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AN EXPERIMENTAL SURVEY OF THE FACTORS THAT AFFECT LEACHING FROM LOW-LEVEL RADIOACTIVE WASTE FORMS

TOPICAL REPORT

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TABLE OF CONTENTS

	Page
ABSTRACT.....	xxxi
1. INTRODUCTION.....	1
1.1 Leaching Mechanisms and Long-Term Leachability.....	1
1.2 Effects of Waste Form Composition.....	2
2. FACTORS THAT AFFECT LEACHING OF LOW-LEVEL WASTE FORMS.....	3
2.1 Temperature.....	4
2.2 Ratio of the Surface Area of the Waste Form to Leachant Volume.....	5
2.3 Leachant Composition.....	5
2.4 Leachant pH.....	5
2.5 Leachant Flow Rate or Replacement Frequency.....	6
2.6 Composition of the Waste Form.....	6
2.7 Volume to Surface Area Ratio of the Waste Form.....	7
2.8 Porosity of the Waste Form.....	8
3. MATERIALS AND METHODS.....	11
3.1 Waste Form Types.....	16
3.1.1 Portland I Cement Containing Sodium Sulfate as Simulated Waste.....	16
3.1.2 Portland I Cement Containing Incinerator Ash Simulated Waste.....	16
3.1.3 Vinyl Ester-Styrene Emulsion with Aqueous Sodium Sulfate as Simulated Waste.....	17
3.1.4 Vinyl Ester-Styrene Containing Sodium Sulfate as Simulated Waste.....	17
3.1.5 Bitumen Containing Sodium Tetraborate as Simulated Waste.....	17
3.1.6 Soda-Lime Glass Containing Incinerator Ash as Simulated Waste.....	17
3.2 Sample Preparation.....	17
3.3 Leaching Tests.....	18
3.3.1 ANS 16.1 Leaching Test.....	18
3.3.2 MCC-3s Leaching Test.....	
3.3.3 MCC-4s Leaching Test.....	20

TABLE OF CONTENTS (cont.)

	Page
3.4 Analytical Methods.....	20
3.4.1 Radiochemical Analysis.....	20
3.4.2 Elemental Leachate Analysis.....	20
3.4.3 Alkalinity.....	20
3.4.4 Analysis for pH.....	20
3.4.5 Conductivity.....	20
3.4.6 SEM/EDS.....	20
4. PORTLAND TYPE I CEMENT CONTAINING SODIUM SULFATE SALT AS SIMULATED WASTE.....	21
4.1 Leaching Mechanisms.....	21
4.2 Factors that Affect Leaching.....	22
4.2.1 Temperature.....	23
4.2.2 Ratio of the Surface Area of the Waste Form to Volume of Leachant.....	30
4.2.3 Composition of the Leachant.....	30
4.2.4 pH of the Leachant.....	32
4.2.5 Leachant Flow Rate or Replacement Frequency.....	33
4.2.6 Composition of the Waste Form.....	34
4.2.7 Ratio of the Volume to Surface Area of the Waste Form.....	36
4.2.8 Effect of Surface Condition and Porosity.....	37
5. PORTLAND TYPE I CEMENT CONTAINING INCINERATOR ASH AS SIMULATED WASTE.....	71
5.1 Leaching Mechanisms.....	71
5.2 Factors that Affect Leaching.....	71
5.2.1 Temperature.....	71
5.2.2 Ratio of Waste Form Surface Area to Leachant Volume.....	75
5.2.3 Composition of the Leachant.....	75
5.2.4 pH of the Leachant.....	76
5.2.5 Leachant Flow Rate or Replacement Frequency.....	77
5.2.6 Composition of the Waste Form.....	77
5.2.7 Ratio of Volume to Surface Area in the Waste Form.....	78
5.2.8 Surface Condition and Porosity.....	79
6. VINYL ESTER-STYRENE EMULSION WITH AQUEOUS SODIUM SULFATE AS SIMULATED WASTE.....	103
6.1 Leaching Mechanisms.....	103

TABLE OF CONTENTS (cont.)

	Page
6.2 Factors that Affect Leaching.....	104
6.2.1 Temperature.....	104
6.2.2 Ratio of Leachant Volume to Waste Form Surface Area.....	105
6.2.3 Composition of the Leachant.....	105
6.2.4 pH of the Leachant.....	105
6.2.5 Effect of the Flow Rate or Replacement Frequency of the Leachant on VES Emulsion with Sodium Sulfate Solution.....	106
6.2.6 Composition of the Waste Form.....	106
6.2.7 Ratio of Volume to Surface Area of the Waste Form.....	107
6.2.8 Porosity and Surface Condition of the Waste Form.....	108
7. VINYL ESTER-STYRENE CONTAINING SODIUM SULFATE SALT AS SIMULATED WASTE.....	123
7.1 Mechanisms of Leaching.....	123
7.2 Factors that Affect Leaching.....	124
7.2.1 Temperature.....	124
7.2.2 Ratio of Waste Form Surface Area to Leachant Volume.....	124
7.2.3 Composition of the Leachant.....	125
7.2.4 pH of the Leachant.....	125
7.2.5 Flow Rate or Replacement Frequency of the Leachant.....	126
7.2.6 Composition of the Waste Form.....	126
7.2.7 Waste Form Volume to Surface Area Ratio.....	126
7.2.8 Porosity and Surface of the Waste Form.....	127
8. BITUMEN CONTAINING SODIUM TETRABORATE SALT AS SIMULATED WASTE.....	147
8.1 Leaching Mechanisms.....	147
8.2 Factors that Affect Leaching.....	148
8.2.1 Temperature.....	148
8.2.2 Surface Area of the Waste Form to Leachant Volume.....	149
8.2.3 Leachant Composition.....	149
8.2.4 pH of the Leachant.....	150
8.2.5 Flow and Replacement Frequency of the Leachant.....	151
8.2.6 Composition of the Waste Form.....	152
8.2.7 Ratio of Surface to Volume (V/S) in the Waste Form.....	153
8.2.8 Porosity and Surface Condition of the Waste Form.....	154
9. SODA-LIME GLASS CONTAINING INCINERATOR ASH AS SIMULATED WASTE.....	177

TABLE OF CONTENTS (cont.)

	Page
10. SUMMARY AND CONCLUSIONS.....	179
10.1 Prelude to Future Work.....	181
REFERENCES.....	185
APPENDIX A	
APPENDIX B	

LIST OF FIGURES

	Page
Figure 3.1 Schematic summary of waste form types listed by solidification agent, waste type and waste loading(s).....	12
Figure 4.1 Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.....	39
Figure 4.2 Linear correlation plots for Cs-137 leaching from portland I cement containing 5 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.....	39
Figure 4.3 Arrhenius plot of Cs-137 incremental leach rates from portland I cement containing 5 wt% sodium sulfate leached at 20, 40 and 50°C in deionized water.....	40
Figure 4.4 Linear correlation plots for Cs-137 leaching from pure portland I cement at 20, 30, 40, 50 and 70°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.....	40
Figure 4.5 Arrhenius plot of Cs-137 incremental leach rates from pure portland I cement leached at 20, 30, 40, 50 and 70°C in deionized water.....	41
Figure 4.6 Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20, 40 and 50°C leached in deionized water.....	41
Figure 4.7 Linear correlation plots for Sr-85 leaching from portland I cement containing 5 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.....	42
Figure 4.8 Arrhenius plot of Sr-85 incremental leach rates from portland I cement containing 5 wt% sodium sulfate leached at 20, 40 and 50°C leached in deionized water.....	42
Figure 4.9 Sodium cumulative amount (mg) leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20 and 50°C. Samples were leached in deionized water.....	43

LIST OF FIGURES (cont.)

	Page
Figure 4.10 Potassium cumulative amount (mg) leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20 and 50°C. Samples were leached in deionized water.....	43
Figure 4.11 Calcium cumulative amount (mg) leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20 and 50°C. Samples were leached in deionized water.....	44
Figure 4.12 Strontium cumulative amount (mg) leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20 and 50°C. Samples were leached in deionized water.....	44
Figure 4.13 Linear correlation plot for Sodium, Potassium and Cs-137 leaching at 20 and 50°C from portland I cement containing 5 wt% sodium sulfate. Correlations are relative to the Cs-137 data. Samples were leached in deionized water.....	45
Figure 4.14 Linear correlation plot for Strontium and Sr-85 leaching at 20 and 50°C from portland I cement containing 5 wt% sodium sulfate. Correlations are relative to the Sr-85 data. Samples were leached in deionized water.....	45
Figure 4.15 Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.....	46
Figure 4.16 Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.....	46
Figure 4.17 Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW, oxic and anoxic groundwaters at 20°C.....	47

LIST OF FIGURES (cont.)

	Page
Figure 4.18 Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.....	47
Figure 4.19 Linear correlation plots for Cs-137 leached from portland I cement containing 5 wt% sodium sulfate leached in DIW, oxic and anoxic groundwaters at 20°C. Correlations are relative to the DIW data.....	48
Figure 4.20 Linear correlation plots for Cs-137 leached from portland I cement containing 5 wt% sodium sulfate leached in DIW and DIW containing 100 ppm disodium EDTA at 20°C. Correlations are relative to the DIW data.....	48
Figure 4.21 Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW, oxic and anoxic groundwaters at 20°C.....	49
Figure 4.22 Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.....	49
Figure 4.23 Linear correlation plots for Sr-85 leached from portland I cement containing 5 wt% sodium sulfate in DIW, oxic and anoxic groundwaters. Correlations are relative to the DIW data. Samples were leached at 20°C.....	50
Figure 4.24 Linear correlation plots for Sr-85 leached from portland I cement containing 5 wt% sodium sulfate in DIW and DIW containing 100 ppm disodium EDTA at 20°C. Correlations are relative to the DIW data.....	50
Figure 4.25 Sodium cumulative amount leached (ppm) vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and oxic groundwater at 20°C.....	51
Figure 4.26 Potassium cumulative amount leached (ppm) vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and oxic groundwater at 20°C.....	51

LIST OF FIGURES (cont.)

	Page
Figure 4.27 Calcium cumulative amount leached (ppm) vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and oxic groundwater at 20°C.....	52
Figure 4.28 Strontium cumulative amount leached (ppm) vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and oxic groundwater at 20°C.....	52
Figure 4.29 Linear correlation plots for Sodium leached from portland I cement containing 5 wt% sodium sulfate in DIW and oxic groundwater at 20°C. Correlations are relative to the DIW data.....	53
Figure 4.30 Linear correlation plots for Potassium leached from portland I cement containing 5 wt% sodium sulfate in DIW and oxic groundwater at 20°C. Correlations are relative to the DIW data.....	53
Figure 4.31 Linear correlation plots for Calcium leached from portland I cement containing 5 wt% sodium sulfate in DIW and oxic groundwater at 20°C. Correlations are relative to the DIW data.....	54
Figure 4.32 Linear correlation plots for Strontium leached from portland I cement containing 5 wt% sodium sulfate in DIW and oxic groundwater at 20°C. Correlations are relative to the DIW data.....	54
Figure 4.33 Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.....	55
Figure 4.34 Linear correlation plots for Cs-137 leached from portland I cement containing 5 wt% sodium sulfate in leachants with initial pH values of 3, 4, 5, 6 and 8. Correlations are relative to the pH 6 (DIW) data. Samples were leached at 20°C.....	55
Figure 4.35 Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.....	56

LIST OF FIGURES (cont.)

	Page
Figure 4.36 Linear correlation plots for Sr-85 leached from portland I cement containing 5 wt% sodium sulfate in leachants with initial pH values of 3, 4, 5, 6 and 8. Correlations are relative to the pH 6 (DIW) data. Samples were leached at 20°C.....	56
Figure 4.37 Cs-137 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for portland I cement waste forms containing 5 wt% sodium sulfate leached at 20°C.....	57
Figure 4.38 Linear correlation plots for Cs-137 leached at 20°C using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule for portland I cement waste forms containing 5 wt% sodium sulfate.....	57
Figure 4.39 Sr-85 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for portland I cement waste forms containing 5 wt% sodium sulfate leached at 20°C.....	58
Figure 4.40 Linear correlation plots for Sr-85 leached at 20°C using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule for portland I cement waste forms containing 5 wt% sodium sulfate. Correlations are relative to the ANS 16.1 data.....	58
Figure 4.41 Portland I cement waste forms containing 5 weight % sodium sulfate. The one at left is as fabricated. The one at right was leached for 403 days in deionized water at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.....	59
Figure 4.42 Cs-137 cumulative fraction leached vs. time from portland I cement waste forms containing 5 wt% sodium sulfate and from pure portland I cement at 20°C.....	59
Figure 4.43 Linear correlation plots for Cs-137 leached at 20°C for portland I cement waste forms containing 5 wt% sodium sulfate and pure portland I cement. Correlations are relative to pure cement.....	60

LIST OF FIGURES (cont.)

