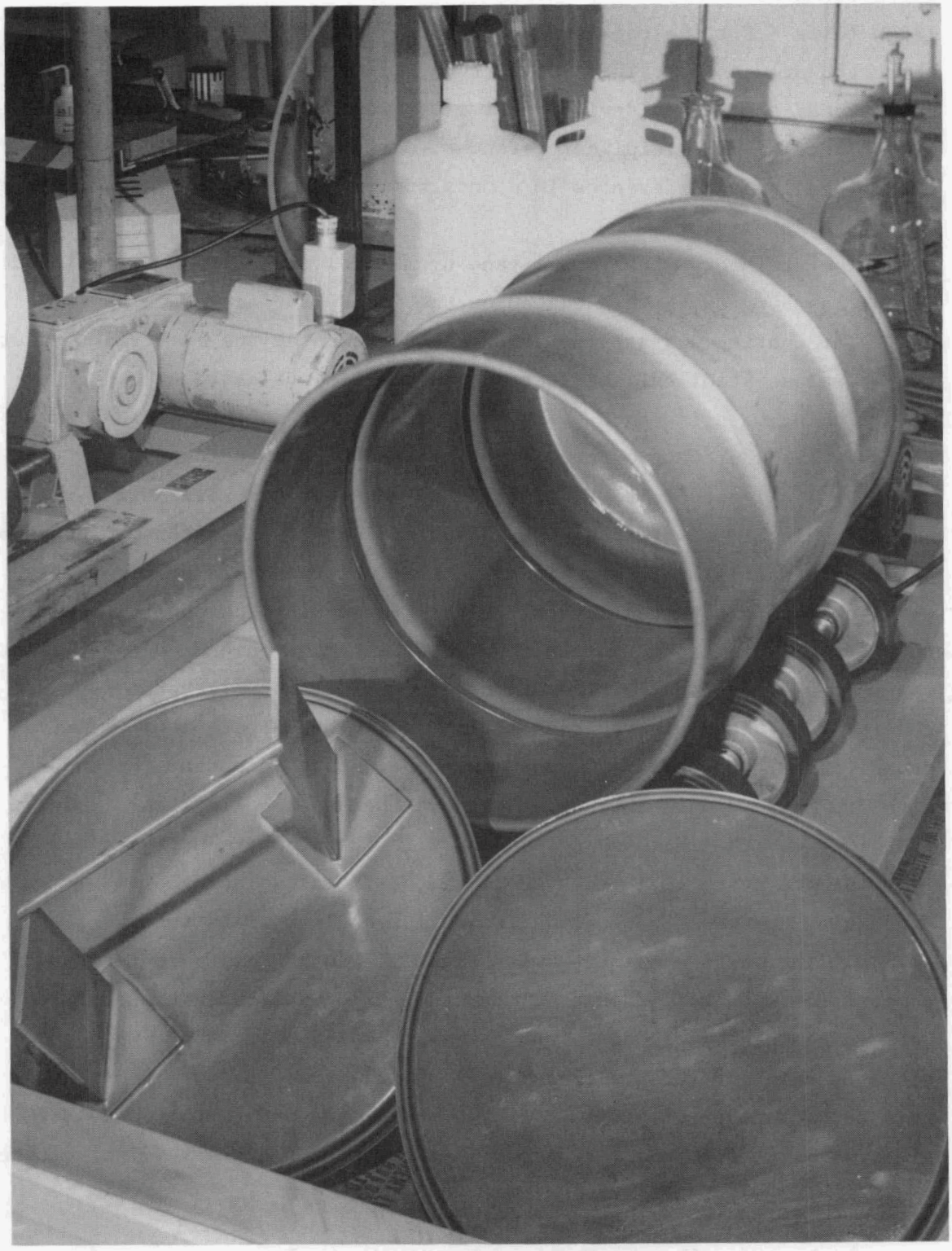

Fig. D.8. Teflon®-lined 30-gal drum and lids used in experiments.

drum was measured to determine the weight of the waste. Once the waste weight was determined, an appropriate weight of leachant was added to the drum while on the electronic scale. The drum was then removed from the scale and sealed. About 50 lb of torque was applied to the sealing bolt. Before being placed on the drum rotator, the drum was inverted with the drum handler and visually checked for leaks. (In all the leach tests conducted, only one minor leak occurred.) After leak-checking, the drum was placed on the drum rotator, the leaching started, and the date and time recorded.