	Page
Figure 4.44 Sr-85 cumulative fraction leached vs. time from portland I cement waste forms containing 5 wt% sodium sulfate and from pure portland I cement at 20°C.....	60
Figure 4.45 Linear correlation plots for Sr-85 leached at 20°C for portland I cement waste forms containing 5 wt% sodium sulfate and pure portland I cement. Correlations are relative to pure cement.....	61
Figure 4.46 Linear correlation plot for Sr-85 versus Cs-137 leaching at 20°C for pure portland I cement.....	61
Figure 4.47 Linear correlation plot for Sr-85 versus Cs-137 leaching at 20°C for portland I cement containing 5 weight % sodium sulfate.....	62
Figure 4.48 Leaching curves of cumulative release (ppm) vs. time of sodium, potassium, calcium and strontium from portland I cement containing 5 weight % sodium sulfate. Samples were leached at 20°C in deionized water.....	62
Figure 4.49 Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.61, 0.85 and 1.85. Samples were leached in deionized water at 20°C.....	63
Figure 4.50 Linear correlation plots for Cs-137 leached from portland I cement containing 5 wt% sodium sulfate at waste form volume to surface area ratios of 0.42, 0.61, 0.85 and 1.85. Correlations are relative to V/S = 0.85. Samples were leached in deionized water at 20°C.....	63
Figure 4.51 Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.61, 0.85 and 1.85. Samples were leached in deionized water at 20°C.....	64

LIST OF FIGURES (cont.)

	Page
Figure 4.52 Linear correlation plots for Sr-85 leached from portland I cement containing 5 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.61, 0.85 and 1.85. Correlations are relative to V/S = 0.85. Samples were leached in deionized water at 20°C.....	64
Figure 4.53 Outer surface of an unleached cement sample containing 5% sodium sulfate at a magnification of 400 times. This surface is indistinguishable from that of unleached pure cement.....	65
Figure 4.54 Outer surface of an unleached cement sample containing 5% sodium sulfate at a magnification of 4700 times.....	65
Figure 4.55 Outer surface of a cement sample containing 5% sodium sulfate after static leaching for 55 days at 50°C. Magnification is 400 times. Profuse crystal growth covers the surface.....	66
Figure 4.56 Outer surface of a cement sample containing 5% sodium sulfate after static leaching for 55 days at 50°C. Magnification is 1900 times.....	66
Figure 4.57 Interior of a cement sample containing 5% sodium sulfate after static leaching for 55 days at 50°C. This is a cut sample from 2 mm inside the outer edge. Note the many cracks.....	67
Figure 4.58 A bubble that after leaching was full of crystals. This was typical of voids in the sample.....	67
Figure 4.59 EDS spectrum of the outer surface of unleached cement sample containing 5% sodium sulfate. Note that s^{+11} sodium and potassium peaks are present and that sulfur is enriched compared to pure cement.....	68
Figure 4.60 EDS spectrum of one of the crystals from Figure 4.58. This spectrum is significantly different from that of the unleached cement containing sodium sulfate shown in Figure 4.59. Sulfur and aluminum are enriched while silicon is depleted relative to the unleached composition.....	68

LIST OF FIGURES (cont.)

	Page
Figure 4.61 EDS spectrum of the leached surface of cement containing 5% sodium sulfate using a large analytical area. This spectrum is identical to that in Figure 4.60 from a single crystal in a pore.....	69
Figure 4.62 EDS spectrum of the center of the leached specimen. This more closely resembles the spectrum of the unleached material, Figure 4.59, than it does the leached surface, Figure 4.60.....	69
Figure 5.1 Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash at 20, 40 and 50°C in deionized water.....	80
Figure 5.2 Linear correlation plots for Cs-137 leaching at 20, 40 and 50°C in deionized water from portland I cement containing 15 wt% incinerator ash. Correlations are relative to the 20°C data.....	80
Figure 5.3 Arrhenius plot of Cs-137 incremental leach rates from portland I cement containing 15 wt% incinerator ash leached at 20, 40 and 50°C in deionized water.....	81
Figure 5.4 Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash at 20, 40 and 50°C in deionized water.....	81
Figure 5.5 Linear correlation plots for Sr-85 leaching at 20, 40 and 50°C in deionized water from portland I cement containing 15 wt% incinerator ash. Correlations are relative to the 20°C data.....	82
Figure 5.6 Arrhenius plot of Sr-85 incremental leach rates from portland I cement containing 15 wt% incinerator ash leached at 20, 40 and 50°C in deionized water.....	82
Figure 5.7 Sodium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash at 20 and 50°C in deionized water.....	83
Figure 5.8 Potassium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash at 20 and 50°C in deionized water.....	83

LIST OF FIGURES (cont.)

	Page
Figure 5.9 Calcium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash at 20 and 50°C in deionized water.....	84
Figure 5.10 Strontium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash at 20 and 50°C in deionized water.....	84
Figure 5.11 Linear correlation plots for Sodium, Potassium and Cs-137 leaching at 20 and 50°C in deionized water from portland I cement containing 15 wt% incinerator ash. Correlations are relative to the Cs-137 data.....	85
Figure 5.12 Linear correlation plots for Strontium and Sr-85 leaching at 20 and 50°C in deionized water from portland I cement containing 15 wt% incinerator ash. Correlations are relative to the Sr-85 data.....	85
Figure 5.13 Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic groundwater at 20°C.....	86
Figure 5.14 Linear correlation plots for Cs-137 leached at 20°C from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic groundwater. Correlations are relative to the DIW data.....	86
Figure 5.15 Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic groundwater at 20°C.....	87
Figure 5.16 Linear correlation plots for Sr-85 leached at 20°C from portland I cement containing 15 wt% incinerator ash in DIW and oxic groundwater. Correlations are relative to the DIW data.....	87
Figure 5.17 Sodium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic groundwater at 20°C.....	88
Figure 5.18 Potassium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic groundwater at 20°C.....	88

LIST OF FIGURES (cont.)

	Page
Figure 5.19 Calcium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic groundwater at 20°C. incinerator ash in DIW and oxic groundwater. Correlations are relative to the DIW data.....	89
Figure 5.20 Strontium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic groundwater at 20°C.....	89
Figure 5.21 Linear correlation plots for Sodium leached at 20°C from portland I cement containing 15 wt% incinerator ash in DIW and oxic groundwater. Correlations are relative to the DIW data.....	90
Figure 5.22 Linear correlation plots for potassium leached at 20°C from Portland I cement containing 15 wt% incinerator ash in DIW and oxic groundwater. Correlations are relative to the DIW data.....	90
Figure 5.23 Linear correlation plots for Calcium leached at 20°C from portland I cement containing 15 wt% incinerator ash in DIW and oxic groundwater. Correlations are relative to the DIW data.....	91
Figure 5.24 Linear correlation plots for Strontium leached at 20°C from portland I cement containing 15 wt% incinerator ash in DIW and oxic groundwater. Correlations are relative to the DIW data.....	91
Figure 5.25 Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash leached at 20°C in leachants with initial pH values of 4, 6 and 8.....	92
Figure 5.26 Linear correlation plots for Cs-137 leached at 20°C from portland I cement containing 15 wt% incinerator ash in leachants with initial pH values of 4, 6 and 8. Correlations are relative to the pH 6 (DIW) data.....	92
Figure 5.27 Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash leached at 20°C in leachants with initial pH values of 4, 6 and 8.....	93

LIST OF FIGURES (cont.)

	Page
Figure 5.28 Linear correlation plots for Sr-85 leached at 20°C from portland I cement containing 15 wt% incinerator ash in leachants with initial pH values of 4, 6 and 8. Correlations are relative to the pH 6 (DIW) data.....	93
Figure 5.29 Cs-137 incremental leach rate vs. time from portland I cement containing 15 wt% incinerator ash comparing results of MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C.....	94
Figure 5.30 Sr-85 incremental leach rate vs. time from portland I cement containing 15 wt% incinerator ash comparing results of MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C.....	94
Figure 5.31 Portland I cement containing 15 weight % incinerator ash. The form at left is as fabricated. The one at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.....	95
Figure 5.32 Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash and from pure portland I cement at 20°C.....	95
Figure 5.33 Linear correlation plots for Cs-137 leached at 20°C for portland I cement containing 15 wt% incinerator ash and pure portland I cement. Correlations are relative to pure cement.....	96
Figure 5.34 Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash and from pure portland I cement leached in DIW at 20°C.....	96
Figure 5.35 Linear correlation plots for Sr-85 leached from portland I cement containing 15 wt% incinerator ash and from pure portland I cement. Correlations are relative to pure cement. Samples were leached in deionized water at 20°C.....	97
Figure 5.36 Linear correlation plot for Sr-85 versus Cs-137 leached from portland I cement containing 15 wt% incinerator ash in deionized water at 20°C.....	97

LIST OF FIGURES (cont.)

	Page
Figure 5.37 Leaching curves of cumulative release (ppm) vs. time for sodium, potassium, calcium and strontium from portland I cement containing 15 weight % incinerator ash. Samples were leached at 20°C in deionized water.....	98
Figure 5.38 Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash at waste form volume to surface area (V/S) ratios of 0.42, 0.61 and 0.91. Samples were leached in deionized water at 20°C.....	98
Figure 5.39 Linear correlation plots for Cs-137 leached from portland I cement containing 15 wt% incinerator ash at waste form volume to surface area (V/S) ratios of 0.42, 0.61 and 0.91. Correlations are relative to V/S = 0.91. Samples were leached in deionized water at 20°C.....	99
Figure 5.40 Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash at waste form volume to surface area (V/S) ratios of 0.42, 0.61 and 0.91. Samples were leached in deionized water at 20°C.....	99
Figure 5.41 Linear correlation plots for Sr-85 leached from portland I cement containing 15 wt% incinerator ash at waste form volume to surface area (V/S) ratios of 0.42, 0.61 and 0.91. Correlations are relative to V/S = 0.91. Samples were leached in deionized water at 20°C.....	100
Figure 5.42 The ash itself is often more porous than the cement matrix in which it is solidified.....	100
Figure 5.43 Large voids form possibly due to gas generation or differential water sorption between the cement and the ash.....	101
Figure 6.1 Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.....	109
Figure 6.2 Linear correlation plots for Cs-137 leaching from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.....	109

LIST OF FIGURES (cont.)

Page

Figure 6.3	Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.....	110
Figure 6.4	Linear correlation plots for Sr-85 leaching from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.....	110
Figure 6.5	Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.....	111
Figure 6.6	Linear correlation plots for Co-57 leaching from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.....	111
Figure 6.7	Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached in DIW and oxic groundwater at 20°C.....	112
Figure 6.8	Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached in DIW and oxic groundwater at 20°C.....	112
Figure 6.9	Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached in DIW and oxic groundwater at 20°C.....	113
Figure 6.10	Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached at 20°C in leachants with initial pH values of 4, 6 and 8.....	113
Figure 6.11	Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached at 20°C in leachants with initial pH values of 4, 6 and 8.....	114
Figure 6.12	Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached at 20°C in leachants with initial pH values of 4, 6 and 8.....	114

LIST OF FIGURES (cont.)

Page

Figure 6.13 Cs-137 incremental leach rate vs. time from VES emulsion with sodium sulfate comparing results from MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C in deionized water.....	115
Figure 6.14 Sr-85 incremental leach rate vs. time from VES emulsion with sodium sulfate comparing results from MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C in deionized water.....	115
Figure 6.15 Co-57 incremental leach rate vs. time from VES emulsion with sodium sulfate comparing results from MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C in deionized water.....	116
Figure 6.16 VES emulsion with aqueous sodium sulfate. The form at left is as fabricated. The one at right was leached for 403 days in deionized water at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.....	116
Figure 6.17 Sectioned specimen of VES emulsion with sodium sulfate solution that was leached for 100 days at 50°C showing delamination of surface.....	117
Figure 6.18 Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate and from VES emulsion with DIW. Samples were leached at 20°C in deionized water.....	117
Figure 6.19 Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate and from VES emulsion with DIW. Samples were leached at 20°C in deionized water.....	118
Figure 6.20 Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate and from VES emulsion with DIW. Samples were leached at 20°C in deionized water.....	118

LIST OF FIGURES (cont.)

	Page
Figure 6.21 Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.....	119
Figure 6.22 Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leach in deionized water at 20°C.....	119
Figure 6.23 Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.....	120
Figure 6.24 Surface of a VES emulsion sample at a magnification of 400 times. Most pores are approximately 5-10 microns in diameter.....	120
Figure 6.25 Interior section of a VES emulsion sample at a magnification of 400 times. The interior structure appears similar to that of the surface shown in Figure 6.24.....	121
Figure 6.26 Surface of a VES emulsion sample at a magnification of 1900 times. Much smaller pores are visible with diameters less than one micron.....	121
Figure 6.27 Interior section of a VES emulsion sample at a magnification of 1900 times. There is considerable saw debris, but the pores are in the same size range as those at the surface, shown in Figure 6.26.....	122
Figure 7.1 Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.....	128
Figure 7.2 Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C leached in deionized water. Initial 35 days.....	128

LIST OF FIGURES (cont.)