Two types of leaching protocol were followed – sequential and batch. In the sequential protocol, the leachate was removed and replaced with fresh leachant at selected times (once each day for 4 d and then after 3 d for the last contact). The volume of leachant was geometrically increased to yield the following series of L/S ratios: 2, 4, 8, 16, and 32 for the five replacement times. This sequence yielded a cumulative L/S ratio of 2, 6, 14, 30, and 62, respectively, for the sequential leach protocol. The batch leach protocol involved only a single contact under the selected test parameters of 2:1 or 20:1 L/S. The batch tests were sampled at 1, 2, 3, 4, and 7 d. For the four bulk wastes (production trash, combined waste, mixed metal chips, and air filters), the test matrix (batch contacts at 2:1 and 20:1 L/S and one sequential leach for both synthetic groundwater and synthetic landfill leachate) required 24 30-gal-size experiments and generated 120 leachate samples for uranium analysis.

Batch tests were always started on Monday and analytical and archive samples of leachate taken each weekday (Tuesday through Friday) and on the following Monday. After each leach period, the drum was removed from the drum rotator and the solids were allowed to settle for 1 to 2 h before sampling. The sampling time marked the end of a given leaching period and the start of the next leaching period. Samples of leachate were removed with a clean stainless steel ladle and poured into cleaned 1-L or 2-L polyethylene bottles and then filtered. Filtration was through a 0.6- to 0.8-μm glass microfiber filter,[m] housed in a

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[m]EPM2000, Whatman, Ltd.

cleaned 1.5-L Teflon®-coated filter assembly,[n] into a clean, weighed polyethylene bottle (see Fig. D.3). Sometimes the leachate could be filtered without applying air pressure; at other times, up to 50 psi air pressure was required to force the filtrate through the filter. When needed, pressure was applied slowly in incremental steps of 10 psi. After filtering, the solids removed from the analytical and archive samples were put back into the leaching drum along with fresh leachant equal to the weight of leachate which was removed. The conductivity, pH, and temperature of the filtered leachate samples were measured; in a few tests, Eh measurements were also made. Leachate samples were stored in a refrigerator at ~4°C.

All the steps described above for the batch tests were also employed in the sequential leach tests. However, after each leach period and the removal of the analytical and archive samples, the major portion of the leachate was removed by vacuum filtration as described in Sect. D.1. The filtration apparatus that was used was different in that two layers of stainless steel screen was used to make the filter chamber. The outer and inner layers were made of 200 × 200 (74-μm openings) and 50 × 50 (297-μm openings) screens, respectively. The selected weight of fresh leachant was then added and the sequential tests continued.

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[n]Catalog No. YT30142W, Millipore Corp.

APPENDIX E
LABORATORY PROCEDURE FOR 2-L-SIZE LEACH TESTS

The procedure for the 2-L-size leaching tests was consistent with the EPA TCLP. Only the uranium oxide powder from the UCOF was leached by this method. First, the as-received sample of uranium oxide powder was blended to ensure homogeneity. This was done using a mixer[a] with a stainless steel mixing bowl and agitator. Three portions of the blended sample were taken for analysis from different positions in the storage bottle to demonstrate the degree of homogeneity. The results were 854.93, 845.85, and 845.70 mg U/g sample, which showed good blending and the ensured preparation of replicate sample aliquots.

The leachants used were either synthetic landfill or synthetic groundwater (see Sect. 7.2). Three different L/S ratios were tested:

50/1 (2000 g leachant and 40 g solid),
20/1 (1700 g leachant and 85 g solid), and
2/1 (1600 g leachant and 800 g solid).

Wide-mouth (100-mm) 2-L borosilicate bottles with Teflon-lined lids[b] were used as extraction vessels in these tests. The procedure for cleaning these bottles and lids was as follows: they were brushed with a solution of Mr. Clean all-purpose cleaner, rinsed several times with deionized water, rinsed with ~3 N HNO_3, and thoroughly rinsed again with deionized water. Afterward, they were filled with deionized water and shaken vigorously. If there was no significant change in the conductivity of the deionized water, the bottles were considered clean. Finally, they were air dried for several days before use.

A calibrated[c] balance[d] was used for all weighing. Periodically, a standard weight was measured to confirm the accuracy of the balance. In each test, the order of measurement was (1) borosilicate bottle and lid, (2) leachant, and (3) uranium oxide powder. Both the leachant and solid

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[a]Hobart Corp., model N 50.
[b]Associated Design and Manufacturing Co., model 3740-WGB.
[c]By ORNL Balance Shop according to ORNL QA procedure.
[d]Sybron Digimetric

were preweighed before addition to the bottle, which served to check the measured weights and to help minimize dusting of the powder.

After weighing, the bottles were tightly sealed and leak checked by inversion. Leaching was started and the time recorded. (Typically, room temperature was 25 ± 1°C.) A rotary device[e] rotated the bottles end-over-end at a rate of 30 rpm. Two types of leaching protocol were followed: batch contact or sequential leachant additions. For either protocol, analytical samples were taken daily except on weekends. After a predetermined leaching period (minimum of ~20 h), the bottle was removed from the rotary extractor, the time recorded, and the solids were allowed to settle for 2 h.

In the batch tests, ~50 mL of leachate was removed for analytical analyses by pipetting, and the sampling time was recorded. An equivalent amount of fresh leachant was added back to the extraction bottle to maintain the desired L/S ratio, and the gross weight was rechecked and recorded. The removed leachate was filtered through a thoroughly cleaned glass suction funnel through 0.6- to 0.8-μm glass microfiber filters.[f] Only a trace of solid was present in these leachate samples as decanted, and filtration easily produced a clear sample for analysis. The end of the leaching period was considered to be the sampling time. This time period included both the rotary leaching and the 2-h settling times. The sampling time was also considered the start time for the next leaching period. The filtrate was divided into three equal samples: two for analyses and one archive sample. Conductivity, pH, and temperature measurements were made, and the samples were stored in a refrigerator at ~4°C. The samples were transported to Analytical Chemistry Division for analyses as soon as possible.

As in the batch tests, the leachates in the sequential leach tests were allowed to settle for ~2 h after the rotary leaching period. However, in these tests all the clear liquid above the solids was

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[e]Associated Design and Manufacturing Co., model 3740-6-BRE.

[f]Whatman Limited, No. EPM 2000.

decanted and filtered through the 0.6- to 0.8-μm glass fiber filter, for these samples housed in a thoroughly cleaned Teflon-coated filter assembly.[g] Again, as in the batch test, very little of the solids was removed from the extraction bottle during the decanting step. While the leachate was filtering, the extraction bottle with lid was reweighed to determine the amount of leachate removed. As a double check, the weight of the filtrate was also weighed later. As quickly as possible, fresh leachant was added to the extraction bottle to replace the removed leachate to maintain the desired L/S ratio, and the next leaching period was started. Larger analytical samples were taken in these tests (~200 mL), and conductivity, pH, and temperature measurements were made. The samples were subsequently stored at ~4°C. The samples were transported to Analytical Chemistry Division for analyses as soon as possible.

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[g]Millipore Corp.

APPENDIX F
DISCUSSION OF THE CHEMISTRY OF URANIUM PERTINENT TO Y-12 PLANT WASTES CONTAMINATED WITH DEPLETED URANIUM

The discussion of the chemistry of uranium in this section is intended to aid in the interpretation and understanding of the uranium leaching data resulting from the laboratory leaching tests and to help guide the future field lysimeter experiments and evaluation of disposal options.

The discussion accents the chemistry of the uranium(VI) and uranium(IV) solution species and the corresponding solid compounds, including fractional- or mixed-valence solids. The discussion emphasizes temperature, pH, and redox conditions relevant to Y-12 Plant waste disposal or treatment situations. The leachants (solutions which may contact disposed wastes and mobilize uranium) considered in the discussion are either natural or synthetic groundwaters (dilute Ca, Mg, Na, K, Cl, Si solutions at near-neutral pH) and a synthetic landfill leachate (0.1 M acetic acid-sodium acetate buffer solution at pH 4.9 as specified in the proposed EPA Toxicity Characteristic Leach Procedure[1]) which is typical or representative of the solution resulting from biodegradation of organic wastes in landfills. Groundwaters may be the leachant in monodisposal situations for Y-12 Plant wastes while, the synthetic landfill leachate may simulate codisposal situations for Y-12 Plant wastes involving biodegradable materials. The discussion in this section deals primarily with the generally oxidizing redox conditions and ambient temperatures which exist in solution in near-surface disposal situations. Because the uranium-containing solids in the Y-12 Plant wastes may range from uranium metal to the higher oxides, solid phases from uranium(0) to uranium(VI) are addressed.