	Page
Figure 7.3 Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C in deionized water.....	129
Figure 7.4 Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C. leached in deionized water.....	129
Figure 7.5 Linear correlation plots for Cs-137 leaching from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data.....	130
Figure 7.6 Linear correlation plots for Sr-85 leaching from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.....	130
Figure 7.7 Linear correlation plots for Co-57 leaching from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.....	131
Figure 7.8 Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.....	131
Figure 7.9 Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.....	132
Figure 7.10 Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.....	132
Figure 7.11 Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW, oxic and anoxic groundwaters at 20°C.....	133

LIST OF FIGURES (cont.)

	Page
Figure 7.12 Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW, oxic and anoxic groundwaters at 20°C.....	133
Figure 7.13 Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW, oxic and anoxic groundwaters at 20°C.....	134
Figure 7.14 Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.....	134
Figure 7.15 Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.....	135
Figure 7.16 Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.....	135
Figure 7.17 Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.....	136
Figure 7.18 Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8. First twenty days.....	136
Figure 7.19 Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.....	137
Figure 7.20 Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.....	137
Figure 7.21 Linear correlation plots for Cs-137 leached from VES containing 40 wt% sodium sulfate in leachants with initial pH values of 3, 4, 5, 6 and 8 at 20°C. Correlations are relative to the pH 6 (DIW) data.....	138

LIST OF FIGURES (cont.)

	Page
Figure 7.22 Cs-137 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for VES waste forms containing 40 wt% sodium sulfate leached at 20°C.....	138
Figure 7.23 Sr-85 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for VES waste forms containing 40 wt% sodium sulfate leached at 20°C.....	139
Figure 7.24 Co-57 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for VES waste forms containing 40 wt% sodium sulfate leached at 20°C.....	139
Figure 7.25 Cs-137 incremental leach rate vs. time from VES containing 40 wt% sodium sulfate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.....	140
Figure 7.26 Sr-85 incremental leach rate vs. time from VES containing 40 wt% sodium sulfate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.....	140
Figure 7.27 Co-57 incremental leach rate vs. time from VES containing 40 wt% sodium sulfate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.....	141
Figure 7.28 Cs-137 cumulative fraction leached vs. time from VES containing 20, 30 and 40 wt% sodium sulfate. Samples were leached in deionized water at 20°C.....	141
Figure 7.29 Sr-85 cumulative fraction leached vs. time from VES containing 20, 30 and 40 wt% sodium sulfate. Samples were leached in deionized water at 20°C.....	142
Figure 7.30 Co-57 cumulative fraction leached vs. time from VES containing 20, 30 and 40 wt% sodium sulfate. Samples were leached in deionized water at 20°C.....	142
Figure 7.31 Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.....	143

LIST OF FIGURES (cont.)

	Page
Figure 7.32 Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.....	143
Figure 7.33 Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.....	144
Figure 7.34 Vinyl ester-styrene forms containing 40 wt% sodium sulfate. The one at left is as fabricated. The one at right was leached for 403 days in deionized water at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.....	144
Figure 7.35 Interior of a sectioned, unleached VES specimen containing 40 wt% sodium sulfate. There appears to be little contact between grains of salt.....	145
Figure 7.36 Unleached surface of a VES specimen containing 40 wt% sodium sulfate. No salt grains are visible but several open pores are evident. A leached surface is similar in appearance. Magnification is 400 times.....	145
Figure 7.37 Two grains of salt separated by VES polymer. This specimen had been leached but no obvious effect from the leaching was noted. No sodium or sulfur was detected by EDS in the polymer between the grains.....	146
Figure 8.1 Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C leached in deionized water.....	155
Figure 8.2 Linear correlation plots for Cs-137 leaching from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C. Correlations are relative to the 20 C data.....	155
Figure 8.3 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C leached in DIW.....	156

LIST OF FIGURES (cont.)

	Page
Figure 8.4 Linear correlation plots for Sr-85 leaching from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C. Correlations are relative to the 20 C data.....	156
Figure 8.5 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C leached in DIW.....	157
Figure 8.6 Linear correlation plots for Co-57 leaching from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C. Correlations are relative to the 20°C data.....	157
Figure 8.7 Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at leachant volume to waste form surface area ratios of 10, 30 and 50:1. Samples were leached in DIW at 20°C.....	158
Figure 8.8 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at leachant volume to waste form surface area ratios of 10, 30 and 50:1. Samples were leached in DIW at 20°C.....	158
Figure 8.9 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at leachant volume to waste form surface area ratios of 10, 30 and 50:1. Samples were leached in DIW at 20°C.....	159
Figure 8.10 Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW, oxic and anoxic groundwaters at 20°C.....	159
Figure 8.11 Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.....	160
Figure 8.12 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW, oxic and anoxic groundwaters at 20°C.....	160

LIST OF FIGURES (cont.)

	Page
Figure 8.13 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.....	161
Figure 8.14 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW, oxic and anoxic groundwaters at 20°C.....	161
Figure 8.15 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.....	162
Figure 8.16 Linear correlation plots for Co-57 leached from bitumen containing 40 wt% sodium tetraborate in DIW, oxic and anoxic groundwaters. Correlations are relative to the DIW data.....	162
Figure 8.17 Linear correlation plots for Sr-85 leached from bitumen containing 40 wt% sodium tetraborate in DIW and DIW containing 100 ppm disodium EDTA. Correlations are relative to the DIW data.....	163
Figure 8.18 Sodium, Boron cumulative amounts leached (ppm) vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW and oxic groundwater at 20°C.....	163
Figure 8.19 Linear correlation plots for Sodium, Boron and Cs-137 leached from bitumen containing 40 wt% sodium tetraborate in DIW and oxic groundwater at 20°C. Correlations are relative to the data for Cs-137 leached in DIW.....	164
Figure 8.20 Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in leachants with initial pH values of 4, 6 and 8 at 20°C.....	164
Figure 8.21 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in leachants with initial pH values of 4, 6 and 8 at 20°C.....	165

LIST OF FIGURES (cont.)

	Page
Figure 8.22 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate in leachants with initial pH values of 4, 6 and 8 at 20°C.....	165
Figure 8.23 Linear correlation plots for Co-57 leached from bitumen containing 40 wt% sodium tetraborate in leachants with initial pH values of 4, 6 and 8. Correlations are relative to the pH 6 (DIW) data.....	166
Figure 8.24 Cs-137 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for bitumen waste forms containing 40 wt% sodium tetraborate leached at 20°C.....	166
Figure 8.25 Linear correlation plots for Cs-137 leached from bitumen waste forms containing 40 wt% sodium tetraborate using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule. Correlations are relative to the ANS 16.1 data.....	167
Figure 8.26 Cs-137 incremental leach rate vs. time from bitumen waste forms containing 40 wt% sodium tetraborate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.....	167
Figure 8.27 Sr-85 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for bitumen waste forms containing 40 wt% sodium tetraborate leached at 20°C.....	168
Figure 8.28 Linear correlation plots for Sr-85 leached from bitumen waste forms containing 40 wt% sodium tetraborate using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule. Correlations are relative to the ANS 16.1 data.....	168
Figure 8.29 Sr-85 incremental leach rate vs. time from bitumen waste forms containing 40 wt% sodium tetraborate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.....	169

LIST OF FIGURES (cont.)

	Page
Figure 8.30 Co-57 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for bitumen waste forms containing 40 wt% sodium tetraborate leached at 20°C.....	169
Figure 8.31 Linear correlation plots for Co-57 leached from bitumen waste forms containing 40 wt% sodium tetraborate using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule. Correlations are relative to the ANS 16.1 data.....	170
Figure 8.32 Co-57 incremental leach rate vs. time from bitumen containing 40 wt% sodium tetraborate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.....	170
Figure 8.33 Bitumen forms containing 40 wt% sodium tetraborate. The one at left is as fabricated. The one at right was leached for 320 days in deionized water at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.....	171
Figure 8.34 Cs-137 cumulative fraction leached vs. time from bitumen containing 0, 20, 30 and 40 wt% sodium tetraborate. Samples were leached in DIW at 20°C.....	171
Figure 8.35 Sr-85 cumulative fraction leached vs. time from bitumen containing 0, 20, 30 and 40 wt% sodium tetraborate. Samples were leached in DIW at 20°C.....	172
Figure 8.36 Co-57 cumulative fraction leached vs. time from bitumen containing 0, 20, 30 and 40 wt% sodium tetraborate. Samples were leached in DIW at 20°C.....	172
Figure 8.37 Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.....	173
Figure 8.38 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.....	173

LIST OF FIGURES (cont.)

	Page
Figure 8.39 Linear correlation plots for Sr-85 leached from bitumen waste forms containing 40 wt% sodium tetraborate at waste form volume to surface area ratios (V/S) of 0.42, 0.62 and 0.91. Correlations are relative to the V/S = 0.91 data.....	174
Figure 8.40 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.....	174
Figure 8.41 Linear correlation plots for Co-57 leached from bitumen waste forms containing 40 wt% sodium tetraborate at waste form volume to surface area ratios (V/S) of 0.42, 0.62 and 0.91. Correlations are relative to the V/S = 0.91 data.....	175

LIST OF TABLES

Table No.		Page
2.1	Factors That Affect Leaching of Low-Level Radioactive Waste Forms That Were Experimentally Investigated in This Program...	4
3.1	Composition (weight %) for Each of the Waste Form Types Containing Simulated Waste.....	13
3.2	Composition of the Waste Forms of Pure Solidification Agent Matrices (weight %).....	15
3.3	Major Cation and Anion Concentrations in Synthetic Oxidic and Anoxic Groundwaters.....	19
4.1	Apparent Activation Energies at Each Leachant Replacement Interval for Cs-137 Leaching from Portland Type I Cement Containing 5 wt% Sodium Sulfate. Values are Listed in SI Units (J/mol) and CGS Units (kcal/mole).....	24
4.2	Cs-137 CFL From Portland Cement at Temperatures of 20, 30, 40, 50 and 70°C*. Each Row Represents a Leachant Replacement Interval (Time of Leachant Replacement in Days).....	25
4.3	Linear Correlations From the Leaching Data for Cs-137 From Pure Portland Cement at Temperatures of 20, 30, 40, 50 and 70°C. The 20°C Data Set is the Standard Against Which the Data at Elevated Temperatures Were Compared. The Slope of the Linear Correlation is Listed One Standard Deviation.....	26
4.4	Activation Energies Calculated for Each Leachant Replacement Interval for Cs-137 Leaching from Pure Cement. Values are Listed in SI Units (J/mol) and CGS Units (kcal/mole).....	27
4.5	Apparent Activation Energies for Sr-85 From Cement Containing Sulfate.....	29
5.1	Apparent Activation Energies at Each Leachant Replacement Interval for Sr-85 and Cs-137 from Portland Type I Cement Containing 15 wt% Incinerator Ash.....	73
10.1	Summary of Acceleration Factor Effects for Cs-137.....	182
10.2	Summary of Acceleration Factor Effects for Sr-85.....	183
10.3	Summary of Acceleration Factor Effects for Co-57.....	184

ABSTRACT

This report presents the results of an experimental survey of the factors that affect leaching from several types of solidified low-level radioactive waste forms. The goal of these investigations was to determine those factors that accelerate leaching without changing its mechanism(s). Typically, although not in every case, the accelerating factors include:

- increased temperature
- increased waste loading (i.e., increased waste to binder ratio)
- decreased size (i.e., decreased waste form volume to surface area ratio)

Additional factors that were studied were: increased leachant volume to waste form surface area ratio, pH, leachant composition (groundwaters, natural and synthetic chelating agents), leachant flow rate or replacement frequency and waste form porosity and surface condition. Other potential factors, including the radiation environment and pressure, were omitted based on a survey of the literature.

Types of waste forms that were investigated included: portland I cement containing sodium sulfate, portland I cement containing incinerator ash, vinyl ester-styrene emulsion (Dow process) with sodium sulfate solution, vinyl ester-styrene with dry sodium sulfate salt, and bitumen containing sodium tetraborate as simulated wastes. Glass waste forms produced by a glass-furnace incinerator under an R&D program at Mound Laboratory also were studied.

Evaluation of the factors as potential accelerating factors was based on comparison of the results from "standard samples," which were defined as nominal 4.8 cm diameter by 6.4 cm tall right cylinders leached in 1300 ml of demineralized water at 20°C. Comparisons included Arrhenius plots for experiments at increased temperature, linear correlations with the data from the standard samples, and microscopic examination.

Generally, accelerated leaching can be accomplished, but statistical variability of the results is increased by acceleration. Further, fabrication of the sample must be tightly controlled, especially for bitumen samples. Cesium-137 leaching from cement was accelerated by increased temperature, with an activation energy of 4 - 6 kcal/mole, which is consistent with diffusion of simple ions in water. For strontium-85 leaching from cement, the results of increased temperature were not clear because leaching does not occur by diffusion alone. Increased waste loading produced either a clear acceleration or an indication of acceleration accompanied by increased statistical variability for every system except Sr-85 from cement, for which there was no acceleration. Decreased size produced increased acceleration for every system, again with increased statistical variability. Cobalt-57 leaching from bitumen was accelerated at pH 8 and in groundwater, and was strongly accelerated in the presence of chelating agents in the leachant.