Several excellent extended critical reviews or evaluations of various aspects of uranium chemistry have been published in recent years, and this discussion has drawn heavily on five of these

articles.* A thorough summary of the information on solution species for uranium(VI) and uranium(IV) for the system uranium–oxygen–water, including hydrolysis products and solubility values, is given in Baes and Mesmer.[2] The solubility of uranium(VI) oxide at near–neutral pH was still uncertain at the time of the Baes and Mesmer study, and a more recent publication by Krupka et al.[3] contains the best experimental data for uranium(VI) oxide solubility as a function of pH. Langmuir[4] has published an excellent review of the groundwater chemistry of uranium relevant to environmental mobility and ore formation. Lemire and Tremaine[5] have published an exhaustive compilation of the relevant thermochemical data for uranium. An extensive review and reanalysis of the information for the system uranium–oxygen–water has been published by Smith et al.[6]

F.1 THE SYSTEM URANIUM-OXYGEN (U-O)

The discussion in this section is principally drawn from the paper by Smith et al. That publication is a critical review of the literature for this system and cites 269 references. Smith et al. state that despite the many investigations completed over decades, there are still U–O compositional ranges where the chemical behavior is not unequivocally understood, and many reported phases are as yet unverified. A summary of the U–O composition range that is of interest to Y–12 waste disposal and treatment problems is given in Figs. 2 and 4 and Table I of Smith et al.

It is important to recognize that the chemistry of the U–O system is unusually complex, and this complexity, in turn, confounds the analysis and understanding of experimental data and/or the prediction of

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*Copies of these publications can be obtained from the ORNL Waste Management Document Library, 4500N, MS–6235 (4–5197).

expected behavior. This complexity results from the many three-dimensional arrangements that can be produced when stacking uranium and oxygen atoms. Further, the crystal structures obtained are capable of maintaining electric neutrality over extended ranges of nonstoichiometric composition, and, therefore, many U-O compounds are stable over a wide span of composition from oxygen-deficient to oxygen-excessive. As a result of these properties, the phases observed experimentally are dependent on not only the U-O ratio, but also the temperature, oxygen fugacity, and total system pressure.

$\underline{UO_4}$. The compound UO_4 contains uranium in the 8+ valence. This compound can be prepared by precipitation from solution as a hydrated oxide in the presence of H_2O_2 but is not obtained by heating U-O mixtures in air. This compound is not relevant to the issues at hand and will not be discussed further.

$\underline{UO_3}$. The compound UO_3 contains uranium in the 6+ valence. At least 10 UO_3 phases and crystal structures have been reported. Two additional UO_{3-x} phases also have been described. Uranium(VI) is the most highly oxidized form of uranium normally observed under environmental conditions, and the solution species of uranium(VI) are the most mobile forms of uranium due to their appreciable solubility (see discussion below). Gamma-UO_3 (the form stable in air) exists from room temperature up to ~600°C; above that temperature, it decomposes to U_3O_8. In the presence of water, however, anhydrous UO_3 is not stable, as discussed below. Because gamma-UO_3 can be formed from uranium metal or lower oxides by air oxidation only below 600°C, low-temperature solid-phase oxidation reactions often are slow, and UO_3 may be thermodynamically unstable in the presence of water, gamma-UO_3 probably is of limited importance in considering uranium behavior in environmental systems.

$\underline{U_3O_8\ (UO_{2.67})}$. The compound U_3O_8 can be considered as a mixed oxide $2(UO_3)\cdot UO_2$ or as the nonstoichiometric compound $UO_{2.67}$ having a formal uranium valence of 5.33+. Many phases and crystal structures having compositions from $UO_{2.67+x}$ to $UO_{2.67}$ and $UO_{2.67-x}$ (where x = -0.06 to +0.25) have been reported (14 are cited in Smith et al.). U_3O_8 phases are stable from room temperature to ~1100°C and are the usual compounds

formed by high-temperature oxidation or ignition of uranium metal or lower oxides in an excess of air. Although U_3O_8 phases may not be thermodynamically stable in the presence of water, as discussed below, experience shows that they may be only slowly converted to other uranium oxides. Understanding the chemistry of U_3O_8 phases is important to environmental applications involving Y-12 Plant wastes because these phases are commonly present in uranium metal or lower-valence uranium oxide-containing wastes which have been heated or ignited. It is less clear if U_3O_8 phases would be readily formed by slow room-temperature oxidation of uranium metal or lower oxide wastes.

U_4O_9 ($UO_{2.25}$). The compound U_4O_9 can be considered as the mixed oxide $UO_3 \cdot 3UO_2$ or as the nonstoichiometric compound $UO_{2.25}$ having a formal uranium valence of 4.5+. Three phases and crystal structures are cited in Smith et al. Some phases are stable from room temperature to ~1100°C. As with U_3O_8, these phases may not be thermodynamically stable in the presence of water. Because U_4O_9 phases cover a broad region of the U-O phase diagram, it would be expected that this compound would be a product of the oxidation or ignition of uranium metal or lower oxides when the air supply (oxygen fugacity) is restricted.

UO_2. UO_2 is one of the best characterized and most stable of the uranium oxides. It occurs widely in nature as the mineral uraninite and, of course, is the oxide composition chosen for LWR reactor fuel pellets. In UO_2, the uranium has a valence of 4+. In addition to the stoichiometric-phase UO_2, variable-composition, oxygen-deficient phases (UO_{2-x}) and oxygen-excess phases (UO_{2+x}) are known. UO_2 has a single cubic crystal structure and is very stable (melting point of 2860°C). The compound UO_2 covers a broad region of the U-O phase diagram and would be expected to be formed by the oxidation or ignition of uranium metal under conditions such that the air supply is severely restricted and higher oxides such as U_3O_8 can not form. UO_2 prepared at high temperature may approach theoretical density and may be very unreactive toward oxidants such as air or water; thus, its application as a fuel form for LWR reactors. UO_2 is stable in the presence of water under reducing redox conditions. Knowledge of the chemistry of UO_2 is

important in understanding the behavior of uranium-containing wastes under reducing or, at least, nonoxidizing environmental conditions.

UO. The oxide UO has been reported, but Smith et al. state that its existence is doubtful. It is not further discussed.

F.2 THE SYSTEM URANIUM-OXYGEN-WATER

F.2.1 Solid Phases

The discussion in this section also is drawn primarily from Smith et al. Only one hydrated U-O compound and one anhydrous oxide are described as equilibrium solid phases in the system uranium-oxygen-water. Knowledge of the reactions involving these two solids is of importance to (1) understanding the reactions that may occur during waste disposal or treatment options and (2) quantifying the mobility of uranium in groundwater or landfill leachate systems.

Schoepite ($UO_3 \cdot H_2O$). The only hydrated U-O compound containing uranium in the 6+ valence is $UO_3 \cdot H_2O$. This compound may occur naturally as the mineral schoepite or may be prepared synthetically. Eight forms or crystal structures of schoepite have been reported. Under oxidizing redox conditions involving aqueous solutions which do not contain species of other elements capable of forming complexes or other uranium(VI)-containing compounds (see discussion below), schoepite would be the equilibrium solid phase controlling the uranium(VI) solubility.

Uraninite (UO_2 to UO_{2+x}). Uraninite, containing uranium in the 4+ valence, is found widely in nature. The compound also has been identified as the mineral pitchblende when it is poorly crystallized. Hydrated forms have been reported but are not well documented (Smith et al.). Uraninite would be the equilibrium solid phase controlling the solubility of uranium(IV) under strongly reducing redox conditions. Because UO_2 solids may be very resistant to oxidation by air or water at ambient temperatures, UO_2 may also exist for long periods of time under oxidizing environmental conditions, although it would not be the equilibrium solid phase under such conditions.

F.2.2 Solution Species

This discussion is based primarily on information in Baes and Mesmer,[2] and in Langmuir[4]. In this section, only species (solute or dissolved solution forms of uranium) containing uranium, oxygen, and hydrogen are considered. The solution chemistry of uranium becomes considerably more complex when some other elements or ions are present in solution, and that situation is addressed in a following section.

Uranium(VI). In the system uranium-oxygen-water, the species UO_2^{2+} is the simplest ion formed that contains uranium(VI). However, UO_2^{2+} may undergo both hydrolysis and condensation reactions to form other species. The species formed are primarily dependent on the total uranium concentration and the system pH. In the pH range of interest to environmental waste disposal concerns (pH of ~5 to 8), the following species (Fig. 9.3 and Table 9.5 of Baes and Mesmer) form (left to right) at increasing uranium concentrations and/or higher pH:

$$UO_2^{2+} \qquad UO_2(OH)^+ \qquad (UO_2)_2(OH)_2^{2+} \qquad (UO_2)_3(OH)_5^+$$

The condensed species are of importance in considering waste disposal or treatment situations. For example, at pH 6 or higher and at either high (0.1 M U) or low (10^{-5} M U) uranium concentrations, $(UO_2)_3(OH)_5^+$ is the dominant species (Baes and Mesmer). Langmuir also states that in pure water at pH 6 and at 10^{-6} M total uranium, the dominant species is $(UO_2)_3(OH)_5^+$, while at 10^{-8} M total uranium, the species UO_2OH^+ becomes dominant. At 10^{-8} M total uranium, there is too little uranium present to favor condensation reactions at pH 6, and thus the species UO_2OH^+ predominates.