1. INTRODUCTION

This report presents the results of investigations of factors that affect the leaching of solidified low-level radioactive waste (LLW) forms. The results continue earlier work that included a literature survey [1] of leaching mechanisms, and two annual reports [2,3] that gave our interim results. Our literature survey [1] identified thirteen individual factors contained in three categories that affect leaching. However, most of the experimental work associated with the identification and specification of these categories came from studies of glass waste forms under consideration for high-level waste. Little of the work on glass was applicable to low-level waste forms, which typically are fabricated from cement, bitumen or polymer solidification agents and contain different types of waste than the high-level waste. Glass solidification of LLW was investigated [4] under a DOE R&D effort and remains an option for future application; however, glass is not currently used for solidification of LLW.

The principal types of waste forms selected for investigation in this program are typical of those currently produced by government and commercial nuclear activities.

The particular reason for investigating factors that affect LLW leaching is to provide a technical basis for development of accelerated leach tests that can predict the long-term leachabilities of LLW forms in disposal conditions. Also, since long-term prediction of leachabilities must be based on a knowledge of leaching mechanisms, these mechanisms are reviewed for the specific waste forms investigated in this task.

Sections 4 through 9 presents the results of leaching experiments and solid phase analysis for each combination of waste type/solidification agent investigated. Section 10 has tables that summarize the effectiveness of each factor. It may be useful for the reader to refer to these tables while reading the individual sections.

1.1 Leaching Mechanisms and Long-Term Leachability

If the long-term prediction of the leaching behavior of waste forms must be based on knowledge of leaching mechanisms, then the validity of characterizing a waste form by an effective diffusion coefficient, D_e , depends on diffusion being the leaching mechanism over the time of the prediction. If diffusion is not the leaching mechanism, then the following question must be answered: Of what use is an effective diffusion coefficient measured from short-term tests for the long-term prediction of leachabilities of waste forms?

This question was addressed quantitatively for waste forms in which the short-term leaching mechanism is well represented as diffusion, but for which the long-term leachability is controlled by dissolution of a slightly soluble contaminant [5]. Specifically, at long times the release by leaching is underestimated by diffusion when dissolution becomes the controlling mechanism. If dissolution replaces diffusion control of leaching release before

the latter is affected by depletion, which occurs at approximately 20% for diffusion [6], then long-term predictions of leachability from the semi-infinite medium model, as well as diffusion models that account for waste-form depletion, will underestimate the release at long times. The underestimation grows with time since the dissolution-controlled release remains constant (until depletion begins to decrease it) while diffusion-controlled release decreases steadily (i.e., as the inverse of the square root of time). Underestimation by diffusion model can become large if the contaminant inventory consists of relatively little of the initially mobile form compared to a relatively large amount of the slightly soluble form.

Another long-term problem can result from loss of integrity of the initial monolithic waste form by cracking, swelling, surface spalling and other processes that increase surface area. Such problems commonly occur when the solidification agent and the waste are not compatible, either physically or chemically. Waste forms consisting of ion exchange resins in cement generally disintegrate sometime after exposure to water due to swelling of the resins and the brittle nature of cement [7]. Sulfate salts in cement react to form the mineral ettringite, which may degrade the waste form over time by cracking [8].

Finally, authigenic mineral formation on the waste form surface and/or within the waste form may change the controlling leaching mechanism over time. Carbonate deposition on cement waste forms is well known, as is ettringite formation in cement waste forms containing sulfate salt.

1.2 Effects of Waste Form Composition

Our initial studies involved leaching experiments on pure solidification agents incorporating radioactive tracers of cesium, strontium and cobalt as the only "waste". These studies provided baseline information on the leaching behavior of the matrices of the pure solidification agent. Studies on more realistic waste forms incorporating simulated waste were started after the baseline experiments were well underway. The comparison between these two studies showed the importance of waste effects (i.e., chemical reaction) and of waste loading effects (i.e., physical consequences of composite waste forms) on both the short- and long-term leaching behavior of low-level waste forms. Indeed, the waste and waste loading effects were so dominant that substantially more effort was directed at these investigations than was initially planned.

2. FACTORS THAT AFFECT LEACHING OF LOW-LEVEL WASTE FORMS

In 1981 Stone [9] reviewed the factors that might affect leachability. These factors were listed under three categories: (i) system factors, (ii) leachant factors, and (iii) waste form factors. System factors included time, temperature, pressure, radiation environment and the ratio of waste form surface area to leachant volume. Leachant factors included composition, pH, Eh and flow rate or replacement frequency. Waste form factors included composition, surface condition and porosity. Some or all of these individual factors could be important for any given type of waste form.

A literature review of the factors affecting leachability specifically for LLW forms [1] concluded that pressure and the radiation environment were probably not significant for LLW forms. The relatively small overburden pressures (20-50 psi) in shallow land burial seemed unlikely to affect the leachability of LLW forms, with the possible exception of bitumen forms which could deform by creep. Studies of radiation effects on LLW forms showed that there were no changes in leachability up to 100 Mrad, although generation of radiolytic gas from organic materials occurred. Cement waste forms withstood substantially greater doses with no adverse effect on leachability.

Recently, two factors were noted that were not in Stone's original list which may have a substantial effect on LLW form leachability: wet-dry cycling [10,11] and container effects [12]. Wet-dry cycling of leaching conditions is important for cement and other porous waste forms because it allows direct transport of solubilized radionuclides to the surface as the wet waste form dries. Container effects may result from damage due to swelling of a waste form inside a container. Wet-dry cycling has been well substantiated as affecting cement waste forms. Container effects were observed in leach tests made on partially exposed test samples, as in the original IAEA leach test [13], but have not been studied directly. The procedure for the IAEA leach test recommends using a containerized waste form with one face exposed to the leachant. The effects of wet-dry cycling and container effects may be important factors in the long-term behavior of LLW forms in actual disposal environments. However, because cognizance of these factors is relatively recent, little work on them is included in this program and in this report.

Table 2.1 lists the factors specifically addressed in this report. Time is not listed as a factor because each factor includes time in the leaching results. Additionally, Eh is not considered independently because it is dependent on leachant composition and cannot be experimentally isolated; therefore, Eh is considered to be an aspect of leachant composition. Since the initial pH of the leachant is easily adjusted, pH is evaluated as an independent factor, although it is also an aspect of leachant composition.

Evaluation of the factors is based on comparison with leaching data for nominally identical waste forms (except for the factor being varied) at 20°C in deionized water (DIW) for a standard sample designated as a right cylinder with nominal dimensions of 4.8 cm diameter by 6.4 cm high. Data from the standard samples gives the baseline figures listed in Table 2.1. The baseline data were taken for long times to assure that they are representative of the

leaching behavior of the sample over its, i.e., until depletion and/or degradation of the waste form occurs.

Table 2.1

Factors That Affect Leaching of Low-Level Radioactive Waste Forms That
Were Experimentally Investigated in This Program

System Factors

- Temperature
- Ratio of Leachant Volume to Waste Form Surface Area

Leachant Factors

- Composition
- pH
- Flow Rate or Replacement Frequency

Waste Form Factors

- Composition
- Volume to Surface Area Ratio
- Porosity
- Surface Condition

2.1 Temperature

Temperature is usually the first variable considered in attempts to change or analyze rate processes. This is because: (i) small changes in temperature often lead to large changes in the observed rates of many processes, and (ii) the variation of the rate with temperature often is well represented by the Arrhenius equation, shown in Equation 2.1 and stated in terms of the rate rather than the rate constant.

$$R(T) = A \exp (-E_a/RT) \quad (2.1)$$

where $R(T)$ is the rate at (absolute) temperature T , A is a constant, R is the gas constant and E_a is the 'Apparent Activation Energy' of the rate process. Equation 2.2 results from the logarithm of Equation 2.1:

$$\ln (R(T)) = \ln (A) - \frac{E_a}{RT} \quad (2.2)$$

A plot of the log of the rate parameter versus $(1/T)$ from Equation 2.2 produces a straight line of slope $(-E_a/2.303R)$ for an activated process. A change in slope is indicative of a change in activation energy associated with a change in mechanism.

2.2 Ratio of the Surface Area of the Waste Form to Leachant Volume

The ratio of the surface area of the waste form to leachant volume affects how fast the leaching system can approach steady state as the leachant becomes saturated with leached material. This factor is not independent of leachant flow rate and replacement frequency, nor of the surface area to volume ratio of the waste form.

2.3 Leachant Composition

Standard leachants include demineralized water (DIW) and brine, although testing is also done with tap water, whose composition may or may not be specified, and other aqueous solutions. DIW generally results in higher leach rates than brine except for ion-exchange-resin wastes, in which the cationic radionuclides on the resin exchange for cations in the brine.

Some elements of concern to LLW management exhibit more than one chemical oxidation state, e.g., Co and Tc. In the absence of chelation complexes, the solubility of these elements depends on the chemical oxidation state, which is a function of Eh. The two most important oxidation states of cobalt are II and III. Cobalt(II) is the only significant oxidation state in aqueous solutions without complexing agents. Few simple Co(III) salts exist, since Co(III) oxidizes water. On the other hand, cobalt(II) forms an extensive group of simple and dehydrated salts. Few compounds of Co(I) are known since Co(I) readily oxidizes to Co(II). For elements with only one oxidation state, such as Cs and Sr, Eh conditions probably have little effect on the solubility of the ions.

2.4 Leachant pH

Since LLW forms are typically two-phase systems, pH effects result from the interaction between the leachant, waste and solidification agent.

Percolate water from rain and runoff may be expected to be close to neutral, depending on dissolved atmospheric gases such as carbon dioxide and interaction with the overburden soil.

2.5 Leachant Flow Rate or Replacement Frequency

Leachant flow rate or, approximately equivalently [14], the replacement frequency of a specific volume of leachant in semi-dynamic leach tests is a major factor in determining leachability: it also determines the boundary conditions which apply to any data analysis.

Static leach tests, such as the MCC-1 [15], ideally are of long enough to allow the leachant and sample to attain equilibrium. Information from static tests includes solubility limits for the specific leachant-waste form under the conditions of the test, and kinetic data if the approach to equilibrium is followed. Knowledge of saturation levels and the kinetic approach to saturation are important not only for static leaching but also for estimating adherence to boundary conditions in flowing and semi-dynamic tests.

Flowing and semi-dynamic leach tests ideally maintain the leachant at such low concentrations of leached substances that redeposition onto the sample is insignificant. However, this condition is seldom assured since experiments rarely vary the fixed schedule of leachant replacement in most tests, and there are no specific test procedures to assure that concentration effects are not significant.

2.6 Composition of the Waste Form

The composition of a waste form determines its fundamental nature, including its physicochemical properties and the mechanism of leaching. A waste form consists of a type and quantity of waste fixed in a solidification agent. Other materials such as sorbents often are added to cemented waste forms to improve performance in specific ways. The nature of the waste also affects the selection of the solidification agent. The waste stream may need treatment to become compatible with a solidification process. Such treatments may include adjustment of pH and/or water content or, in the case of glass, incineration.

Low-level waste forms are generally two or more phase systems in which the solidification agent matrix is physically and chemically distinct from the incorporated waste. Because LLW forms are inherently not 'one substance' there is the possibility of interaction between the waste and the solidification agent.

Generally, the leachability of a waste form increases as the waste loading is increased. If increased waste loading produces a reproducible increase in leachability, then waste loading may provide an acceleration factor.

2.7 Volume to Surface Area Ratio of the Waste Form

When certain conditions are met, increasing the sample surface area to volume ratio may be useful as an accelerating factor in leach testing. There are different requirements for leaching which is diffusion-controlled to those for corrosion-controlled.

The argument for corrosion-controlled leaching is contained in Reference 1.11-1.12 [16]. Briefly, the concentration of species, i , in the leachant, C_i , may be related to the leach rate, L_i , the fraction of species in the waste form, f_i , the surface area to volume ratio of the waste form, (S/V) , and the contact time of the leachant with the waste form, t , as in Equation 2.3.

$$C_i = L_i f_i (S/V) t \quad (2.3)$$

L_i depends on the chemical composition of the leachant and may also be a function of time and/or (S/V) explicitly [17]. If L_i depends only on leachant composition and Equation 2.3 holds, then increasing (S/V) will effectively shorten the time required to reach a given concentration level in the leachant thus accelerating the leaching process. This is shown in Equation 2.4.

$$(S/V)_1 t_1 = (S/V)_2 t_2 \quad (2.4)$$

The subscripts 1 and 2 in Equation 2.4 indicate different conditions of (S/V) and t . The validity of Equation 2.4 for glass leaching was experimentally demonstrated once the leach rate has become linear with time [16,18,19,20].

Alternatively, under diffusion-controlled conditions, the relationship of the cumulative fraction leached from different sized samples, which are otherwise identical and are leached under identical conditions, can be shown to be:

$$\left\{ \frac{\Sigma a_n}{a_0} \right\}_1 \left\{ \frac{V}{S} \right\}_1 = \left\{ \frac{\Sigma a_n}{a_0} \right\}_2 \left\{ \frac{V}{S} \right\}_2 \quad (2.5)$$

a_n = amount of substance of interest leached in interval n

a_0 = total amount of substance of interest originally present

$\frac{\Sigma a_n}{a_0}$ = cumulative fraction leached through interval n .

where subscripts 1 and 2 indicate the different size samples. This conclusion is based on the solution to the problem of diffusional release from the semi-infinite medium (Reference 21, p. 32), which may be stated as in Equation 2.6.

$$\left(\frac{\Sigma a_n}{A} \right) \left(\frac{V}{S} \right) = 2 \left(\frac{Dt}{\pi} \right)^{1/2} \quad (2.6)$$

For samples which are nominally identical, except for size, D should be the same. If they are leached under similar conditions for the same length of time, t, then the right-hand side of Equation 2.6 is the same for both samples and Equation 2.5 follows. There is experimental evidence supporting Equation 2.5 [22,23,24]. However, the leaching results used to validate Equation 2.5 were limited to a relatively small range of fractional release early in the leach test, such that the semi-infinite medium approximation might be valid.

To summarize, based on diffusion theory and supported by experiments, it has been shown that leaching from small-scale test samples can be used to predict leaching release of larger waste forms under certain conditions. The complete set of conditions under which this result may be valid include the conditions set forth above, plus those which lead to Equation 2.6 as the quantitative expression of cumulative release versus the square root of time. These conditions include:

- Diffusion is the mass transport mechanism and the diffusion coefficient is constant.
- The diffusant is uniformly distributed throughout an effectively homogeneous medium before leaching.
- The leachant and the surface of the waste form are maintained at effectively zero concentration with respect to the diffusant during leaching.

If test conditions on small-scale samples can be controlled to effectively simulate actual burial conditions and Equation 2.6 holds, then it should be possible to predict long-term leaching release for the specified conditions. Thus, small-scale tests would provide an accelerating factor to estimate long-term release.

2.8 Porosity of the Waste Form

An inert matrix which is physically porous can only retard the leachability of other substances embedded in the matrix compared to simply exposing the substances directly to the leachant. This is not equivalent to the effect of porosity acting to increase surface area because of microscopic surface roughness, as was found to be important for glass [9,16]. Porous LLW forms in which the waste and matrix of the solidification agent are distinct may be better described by formally considering the effect of the porous matrix,

rather than considering the effect of porosity as simply increasing surface area.

The physical considerations necessary to account for the effect of porosity on diffusion in a porous matrix along with mathematical models incorporating these considerations were reviewed by Van Brakel and Heertjes [25]. In general, the diffusibility, Q , of a porous matrix is described as:

$$Q = \frac{PC}{T^2} \quad (2.7)$$

where P is the porosity, C is the constrictivity and T is the tortuosity. P and T depend only on the porous matrix, whereas C depends both on the porous matrix and the diffusant since the relative sizes of porosity and diffusing species are important. Q is defined as the ratio of the effective diffusion coefficient in the porous medium to the diffusion coefficient in the absence of the porous medium.

3. MATERIALS AND METHODS

The materials for making waste form, the leach test methods and the analytical methods used in the experimental studies are summarized in this section. Previous reports [2,3] from this program also contain similar descriptions. The solidification agents, portland type I cement, bitumen, vinyl ester-styrene copolymer and glass, were selected because they were either in use or being considered for use by the defense or commercial nuclear industries. The (simulated) waste types chosen for study are common waste streams produced by power reactors--the sulfate and borate salts--plus incinerator ash, which is likely to become a major waste stream as advanced processes for volume reduction become common.

Four classes of waste forms were investigated:

- (i) Solidification agent matrices incorporating only radiotracers as simulated waste.
- (ii) Solidification agent matrices without radiotracers. These are nominally identical to the samples in (i) except for the absence of radiotracers and are termed, "Solidification Agent Blanks."
- (iii) Waste forms incorporating simulated bulk waste plus radiotracers.
- (iv) Waste forms incorporating simulated bulk waste without radiotracers. These are nominally identical to the samples in (iii) except for the absence of radiotracers. These samples are termed, "Waste Form Blanks."

The samples in class (i) were fabricated to investigate the leaching behavior of the radionuclides of cesium, strontium and cobalt from pure solidification agent matrices. The samples in (ii) were used to study the leaching of the components of the solidification agent. The samples in (i) could not be used for both studies because of the possibility of radioactive contamination of the instruments used for analysis of the samples in (ii).

The samples in (iii) and (iv) were made to investigate the leaching of the radionuclides listed above and of solidification agent and waste components, respectively. Again, the samples in (iii) could not be used for both investigations because of the possibility of contaminating the analytical instrument with radioactivity.

Figure 3.1 summarizes the waste form types containing simulated wastes that were selected for study. Table 3.1 lists the compositional parameters for these waste forms corresponding to the abbreviated summary in Figure 3.1. Table 3.2 lists compositional parameters for the samples consisting of the pure solidification agent with no otherwise bulk waste. The "blanks," i.e., those samples without radiotracers, are nominally identical to the sample formulations listed in Tables 3.1 and 3.2.

Figure 3.1 Schematic summary of waste form types listed by solidification agent, waste type and waste loading(s).

Table 3.1

Composition (weight %) for Each of the Waste Form Types
Containing Simulated Waste

<u>Component</u>	<u>Weight %</u>	<u>Activity (μCi)</u>	<u>Component</u>	<u>Weight %</u>	<u>Activity (μCi)</u>
Portland Type I Cement/Sodium Sulfate			Vinyl Ester-Styrene/Sodium Sulfate		
Cement Powder	65	-	Vinyl Ester-	54.7	-
Sodium Sulfate	5	-	Styrene Monomer		
(anhydrous)			Sodium Sulfate	39.3	-
Water	30	-	(anhydrous)		
Co-157	-	6.3	Water	1.8	-
Cs-137	-	6.3	Catalyst	1.5	-
Sr-85	-	12.5	Promoter	0.06	-
			Co-57	-	100
			Cs-137	-	100
			Sr-85	-	200
Portland I Cement/Incinerator Ash			Vinyl Ester-Styrene/Sodium Sulfate		
Cement Powder	60	-	Vinyl Ester-	67.6	-
Incinerator Ash	15	-	Styrene Monomer		
Water	25	-	Sodium Sulfate	30.0	-
Co-57	-	100	(anhydrous)		
Cs-137	-	100	Water	0.6	-
Sr-85	-	200	Catalyst	1.7	-
			Promoter	0.07	-
			Co-57	-	16.5
			Cs-137	-	16.5
			Sr-85	-	25.5
Vinyl Ester-Styrene/Aqueous Sodium Sulfate Emulsion					
Vinyl Ester-	39.0	-			
Styrene Monomer					
Sodium Sulfate	15.0	-	Vinyl Ester-Styrene/Sodium Sulfate		
(anhydrous)					
Water	45.0	-	Vinyl Ester-	77.3	-
Catalyst	1.0	-	Styrene Monomer		
Promoter	0.04	-	Sodium Sulfate	20.0	-
Co-57	-	100	(anhydrous)		
Cs-137	-	100	Water	0.6	-
Sr-85	-	100	Catalyst	2.0	-
			Promoter	.08	-
			Co-57	-	16.5
			Cs-137	-	16.5
			Sr-85	-	25.5

Table 3.1 (cont.)

Composition (weight %) for Each of the Waste Form Types
Containing Simulated Waste

<u>Component</u>	<u>Weight %</u>	<u>Activity (μCi)</u>	<u>Component</u>	<u>Weight %</u>	<u>Activity (μCi)</u>
Bitumen/Sodium Tetraborate			Glass/Incinerator Ash		
Bitumen	60.0	-	Soda-Lime Glass	a	-
Sodium	40.0	-	Incinerator Ash	a	-
Tetraborate (anhydrous)			Co-60	-	0.01-0.05
Co-57	-	91	Cs-137	-	0.01-0.05
Cs-137	-	91	Mn-54	-	0.01-0.04
Sr-85	-	182			

Bitumen/Sodium Tetraborate

a. The waste form composition was not determined.

Bitumen	70.0	-
Sodium	30.0	-
Tetraborate (anhydrous)		
Co-57	-	39
Cs-137	-	39
Sr-85	-	78

Bitumen/Sodium Tetraborate

Bitumen	80.0	-
Sodium	20.0	-
Tetraborate (anhydrous)		
Co-57	-	100
Cs-137	-	100
Sr-85	-	200

Table 3.2

Composition of the Waste Forms of
Pure Solidification Agent Matrices (weight %)

<u>Component</u>	<u>Weight %</u>	<u>Activity (μCi)</u>
Portland I Cement		
Cement Powder	70	-
Water	30	-
Co-60	-	16.3
Cs-137	-	9.9
Sr-85	-	23.6
Pioneer 321 Bitumen		
Bitumen	100	-
Co-60	-	13.8
Cs-137	-	8.4
Sr-85	-	20.0
Vinyl Ester-Styrene/Water Emulsion		
Vinyl Ester- Styrene	49.2	-
Water	49.5	-
Catalyst	1.26	-
Promoter	0.05	-
Co-60	-	15.4
Cs-137	-	9.3
Sr-85	-	22.3
Vinyl Ester-Styrene		
Vinyl Ester- Styrene	97.9	-
Water Comonomer	0.7	-
Catalyst	1.3	-
Promoter	0.05	-
Co-60	-	13.9
Cs-137	-	8.4
Sr-85	-	20.0

The choice of solidification agents was based on two criteria: (i) That they were either in use or being considered for in low-level waste management, and (ii) that the solidification agents cover a range of materials properties. By providing detailed knowledge of several types of materials, e.g., hydraulic cement, thermoplastic binders, and thermosetting polymers, we hoped that these results would apply in a general way to solidification agents that may be developed in the future. The glass solidification process for low-level waste was investigated at the Mound Laboratory [4], and the glass waste-form samples used in this program were provided by Mound.

3.1 Waste Form Types

Studies were made to select the best formulation of solidification agent and waste type. Since many waste types are incompatible with their solidification agents (e.g., cement and sodium sulfate, bitumen and dried salts), formulations were optimized to provide stability for 90 days in immersion while maximizing the waste loading.

3.1.1 Portland I Cement Containing Sodium Sulfate as Simulated Waste.
The compositional phase diagram for the solidification of aqueous sodium sulfate with portland type I cement is available [26].

Sodium sulfate waste is a product of the regeneration of ion exchange resin at BWR power stations. The waste is usually concentrated to an approximately 22 wt% solution at 25°C. Evaporation of this solution to dryness results in sodium sulfate decahydrate (Glauber's salt): Glauber's salt dehydrates to anhydrous sodium sulfate at temperatures above 32°C.

Up to approximately 45 wt% sodium sulfate can be solidified with cement. However, waste forms containing more than approximately 8 wt% sodium sulfate were unstable on immersion in deionized water and disintegrated before a 90-day immersion test was completed. A waste form formulation of 5 wt% sodium sulfate, 30 wt% water and 65 wt% cement was selected for testing, corresponding to a waste-to-binder ratio, i.e., evaporator concentrate to cement of 0.54.

3.1.2 Portland I Cement Containing Incinerator Ash as Simulated Waste.
The solidification of incinerator ash with portland type I cement and its compositional phase diagram have been reported [3,27-30]. Up to 50 wt% incinerator ash can be solidified by portland I cement without free standing water being present. However, on curing specimens swell with the development of large voids. A waste form formulation of 15 wt% ash, 25 wt% water and 60wt% cement was selected for leach testing because this composition produced waste forms with few voids.

Incinerator ash was obtained from the Tennessee Valley Authority's waste incinerator. The major components of incinerator ash are typically uncombusted carbon, aluminum oxide (Al_2O_3), ferric oxide (Fe_2O_3) and silicon dioxide (SiO_2). The ash was passed through a 2.38 mm sieve to produce a uniform powder free of large clinkers and metal objects.

3.1.3 Vinyl Ester-Styrene Emulsion With Aqueous Sodium Sulfate as Simulated Waste. The amount of sodium sulfate that can be solidified by the vinyl ester-styrene polymer emulsion is limited by the 22 wt% solubility at 25°C of sodium sulfate in water. A mixture of 15 wt% sodium sulfate, 45 wt% water and 37 wt% vinyl ester-styrene monomer produced a satisfactorily polymerized form with hard surfaces that was stable when immersed in water.

3.1.4 Vinyl Ester-Styrene Containing Sodium Sulfate as Simulated Waste. Mixtures of up to 60 wt% dry sodium sulfate with vinyl ester-styrene monomer polymerized satisfactorily to produce waste forms with hard surfaces. The leaching of sodium sulfate from solidified waste forms was used to select a composition which maximized the amount of incorporated waste, while minimizing its leaching. The amount of sodium leached at waste loadings above 40 wt% rapidly increased, so this value was the maximum used.