Uranium(IV). The solubility of uranium(IV) species [assuming the redox condition of the system is reducing enough (low system Eh) to conserve uranium(IV) species without oxidation to uranium(VI) species] is much lower than that of uranium(VI) species at near-neutral pH, and this lower solubility limits the consideration of relevant species (Fig. 9.3 of Baes and Mesmer) to only the following (left to right with increasing pH) as being important under environmental conditions:

$$U(OH)_3^+ \qquad U(OH)_4 \qquad U(OH)_5^-$$

At near-neutral pH, the dominant solution species is the uncharged molecule $U(OH)_4$. The existence of the anion $U(OH)_5^-$ has recently been questioned,[7] based on a careful remeasurement of the solubility of U(IV) species at near-neutral pH.

F.3 SOLUTION SPECIES INVOLVING ADDITIONAL ELEMENTS OR IONS

Uranium(VI) and, to a lesser extent, uranium(IV) are capable of forming a wide range of complexes with certain anions in solution. The presence of such complexes may increase uranium solubility. Conversely, reaction of uranium with some elements or ions may result in the formation of new, lower-solubility, equilibrium solid phases. It is beyond the scope of this paper to present an extensive discussion of these complexes and solids; however, several solution species are important in controlling the solubility or mobility of uranium in groundwater systems, and these are described briefly below. Much of this discussion is drawn from the review by Langmuir. Detailed calculation of the uranium speciation and solubility and of the equilibrium solid phases, as a function of groundwater composition and geochemical parameters such as pH and Eh, can be made using geochemical computer codes such as EQ3/EQ6[8] or MINTEQ.[9,10]

F.3.1 Uranium(VI) Complexes With Anions

The discussion of uranium(VI) complexes in the following sections is ranked according to the strength of the formation constants: phosphate complexes are most stable, and fluoride complexes are the least stable of those discussed.

Uranium(VI)-Phosphate Complexes. Phosphate is frequently present at low concentrations in most groundwaters, primarily as the biphosphate anion HPO_4^{2-}. Langmuir reports the formation of the very stable uranyl biphosphate complex $UO_2(HPO_4)_2^{2-}$ at solution pHs ≥ 5. The formation constant for $UO_2(HPO_4)_2^{2-}$ is greater than for any other uranium(VI) complex usually anticipated in natural groundwaters. Therefore, uranium(VI) in groundwaters would be expected to exist as this anionic complex in stoichiometric amounts equivalent to the phosphate content of

the groundwater. The equilibrium solid phase containing phosphate, UO_2HPO_4 (see below), is important when considering the solubility or mobility of uranium(VI) in groundwater due to the greatly reduced solubility of uranium(VI).

Uranium(VI)-Carbonate Complexes. Carbonate anions, CO_3^{2-}, are frequently present in alkaline groundwaters at pHs ≥ 8 due to groundwater contact with limestone or dolomite formations. Stable carbonate complexes are formed with UO_2^{2+} when CO_3^{2-} ions are present. Complexes with the bicarbonate anion, HCO_3^- (which predominates at pHs ≤ 8), either are much less stable or may not exist. According to Langmuir, at pH 5 to 6, a total uranium concentration of 10^{-8} M, and at atmospheric partial pressure of CO_2, the neutral species UO_2CO_3 predominates both in solution and as the equilibrium solid phase. At pH 7, the predominant species becomes $UO_2(CO_3)_2^{2-}$; at pH 8 or higher, $UO_2(CO_3)_3^{4-}$ becomes controlling. These carbonate complexes have important implications for uranium mobilization considerations because they can substantially increase the effective solubility of uranium (see discussion below).

Uranium(VI)-Silicate Complexes. All groundwaters contain some amount of dissolved silicate species because all soils contain a variety of silicate minerals. A number of solution species of silicate may exist, and interchange between these often is slow; therefore, that metastable silicate systems may be present. Unfortunately, this complicated silicate chemistry considerably confounds consideration of the chemistry of uranium(VI) in groundwater due to the existence of stable uranyl-silicate complexes. Langmuir identifies the species $UO_2SiO(OH)_3^+$ as an important complex in groundwaters in the pH range of 5 to 7.

Uranium(VI)-Fluoride Complexes. Uranium(VI) also forms the complex UO_2F^+ under acidic conditions of pH <5 (Langmuir). This complex may be of less importance in considering the chemistry of Y-12 wastes in ground- waters unless the wastes also contain appreciable amounts of soluble fluoride compounds.