3.1.5 Bitumen Containing Sodium Tetraborate as Simulated Waste. Boric acid waste generated at a typical PWR Plant contains approximately 12 wt% boric acid in aqueous solution. Solidification of the waste with bitumen requires the removal of water by evaporation. Because boric acid dehydrates at 160°C, the loss of water would cause foaming of the bitumen mixture.

A satisfactory method of solidification is to neutralize the boric acid solution with sodium hydroxide. Sodium tetraborate is the predominant product when the waste stream is neutralized to pH 9.3 [31]. Evaporation of the solution to dryness results in the hydrated crystalline substance, sodium tetraborate decahydrate (borax). The borax must be further dried at 200°C to produce the anhydrous borate.

A uniform solid waste can be produced by mixing the anhydrous sodium tetraborate with molten bitumen. Waste loadings of 20%, 30% and 40% by weight sodium tetraborate in bitumen were used.

3.1.6 Soda-Lime Glass Containing Incinerator Ash as Simulated Waste. The glass-waste form has been used at the Monsanto-Mound Facility in a process that simultaneously incinerates low-level waste and incorporates the ash in the glass [4]. The glass waste form consists of two solid phases:

- (i) the glass matrix in which part of the waste components are dissolved, and
- (ii) particulates of ash residue.

3.2 Sample Preparation

The samples prepared for leaching experiments were cylindrical with approximate dimensions of 4.8 cm diameter and 6.4 cm length ($V/S=0.91$). Based on past experience this sample size is convenient for laboratory studies. Additional samples were prepared for configurational studies; these included smaller cylinders, approximately 2.5 cm diameter by 2.5 cm tall ($V/S=0.42$), a disk, approximately 14 cm diameter by 1.2 cm ($V/S=0.61$) tall and a larger cement cylinder that was approximately 10 cm diameter by 13 cm tall ($V/S=1.85$).

Radioactive samples prepared for leach testing had radioactive tracers incorporated into the waste. The radioisotopes were Co-57, Cs-137 and Sr-85. The low energy gamma ray emitted by Co-57 ($T_{1/2}=270$ days) is better suited to the automated NaI counting system than is Co-60 and works well with the Geli counting system.

The cylinders of soda-lime silica glass, which were produced at the Mound facility, were approximately 2.5 cm diameter and 2.5 cm in height, which contained Cs-137, Mn-54 and Co-60.

3.3 Leaching Tests

Three leach tests were used to determine the leachability of various radionuclides and constituents of solidification agents.

3.3.1 ANS 16.1 Leaching Test. The ANS 16.1 Leach Tests is a semi-dynamic leaching test in which the leachate is replaced after intervals of static leaching [32]. Specimens are placed into the leachant solution with all the external surface area directly exposed. Specimens are tested in individual containers containing sufficient leachant to provide a leachant/specimen external geometric surface area ratio of 10 cm unless otherwise specified. Specimen formulations are usually tested in duplicate or triplicate to determine the extent of specimen variation in leaching. Leach test data are expressed as incremental fraction release, as cumulative fraction release or as a release rate to facilitate alternative methods of treating the data.

The leachant is typically distilled water with a conductance of less than 5 μ mhos/cm. The sampling interval was modified to more frequent intervals and to extend the duration of the test beyond the 90-day standard.

In addition to DIW, two simulated groundwaters and a 100 ppm solution of EDTA (disodium ethylenediaminetetraacetate hexahydrate) were used as leachants. The groundwaters were of two types: An oxygen-saturated groundwater (oxic) based on the composition of an ORNL groundwater from a potential waste burial site [3,33] and an oxygen-deficient groundwater (anoxic) which could be formed by the biodegradation of waste in the presence of the former groundwater. The compositions of these leachants are shown in Table 3.3.

3.3.2 MCC-3s Leaching Test. The MCC-3s Agitated Powder Leach Test Method is a static leach test developed for determining the solubility limits and the dissolution rates of materials used for the encapsulation of high-level wastes [34].

This method was adapted for use with low-level waste materials to determine solubilities of sample components in the leachate. Leachate elemental concentration must be monitored for chemical saturation to eliminate retardation of leach rates, or mechanistic variations due to saturation conditions.

Table 3.3

Major Cation and Anion Concentrations in Synthetic Oxidic and Anoxic Groundwaters^a

Species	Concentration (ppm)	
	Oxidic GW	Anoxic GW
Na ⁺	3.80	5.25
K ⁺	0.46	0.91
Ca ⁺²	57.00	114.02
Mg ⁺²	2.86	5.72
NH ₄ ⁺	0.00	5.95
Fe ⁺²	0.00	6.16
Cl ⁻	2.30	32.59
SO ₄ ⁻²	3.20	0.00
HCO ₃ ⁻	120.00	361.06

-
- a. The composition of an Oak Ridge National Lab groundwater was used as a model for the synthesis of these waters. The concentrations reported for well #313 (6.3 m deep) at ORNL Area C Engineered Test Facility were used [3,33].

3.3.3 MCC-4s Leaching Test. The MCC-4s Low Flow Rate Leach Test Method is a single-pass flow-through test which eliminates the effects of sampling interval and of large changes leachate concentration, providing better control over the boundary conditions of leachant composition [35].

This leaching test was also developed for evaluation of high-level waste forms. Because of the nature of the materials used for this study, some modifications were made in the test procedure by increasing the flow-rates.

3.4 Analytical Methods

Leachates were analyzed for a variety of materials depending on the composition of the solidification agent. Cement leachates had the most analyses, since reactions within the matrix cause significant differences in leaching among different isotopes. Specific analytical methods are given below.

3.4.1 Radiochemical Analysis. The radiochemical component of the leachate such as Cs-137, Sr-85 and Co-60 (or Co-57) was analyzed by gamma-ray spectroscopy using an intrinsic Germanium detector or a sodium iodide detector in accordance with the methods described in ASTM D3648-78 [36] and ASTM D3649-78 [37].

3.4.2 Elemental Leachate Analysis. Analysis of leachates for non-radioactive elements was conducted with standard methods such as ASTM E663 [38] and those in, Analytical Methods for Atomic Absorption Spectrophotometry, revised January 1982, Perkin-Elmer Corporation [39].

3.4.3 Alkalinity. Analysis of leachates for total alkalinity was measured by titration to the phenolphthalein and methyl orange end points according to Method Number 403 from Standard Methods for the Examination of Water and Waste Water, 15th edition, 1980 [40].

3.4.4 Analysis for pH. Analysis of leachates for pH was performed using ASTM D1293 [41] with a platinum combination probe.

3.4.5 Conductivity. Conductivity was measured by ASTM D1125 [42].

3.4.6 SEM/EDS. Waste forms will be analyzed before and after leaching by Scanning/Electron Microscopy (SEM) to observe change in physical morphology and by Energy Dispersive Spectroscopy (EDS) to determine elemental ratios in profile and on waste form surfaces. Methods used will be those discussed by Goldstein and Yakowitz in Practical Scanning Electron Microscopy, Electron and Ion Microprobe Analysis, (1975) [43].

4. PORTLAND TYPE I CEMENT CONTAINING SODIUM SULFATE SALT AS SIMULATED WASTE

Portland cement, either by itself or blended with additives to enhance radionuclide retention, is the most commonly used solidification agent for low-level radwaste. As the result of hydration reactions with water, portland cement solidifies to form a porous, hydrophilic matrix of high surface area. The physical and chemical properties of portland cement have been well documented [44-50].

In general, portland cement evidences a rapid release of cesium in leaching experiments while strontium and cobalt leach substantially less readily [1-3,10,11,29,51-58]. As a result, sorbents for cesium are commonly blended with cement to reduce its leachability [51-61]. These blended cement + sorbent mixtures are often formulated for specific waste streams.

This section presents results obtained from leaching studies investigating the factors deemed potentially important for LLW forms, as discussed in Section 2 of this report, consisting of portland type I cement incorporating 5 wt% sodium sulfate salt as simulated waste.

4.1 Leaching Mechanisms

The following overview summarizes the leaching mechanisms for cement as determined from the literature survey [1] and from the experimental work in this task.

Cesium leaches from cement by diffusion within and out of the porous cement matrix. Cesium is present in the cement matrix in trace quantities as a waste radionuclide. It is not limited by solubility in the cement and is not sorbed to any significant extent on the solid components of the cement. Thus, all of the cesium inventory should be available for leaching immediately. The presence of sulfate waste does not substantially alter these mechanistic observations, even though the sulfate reacts with the cement over time and strongly affects the long-term physical integrity of the waste form. In a practical sense, cesium release is retarded only by the tortuous nature of the porous matrix and not by any significant chemical interaction. Finally, cesium leaching from the cement waste form containing 5% sodium sulfate as simulated waste was not sensitive to variations in the replacement interval of the leachant (i.e., from weekly to daily, Section 4.2.5). This supports the observations in the literature that cesium sorbs only weakly on cement since the cesium concentration in the leachate replaced weekly was substantially greater than in that replaced daily. We recently found that calcium carbonate minerals that form on cement surfaces during leaching have a significant capacity to sorb cesium [62].

Strontium leachability from cement is more complex than that for cesium for several reasons.

- (i) Strontium is present as a minor component in cement; thus the trace amounts of radiostrontium (principally Sr-90) are subject to the common ion effect for solubility and sorption distributions.
- (ii) Strontium may have limitations on its solubility imposed by the hydroxide and/or sulfate concentrations in cement waste forms containing sulfate salts.
- (iii) The sorption of strontium onto cement components is relatively small, but certainly larger than that for cesium [1]. This would be expected to decrease the effective diffusion coefficient but would not otherwise affect diffusion.
- (iv) Strontium leachability was shown to be strongly dependent on the frequency of leachant replacement (Section 4.2.5) in cement waste forms containing 5% sodium sulfate. This suggests a limit on solubility, a sorption equilibrium, or both.
- (v) Strontium leachability appears to be retarded by carbonate buildup on the surface of the cement waste form (reference 1 and references therein). This has the effect of progressively reducing strontium leachability over time; thus a calculated effective diffusion coefficient for strontium would decrease with time as the carbonate builds up.

In sum, strontium leachability from the cement waste forms investigated in this task may be affected by solubility limitations, sorption, and surface effects that grow with time and by the complication that strontium is naturally in cement as a minor, but not insignificant, component. In carbonate-rich environments, the surface buildup of carbonate/bicarbonate precipitates may control strontium leachability through a solubility product (K_{sp}) or sorption equilibrium (K_{eq}) in the long-term.

Cobalt leaching from both the pure cement waste forms and from the cement waste forms containing 5% sodium sulfate was not measurable, because the very low solubility of cobalt in the high pH cement limits leachability. These results are not consistent with the observed leaching of radiocobalt from waste forms containing actual radwaste. The latter appears to result from cobalt having been mobilized by chelation and/or complexation by organic chelating, and/or complexing agents in the waste.

4.2 Factors that Affect Leaching

Results from experiments designed to investigate each of the factors listed in Table 2.1 for the cement waste forms containing sodium sulfate are discussed in the following sections. The basis for evaluating the effect of each of the factors is by comparison with tests on standard samples, i.e., 4.8 cm diameter by 6.4 cm high right cylinders, at 20°C in deionized water.

Replicate tests, generally triplicates, provided a measure of the variability of the data.

4.2.1 Temperature. The effect of temperature on the leachability of portland type I cement waste forms containing 5 wt% sodium sulfate was investigated between 20 and 50°C. Cesium release evidenced Arrhenius behavior with an activation energy of 22 ± 7 J/mol (5.2 ± 1.7 kcal/mole). Strontium release was little affected by temperature and did not evidence Arrhenius behavior; this was not surprising, given the large number of factors affecting strontium leachability (Section 4.1). Temperature had no effect on cobalt leaching; cobalt was not detected in any of the leachates.

Figures 4.1, 4.2 and 4.3 summarize the effect of temperature on the leaching of Cs-137. Figure 4.1 presents the cumulative fraction leached (CFL) versus time, for triplicate samples at 20 and 50°C and for duplicate samples at 40°C. Figure 4.2 plots linear correlations of these data versus the 20°C data. Figure 4.3 is an Arrhenius plot of the incremental leach rates of these data.

Figure 4.1 shows that increasing temperature increases Cs-137 leachability. This figure also shows that the reproducibility, as indicated by the scatter of data, is decidedly better for the 20°C data than for the data at 40 and 50°C. Although temperature clearly accelerates leaching of Cs-137 from these samples, the loss of reproducibility at the higher temperatures reduces the reliability as an accelerating factor.

The correlation plots in Figure 4.2 indicate that the two 40°C data curves remain linear with respect to the 20°C data, while the 50°C data deviate from linearity beyond approximately 0.6 CFL. Since the 40°C data correlate with the 20°C data up to releases of approximately 0.8 CFL, depletion seems unlikely to be the cause of the deviation from linearity for the 50°C data. The reason for this deviation is unknown.

In the Arrhenius plots of Figure 4.3, least-square lines were been drawn through the 20, 40 and 50°C data for each leachant replacement interval. Since the leach rate decreases with time, the least-square lines for each of the replacements proceed down the figure. Table 4.1 lists the apparent activation energies calculated from the slopes of these lines. The data for leachant replacements 12 to 14 of the 50°C set are not included. Scanning down the list in Table 4.1 suggests that the apparent activation energy, E_a , is near 5 kcal/mole through replacement interval 9; a dashed line was drawn between the data for replacement intervals 9 and 10. Starting with interval 10 the E_a values decrease, indicating that factors other than the activated process are beginning to affect the leach rates. Sample depletion of both the 40 and 50°C samples seems the most likely cause. Therefore, the E_a values for the process is taken to be the average of the individual E_a values for leachant replacement intervals 1 through 9, as listed in Table 4.1

Table 4.1

Apparent Activation Energies at Each Leachant Replacement Interval for Cs-137 Leaching from Portland Type I Cement Containing 5 wt% Sodium Sulfate. Values are Listed in SI Units (J/mol) and CGS Units (kcal/mole).

Leachant Replacement Interval	E_a (J/mol)	E_a (Kcal/mole)
1	34	8.1
2	18	4.3
3	24	5.7
4	27	6.4
5	27	6.5
6	13	3.0
7	23	5.4
8	20	4.7
9	11	2.7

10	9.0	2.1
11	4.2	1.0
12	6.7	1.6
13	7.1	1.7
14	-39.0	-9.3

Leaching at elevated temperature was also measured on portland type I cement samples containing radiotracers, but NO simulated bulk waste. The CFL versus time plots for Cs-137 leaching from these pure cement samples are not presented, but linear correlation plots and Arrhenius plots are shown in Figures 4.4 and 4.5, respectively, for comparison with the results in Figures 4.2 and 4.3.

Figure 4.4 shows that the Cs-137 leaching releases at elevated temperature correlated well with that at 20°C, with the exception of the last two points at 70°C. Since over three quarters of the Cs-137 activity had been leached, the deviation of these last two 70°C data points probably results from depletion. There is no estimate of the variability of the releases at the elevated temperatures as replicates were not leached at elevated temperature. The data plotted in Figure 4.4 are listed in Table 4.2 since these data are not listed in Appendix A. Table 4.3 lists the least-squares slopes of the lines in Figure 4.4. These slopes provide a measure of the acceleration of leaching release at each temperature relative to the average leachability at 20°C over the range of validity of the linear correlation.

Table 4.2

Cs-137 CFL From Portland Cement at Temperatures of 20, 30, 40, 50 and 70°C*.
 Each Row Represents a Leachant Replacement Interval
 (Time of Leachant Replacement in Days).

TEMPERATURE (°C)

	20	30	40	50	60	70
1 (.083)	.021 ± .001	.022	.024	.038	-	.053
2 (.29)	.035 ± .001	.039	.045	.061	-	.109
3 (1.0)	.062 ± .001	.074	.093	.138	-	.251
4 (2.0)	.092 ± .001	.108	.141	.211	-	.376
5 (3.0)	.116 ± .003	.133	.177	.274	-	.469
6 (4.0)	.137 ± .005	.157	.210	.320	-	.536
7 (5.0)	.157 ± .007	.176	.240	.366	-	.591
8 (11.0)	.237 ± .015	.255	.345	.527	-	.779
9 (18.0)	.281 ± 0.21	.317	.420	.640	-	.864

* All of the samples were nominally identical. The 20°C data are from triplicate samples which were made and tested separately from those tested at the higher temperatures. The 20°C data are the average CFL one standard deviation for the triplicate samples.

Table 4.3

Linear Correlations From the Leaching Data for Cs-137 From Pure Portland Cement at Temperatures of 20, 30, 40, 50 and 70°C. The 20°C Data Set is the Standard Against Which the Data at Elevated Temperatures Were Compared. The Slope of the Linear Correlation is Listed $\pm$ One Standard Deviation.

	TEMPERATURE (°C)				
	20	30	40	50	70 ^a
slope $\pm$ s	1.0	1.1 $\pm$ .1	1.5 $\pm$ .1	2.3 $\pm$ .2	4.0 $\pm$ .2
intercept	0.0	.003	-.001	-.004	-.016
r ^b	1.0	.999	.999	.999	.996

a. The data for leachant replacement intervals 8 and 9 were not used for calculating the linear relationship for the 70°C data since they deviated substantially from the line determined from the first seven data points.

b. r is the correlation coefficient. A value of 1 represents a perfect correlation while a value of zero indicates no correlation.

Figure 4.5 is an Arrhenius plot of the Cs-137 leach rates during each leachant replacement interval at the various temperatures for the pure cement samples. The apparent activation energies calculated from the least-squares slopes of the lines for each leachant replacement interval are listed in Table 4.4. The average E_a of 5.4 ± 0.9 kcal/mole is consistent with that (4-6 kcal/mole) for diffusion of simple ions in water.

Table 4.4

Activation Energies Calculated for Each Leachant Replacement Interval for Cs-137 Leaching from Pure Cement. Values are Listed in SI Units (J/mol) and CGS Units (kcal/mole)*

Leachant Replacement Interval	E_a (J/mol)	E_a (kcal/mole)
1	17.9	4.3
2	22.6	5.4
3	28.7	6.9
4	25.3	6.0
5	24.3	5.8
6	20.5	4.9
7	19.7	4.7
8	19.7	4.7
9	23.0	5.5
Average $\pm$ s:	22.4 ± 3.4	5.4 ± 0.9

* The 70°C values for intervals 8 and 9 were not used in the calculation of E_a since sample depletion appears to affect the leach rate.

Figures 4.6, 4.7 and 4.8 summarize the effect of temperature on the leaching of Sr-85 from portland type I cement waste forms containing 5 wt% sodium sulfate salt. Figure 4.6 presents the cumulative fraction leached (CFL) versus time for triplicate samples at 20 and 50°C and for duplicate samples at 40°C. Figure 4.7 plots linear correlations of these data versus the 20°C data. Figure 4.8 is an Arrhenius plot of the incremental leach rates of these data.

Figure 4.6 shows that increasing temperature clearly increases Sr-85 leachability. The reproducibility, i.e., the scatter of data at the same temperature, is somewhat better for the 20°C data than for the data at 40 and 50°C. The lack of reproducibility limits the reliability of temperature as an accelerating factor.

Although the initial portions of the 40 and 50°C data curves are linear with respect to the 20°C data, the correlation plots in Figure 4.7 show that they deviate from linearity as the leachant replacement intervals become longer than a week (i.e., approximately at interval 9). Depletion cannot be the cause of the deviation from linearity, as the CFL is less than 20%. It is probable that the deviation results from carbonation of the surface of the waste form, which could reduce the solubility of strontium and thus reduce the leachability of strontium. This is a particularly likely mechanism since strontium is contained naturally in cement in amounts well above the trace levels of radiostrontium present in radwaste.

In the Arrhenius plots of Figure 4.8, least-squares lines were drawn through the 20, 40 and 50°C data for the first nine replacement intervals. Since the leach rate decreases with time, the least-squares lines for each of the leachant replacements proceed down the figure. Table 4.5 lists the apparent activation energies calculated from the slopes of these lines. Early, these E_a values are outside the 4-6 kal/mole range that is typical of diffusion of simple ions in water. Therefore, Sr-85 leaching from this waste form type is not simple diffusion based on the measured E_a values.

No Co-57 activity above background was seen in any of the leachates for the cement samples containing sodium sulfate as simulated waste. This is a reasonable finding since insoluble cobalt hydroxide is presumably precipitated in the high pH cement.

Table 4.5

Apparent Activation Energies for Sr-85 From Cement Containing
5 Wt% Sodium Sulfate

Leachant Replacement Internal	E_a (Kcal/mole)	E_a (J/mol)
1	25	103
2	16	64
3	15	64
4	10	43
5	11	44
6	13	56
7	14	58
8	11	44
9	14	57
10	-3.6	-15
11	12	49
12	6.31	27
13	5.2	22
14	2.6	11

The leaching of sodium, potassium, calcium and strontium was measured from portland type I cement waste forms containing 5 wt% sodium sulfate, but no radiotracers. These "Blanks" were otherwise nominally identical to the samples containing radiotracers. Previous results [2,3,29] showed that the first three elements comprise the bulk of leachable cations from cement, while the strontium that is in cement naturally may affect the leaching of radio-strontium. In the cement waste forms containing sodium sulfate salt, the leached sodium comes from both the cement and from the salt; however, the bulk of it comes from the salt.

Figures 4.9, 4.10, 4.11 and 4.12 show the cumulative amounts leached (mg) versus time plots for, respectively, sodium, potassium, calcium and strontium from duplicate cement blanks. The sodium and potassium data all show "typical" leaching curves--i.e., monotonically increasing at a decreasing rate. However, the leaching of calcium and strontium behave differently. Specifically, calcium leaching starts slowly and then increases to a relatively rapid and linear rate of release. This behavior appears to result from a solubility limit for calcium from the large concentration of sulfate initially present. Calcium leaches rather slowly until the bulk of the sulfate, as the sodium salt, has leached from the sample or has reacted with the calcium that

was available; at this point the leach rate of calcium increases substantially and becomes linear with time. Strontium releases generally parallel those of calcium.

Figure 4.13 is the correlation plot of sodium and potassium leaching from the blanks compared to the Cs-137 leaching from nominally identical portland I cement waste forms containing 5 wt% sodium sulfate. Sodium and potassium releases correlate very well with those of Cs-137.

Figure 4.14 is the correlation plot for strontium leaching from the blanks compared to the Sr-85 leaching from nominally identical portland I cement waste forms containing radiotracers. The strontium releases at 20°C appear to correlate with Sr-85 after a delay, but at 50°C they do not correlate. This may be caused by different rates of carbonation.

4.2.2 Ratio of the Surface Area of the Waste Form to Volume of Leachant. The ANS 16.1 leach test procedure specifies that the ratio of the leachant volume (cubic cm) to the geometric surface area (square cm) of the test specimen be 10 ± 0.2 (cm). To investigate the effect of increasing this ratio on leaching, ratios of 20, 30 and 50 were used. In Figures 4.15 and 4.16, respectively show the results for Cs-137 and Sr-85 leaching from portland I cement waste forms containing 5 wt% sodium sulfate salt.

For the Cs-137 leaching (Figure 4.15) there is no apparent effect of increasing the ratio of leachant volume to waste form surface area. The decrease in Cs-137 leachability with increasing leachant volume is probably an artifact. Specifically, although all of the samples in these experiments were nominally identical, only the three sets at the larger leachant volumes were replicates whereas the samples at 1300 ml (i.e., ratio of 10:1) were made at a different time. Increasing the ratio of leachant volume to surface area was not promising as an accelerating factor for Cs-137, so the experiments were not pursued.

Figure 4.16 shows the results on Sr-85 leaching from increasing the leachant volume to waste form surface area. Although there appears to be a small increase in leachability of strontium, the lack of reproducibility is so dominant that the increase is lost in the scatter. These results were considered marginal at best, and the use of increasing leachant volume to waste form surface area was not pursued as a potential accelerating factor for strontium leachability from these waste forms under the conditions of these tests.

4.2.3 Composition of the Leachant. Deionized water (DIW) was the standard leachant used in the ANS 16.1 Leach Test. The effect of leachant composition on the leaching of portland I cement waste forms containing 5 wt% sodium sulfate was examined with DIW, a simulated groundwater from Oak Ridge National Laboratory (ORNL) [63] and DIW containing 100 ppm disodium EDTA. Table 3.3 gives the composition of the ORNL groundwater. In addition, the ORNL-simulated groundwater was used (i) in a well oxygenated state (i.e., oxic groundwater), and (ii) depleted of oxygen (i.e., anoxic groundwater). Both the oxic and anoxic groundwaters contained soil-extracted humic and fulvic acids to make the compositions more realistic. Humic and fulvic acids have

strong affinities for metal ions and can act as complexing and chelating agents. The experiments using 100 ppm disodium EDTA in the leachant were used to examine the effect of very strong chelating agent on leaching.

Figure 4.17 shows the leaching curves for Cs-137 from portland I cement containing 5 wt% sodium sulfate leached at 20°C in DIW, oxic and anoxic groundwaters. Figure 4.18 shows the same leaching curves for Cs-137 leached in DIW, plus those for leaching in DIW containing 100 ppm disodium EDTA. In both figures Cs-137 leachability is greatest in DIW. This result is in accord with other findings [9] and was expected [3] because of the high ionic strength of the groundwater leachant. However, it is interesting that the DIW leachant containing disodium EDTA also retards leaching of Cs-137 to about the same extent as oxic groundwater. However, this may be within the normal variation for nominally identical but non-replicate samples. Since the disodium EDTA would not affect the solubility of Cs-137 (it would not decrease the solubility), the increase in ionic strength of the leachant is the only obvious affect that it would have. This conclusion is also suggested from the comparison of oxic versus anoxic groundwater leaching since the anoxic groundwater has a substantially greater ionic strength than does the oxic groundwater (Table 3.3). In sum, increasing the ionic strength of the leachant appears to decrease Cs-137 leachability. Further, the presence of chelating agents and the oxic or anoxic state of the leachant make little, if any, difference in Cs-137 leachability from these waste forms.