Combination of Uranium(VI) Complexes in Typical Groundwater. When uranium(VI) is dissolved in typical groundwaters containing various concentrations of these complex-forming anions (most groundwaters contain

at least some concentration of HPO_4^{2-}, CO_3^{2-}, $H_3SiO_4^-$, and F^-), the final concentration of the uranium-containing species is governed by the concentrations of all the constituents as well as the pH. If all the concentrations and the pH are known, geochemical computer codes can be used to calculate the equilibrium uranium speciation. Langmuir has calculated the dominant species for a typical groundwater as a function of pH (Fig. 11 of Langmuir) at low uranium concentrations. Three species predominate in this situation: UO_2F^+ at pHs <5, $UO_2(HPO_4)_2^{2-}$ at pH 5 to 8, and $UO_2(CO_3)_3^{4-}$ at pHs >8. Other species are less important in understanding the chemistry of uranium in groundwater due to lower stability constants or pH ranges of instability.

At higher uranium concentrations, if the amount of the important complexing anions present in the groundwater (F^-, HPO_4^{2-}, and CO_3^{2-}) become consumed, any remaining uranium would then be present as the condensed hydrolysis species UO_2OH^+ at low concentrations or as $(UO_2)_3(OH)_5^+$ at high concentrations.

In considering the chemistry of uranium in waste leachates, it is important to at least qualitatively understand which combination of these species may be present in the solution under consideration. Only then will it be possible to predict the behavior of uranium in the system under consideration.

F.3.2 Uranium(VI) Complexes With Cations

No cation-cation species involving uranyl ions are expected to exist in groundwater solutions.

F.4 URANIUM OXIDE DISSOLUTION REACTIONS

F.4.1 Dissolution of U_3O_8

The dissolution of U_3O_8 in the absence of an oxidant can be considered, for the purposes of discussion, to consist of a number of hypothetical sequential reactions. These are:

(1) Hydrolysis and disproportionation to form schoepite and uraninite –

$$U_3O_{8(solid)} + 2H_2O = 2(UO_3 \cdot H_2O)_{(solid)} + UO_{2(solid)}.$$

(2) Dissolution of the schoepite –

$$UO_3 \cdot H_2O_{(solid)} + 2H_2O = UO_2^{2+} + 3H_2O.$$

(3) Hydrolysis of the uranyl ion, –

$$UO_2^{2+} + H_2O = UO_2OH^+ + H^+.$$

(4) Condensation to the trimeric species –

$$3UO_2OH^+ + 2H_2O = (UO_2)_3(OH)_5^+ + 2H^+.$$

Thus, the overall reaction for the dissolution of U_3O_8 in the absence of an oxidant becomes:

$$3U_3O_{8(solid)} + 2H^+ + 4H_2O = 2(UO_2)_3(OH)_5^+ + 3UO_{2(solid)}.$$

In the above equation, it was assumed that the total concentration of uranium was great enough so that the solubility of uranium(IV) species was insignificant and the uraninite was not oxidized. If the dissolution system contains sufficient oxidant (represented here as O_2) to oxidize the UO_2 portion of the U_3O_8, then the overall reaction becomes:

$$2U_3O_{8(solid)} + 2H^+ + O_2 + 4H_2O = 2(UO_2)_3(OH)_5^+.$$

It is interesting to note that for either the dissolution or oxidation–dissolution reactions, relatively small quantities of acid are consumed during the dissolution process. Therefore, the dissolution of relatively small amounts of uranium from U_3O_8–containing wastes may not be expected to cause a major shift of the groundwater pH to more alkaline values unless the groundwater is very poorly buffered.

F.4.2 Dissolution of UO_2

Consideration of the dissolution of appreciable amounts of uranium from UO_2–containing wastes assumes an oxidation reaction because the solubility of uranium(IV) species (see below) is very low. In the presence of an oxidant (represented here as O_2), the overall reaction is:

$$6UO_{2(solid)} + 3O_2 + 6H_2O = 2(UO_2)_3(OH)_5^+ + 2OH^- .$$

While no acid is consumed in this reaction, hydroxide is formed during the oxidation step and the mixture may become more basic as a result of the oxidation-dissolution of UO_2.

F.5 URANIUM SOLUBILITY LIMITS

The following brief qualitative discussion of uranium solubility may be useful in considering the results of laboratory or field experiments involving uranium leaching.

F.5.1 Uranium(VI)

Figure 1 of the paper of Krupka et al.[3] contains the most recent data for the solubility of schoepite, $UO_3 \cdot H_2O$, in water as a function of pH. At pHs typical of landfill leachates or groundwaters (pH 5 to 7), the measured saturated solution concentration of uranium is ~10^{-3} to $10^{-3.5}$ M, or ~238 to 75 mg/L. This measured value is ~1 to 2 order-of-magnitude higher than the concentrations calculated for these pHs by Krupka et al. using the available thermodynamic data. Krupka et al. state that the calculated value is in good agreement with their experimental results. In comparing experimental with calculated solubility values for systems as complex and poorly studied as uranium(VI) at near-neutral pH, agreement to within 1 to 2 orders of magnitude probably can be considered good.

F.5.2 Uranium(IV)

Figure 9.2 of Baes and Mesmer[2] summarizes information on the solubility of UO_2 in water as a function of pH. At pH 5 to 7, the uranium solubility increases from ~10^{-12} to 10^{-11} M, or from ~2 x 10_{-7} to 2 x 10^{-6} mg/L. The principal solution species is neutral $U(OH)_4$. These are very low solubility values and serve to illustrate the relative insolubility and immobility of uranium in geologic systems under redox conditions reducing enough to form uranium(IV). A recent review by Kertes and Guillaumont[11] of both computed and experimental data for the solubility of uranium(IV) oxide in water reported that solubility values ranged from 10^{-7} to 10^{-13} M, and the calculated solubility minimum ranged

from pH 4 to 8. They concluded that the field is ripe for reinvestigation because, in addition to the uncertain solubility information, there is not even agreement as to the equilibrium solution species, such as $U(OH)_{4(solution)}$, $U(OH)_n^{4-n}$, etc. A recent paper by Parks and Pohl[7] reported a careful remeasurement of the solubility of uraninite in water as a function of pH. The measured solubility did not agree well with solubilities calculated by the computer program EQ3/EQ6. Parks and Pohl suggest that all currently used thermochemical data bases are in error for U(IV) species due to experimental errors in earlier solubility experiments involving possible oxidation to U(VI) and formation of uranyl carbonate species.

F.5.3 Carbonate-Containing Compounds of Uranium(VI)

Figure 1 of Sergeyeva et al.[12] shows the solubility of UO_2CO_3 as a function of pH at 25°C and 1 atm of CO_2. At pH 5, the uranium solubility is ~$10^{-4.5}$ M, or ~7 mg/L. This value is less than the solubility of schoepite in water at this pH due to the high p_{CO_2}. The solubility of UO_2CO_3 increases rapidly with increasing pH above pH 5 due to the formation of the soluble species $UO_2(CO_3)_2^{2-}$. At pHs of ≥8, the solution species $UO_2(CO_3)_3^{4-}$ is formed and the solubility increases still further. The uranium solubility value is, of course, a function of temperature and p_{CO_2} as well as of pH. In general, carbonate complexation may not greatly increase the solubility of uranium, relative to pure water, until the solution pH reaches ≥7.

F.5.4 Phosphate-Containing Compounds of Uranium(VI)

Estimating the solubility of uranium(VI) in the presence of phosphate is complicated by the large number of autunite solid phases which can form. [Uranium precipitates as autunite compounds $M_2(UO_2)_2(PO_4)_2$ where M can be a number of monovalent cations, such as H^+, Na^+, K^+, etc.] Langmuir has calculated the solubility of uranium for some typical groundwater concentrations of PO_4^{3-} as a function of pH (Figs. 21a and 21b of Langmuir). For the pH range of 5 to 7, uranium solubilities of ~10^{-7} to 10^{-6} M, or ~0.02 to 0.2 mg/L, can be

extrapolated from Langmuir's figures. These values are substantially lower than the values for schoepite and illustrate the reduced solubility or increased immobility of uranium in geologic systems containing appreciable levels of phosphate.

F.5.5 Other Relevant Uranium(VI) Compounds

Uranium(VI) can form soluble solution complexes and/or stable solid phases with many other elements, and the chemistry of the system under consideration rapidly becomes more complex as additional elements are involved. It is difficult to generalize about such complex systems. If the necessary thermochemical data are available, geochemical computer codes such as EQ3/EQ6 or MINTEQ can be used to calculate the equilibrium solids and the solution concentration of uranium. Unfortunately, the chemistry of uranium(VI) at near-neutral pH has not been extensively investigated and the needed information is not always available to support the calculations.

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