Figures 4.19 and 4.20 are the linear correlation plots for the data in Figures 4.17 and 4.18, respectively, on the effect of leachant composition on Cs-137 leachability from portland I cement containing sodium sulfate. Figure 4.19 shows that both the oxic and anoxic groundwaters decrease Cs-137 leachability and increase the statistical scatter compared to leaching in DIW. In contrast, Figure 4.20 shows that Cs-137 leaching in the DIW leachant containing 100 ppm disodium EDTA is retarded but is as reproducible as in DIW itself. Buildup of calcium carbonate on the surface of the waste form from the chemical reaction between the carbonate in the groundwaters and calcium from the cement may cause the scatter in the groundwater leaching results. This surface buildup may also retard leachability if the porosity of the cement is reduced or if sorption of Cs-137 is significant on the carbonate surface.

Figure 4.21 shows the leaching curves for Sr-85 from portland I cement containing 5 wt% sodium sulfate leached at 20°C in DIW, oxic and anoxic groundwaters. Figure 4.22 shows the same leaching curves for Sr-85 leached in DIW and in DIW containing 100 ppm disodium EDTA. In Figure 4.21 Sr-85 leachability is greatest in DIW, while in Figure 4.22 it is greater in the EDTA-containing leachant. The results in Figure 4.21 are in accord with other groundwater leaching results [64-65]. Both the high carbonate content of the groundwater and the high ionic strength of the groundwater leachant are expected to reduce Sr-85 leachability. However, it is interesting that the DIW leachant containing the disodium EDTA increases leaching of Sr-85, as could be expected since the disodium EDTA effectively increases the solubility of Sr-85 by forming soluble chelation complexes. This increase in solubility apparently overcomes the tendency to decrease leachability expected from the increased ionic strength of the leachant (the only obvious affect that it

would have). In sum, carbonate content and increased ionic strength of the groundwater leachant appear to decrease Sr-85 leachability. Further, the presence of the natural chelating agents, i.e., the humic and fulvic acids make little, if any, difference in Sr-85 leachability from these waste forms while the chelating agent EDTA increases Sr-85 leachability.

Figures 4.23 and 4.24 plot the linear correlations of the data from Figures 4.21 and 4.22, respectively, showing the effect of leachant composition on Sr-85 leachability from portland I cement containing sodium sulfate.

No measurable Co-57 activity above background was leached from the waste forms in any of these experiments.

As described in Section 4.2.1 the leaching of sodium, potassium, calcium and strontium was measured from non-radioactive "Blank" waste forms containing sodium sulfate. Figures 4.25, 4.26, 4.27 and 4.28 show the cumulative amounts leached (ppm) versus time for, respectively, sodium, potassium, calcium and strontium from duplicate samples in DIW and in oxic groundwater.

While leaching of potassium and sodium is slightly suppressed by groundwater, the basic curve shape of releases in groundwater are similar to those in distilled water: releases of calcium, however, are markedly different. The groundwater contained 57 ppm calcium at the start of the experiment. Nevertheless, calcium releases in the groundwater are much faster during the first seven days of the experiment, than in the distilled water. After one week, the calcium concentrations in the groundwater remains constant at about 145 ppm. Calcium concentration in the distilled water continues to increase, with a significant change in leach rate occurring between 10 and 16 days. The difference in behavior is caused by solubility limits on the calcium in the groundwater; probably by CaCO_3 precipitation.

Strontium releases are not limited by solubility constraints directly but are significantly reduced in the groundwater. This reduction is probably due to inclusion of strontium in the CaCO_3 precipitate.

Figures 4.29, 4.30, 4.31 and 4.32 plot the linear correlations of the data shown in Figures 4.25-4.28, respectively.

4.2.4 pH of the Leachant. The pH of deionized water (DIW), which is the standard leachant in the ANS 16.1 leach test, is nominally 7 at 20°C but is actually about 6 due to dissolution of carbon dioxide from the air, making the DIW slightly acidic. For cement waste forms the initial pH of the leachant is not maintained since dissolution of soluble material in the cement matrix, primarily calcium hydroxide, shifts the pH higher. To investigate the effect of leachant pH, initial values of 3, 4, 5 and 8 were compared with the nominal leaching results obtained in DIW at pH 6. These results for Cs-137 and Sr-85 leaching from portland I cement waste forms containing 5 wt% sodium sulfate salt are shown in Figures 4.33 to 4.36.

Figure 4.33 shows that the leachability of Cs-137 decreases as initial leachant pH values were made more acidic and more basic than the nominal pH of 6. The decrease in Cs-137 leachability with both decreased and increased leachant pH may be due to the increased ionic strength of the leachant solutions at pH values other than 6 (i.e., pure DIW). However, the last point at pH 8 seems notable in that it is below its expected position, based on comparison with other data. This may be due to more rapid carbonation of the system since carbon dioxide dissolves rapidly in basic solutions. This observation is clear in the linear correlation plot of Figure 4.34. Changing the leachant pH was not promising as an accelerating factor for Cs-137, so the experiments were not pursued.

Figure 4.35 shows the results of changing initial leachant pH on Sr-85 leaching. There is an apparent increase in leachability of Sr-85, which is clearer in the linear correlations plotted in Figure 4.36. These correlations show that acidic leachants may be useful for accelerating Sr-85 leaching since the plots at pH values of 3, 4 and 5 remain linear over the course of the experiments. Part of the acceleration effect may result from reducing carbonation of the system, since carbon dioxide from the air dissolves to a much lesser extent in acidic solution.

No measurable Co-57 activity above background was leached from the cement waste forms in any of these experiments.

As described in Section 4.2.1, the leaching of sodium, potassium, calcium and strontium was measured from nonradioactive "Blank" portland I cement waste forms containing sodium sulfate. However, since changing the initial leachant pH was not an accelerating factor for Cs-137 and was somewhat marginal for Sr-85, no experiments were performed on this waste form type.

4.2.5 Leachant Flow Rate or Replacement Frequency. If the buildup of leached material in the leachant affects leachability, then flow rate or replacement frequency is a factor in accelerated test development. The ANS 16.1 leach test requires daily replacement of leachant through day five following replacements at 2 hours and 7 hours on the first day. After day five the replacement intervals are much longer. To investigate the effect of replacement interval on the leachability of the portland I cement waste forms containing 5 wt% sodium sulfate, daily replacements were continued for 32 days. These results for Cs-137 and Sr-85 leachability are shown in Figures 4.37 through 4.40.

Figure 4.37 presents the Cs-137 leaching data for daily replacements compared to data from testing using the standard replacement intervals. Leachability from the daily replacements is less than from the reference data, but the reproducibility is good for both sets of replicate samples. The difference in Cs-137 leachability between the two sets of data is larger than we had hoped, but is consistent with differences between nominally identical samples that are not actual replicates.

Figure 4.38 plots the linear correlations of the data in Figure 4.37. Only corresponding points are used from the daily replacement data. These data are well correlated and there is no evidence that the buildup of leached

material at the longer replacement intervals affects Cs-137 leaching from these samples.

The effect of daily replacement on Sr-85 leaching from portland I cement containing 5 wt% sodium sulfate is shown in Figure 4.39. Sr-85 leaching is notably greater from the daily replacement experiments than from the reference data at longer intervals. Interestingly, this is the reverse of the relative leaching behavior of Cs-137. Although Sr-85 leaching from the daily replacements starts out, and remains, greater than that from the normal replacements, the divergence increases when the replacement intervals lengthen after day five.

In the linear correlations plotted in Figure 4.40, the divergence between Sr-85 CFL from the daily replacements and that from the longer replacement intervals in the reference ANS 16.1 data is more evident. Specifically, the slope of the line through the last three triplicate data points from the daily replacements noticeably increases compared to that for the first seven triplicate data points.

No measurable Co-57 activity above background was leached in any of these experiments.

As described in Section 4.2.1 the leaching of sodium, potassium, calcium and strontium was measured from nonradioactive "Blank" samples. However, since changing the initial leachant pH was not an accelerating factor for Cs-137 and was a marginal accelerating factor for Sr-85, no experiments were performed on this waste form.

4.2.6 Composition of the Waste Form. Sulfate salts are not totally compatible with portland cements since sulfate is known to attack cement [44,45]. Nevertheless solidification of sulfate evaporator bottoms in portland cements has been a common practice.

The presence of 5 wt% sulfate causes cracking of waste forms after about 100 days of leaching. Figure 4.41 shows the cracking after 330 days leaching. The formation of authigenic minerals growing on the surfaces of the specimen and filling the pores causes swelling, cracking, and ultimately, cracking of the waste form.

Radionuclide releases from cement containing 5 wt% sodium sulfate salt are shown in Figure 4.42 for a set of triplicate specimens. Intersample variability is small, for example 1.4% at the 45-day interval, until cracking of the waste form began at about 100 days. Comparison of these data with the baseline samples, (also shown in Figure 4.42) shows that Cs-137 leaching is faster from the samples containing waste than from those without waste.

To determine if the leaching mechanism of cement was altered by inclusion of waste, the CFL for Cs-137 from samples without waste was plotted against the CFL of samples that contained Na_2SO_4 . Figure 4.43 indicates that a linear relationship exists between releases from the two types of samples.

There was no change in leaching mechanism. The slope of the line for specimens containing waste is approximately 1.15, indicating a small increase in leach rate.

Typical of cement, Sr-85 releases are significantly lower than those of Cs-137. Figure 4.44 shows the CFL for Sr-85 from baseline specimens and cement specimens containing Na_2SO_4 . During the first 90 days of the tests, Sr-85 from the specimens with the Na_2SO_4 leached slightly slower than from the baseline specimens. These differences are significant at the 95% confidence interval. After 90 days the scatter in the sulfate samples increases dramatically as do their release rates relative to the baseline: this is caused by cracking of the sample due to the sulfate salt.

Figure 4.45 shows Sr-85 CFL data for sulfate samples plotted against the baseline Sr-85 CFL. The slope of this curve is quite different than that of Cs-137 (Figure 2). Sample depletion is not a factor for Sr-85 since CFL never reached 10%. The relationship between sulfate and baseline samples is linear until a baseline CFL of 0.035 is reached, equivalent to 46 days leaching. After this point the Sr-85 releases from the two types of samples dramatically depart from a linear relationship. Cracking and swelling were observed in these samples shortly after the leach rate began to increase.

Plots of CFL vs Time, as in Figure 4.44 indicate that Sr-85 releases from samples containing Na_2SO_4 are initially slightly lower than the baseline but then begin to increase rapidly, as does the scatter among the samples, when swelling and cracking begins. The effect of disruption of the solid specimen is more acute in the Sr data than in the Cs. By the time the samples begin to crack most Cs has leached out, so that the cracks expose areas already depleted in Cs. However, Sr only lost about 3% of its original concentration so the cracks open areas of high Sr concentrations, leading to greater release rates of this nuclide. Figure 4.46 shows Sr-85 CFL plotted against Cs-137 CFL for a specimen without waste, to clarify the differences in leaching mechanisms of the two radionuclides. This figure shows a linear relationship among the data points representing daily sampling intervals (Region A). With the change in sampling interval, a second linear region (Region B) develops with a lower release rate for strontium. This region extends to the end of the Sr-85 data at 130 days. The causes of this change in behavior are probably related to carbonate formation on the surface of the specimen [1] and is discussed further in the solid phase section of this report.

Treating the data from a specimen containing sulfate waste in the same manner illustrates the difference in Sr-85 leaching behavior between specimens with and without waste. Figure 4.47 shows that Regions A and B are also present in a specimen containing waste. In both regions, however, the slopes are lower than in their respective regions for the base line specimen indicating that Sr-85 releases are lower (relative to Cs-137 releases) from specimens containing sulfate than from the baseline. More importantly, a third region developed where Sr-85 leaching accelerated relative to Cs-137, illustrating the affects of cracking.

No measurable Co-57 activity above background was leached from the cement waste forms in any of these experiments.

Elemental composition data for leachate from nonradioactive samples of portland cement containing Na_2SO_4 are presented in Figure 4.48. The calcium concentrations are of particular interest. During the first 40 to 60 days of leaching, calcium releases from the sulfate samples are significantly lower than calcium from the baseline. Later, release rates are much higher. Sulfate in the specimen probably reacts with free calcium to form $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or with aluminum and calcium to form ettringite. Only later, when the sulfate causes the cement to crack, does calcium leaching increase. Conductance values for samples containing Na_2SO_4 salt were extremely high compared to those of the baseline indicating that large quantities of additional ions from the salt were released.

4.2.7 Ratio of the Volume to Surface Area of the Waste Form (V/S). As reviewed in section 2.7, under certain conditions, small-scale test specimens can be used to accelerate the leaching that would be expected from full-scale waste forms. There are data that support the use of small-scale test samples to accelerate leaching from cement waste forms containing various types of bulk waste, including sulfate salts [19,20,22]. The ANS 16.1 leach test specifies that the minimum dimensions of the sample must be one cm. Experiments were performed using small-scale samples of various sizes to evaluate decreasing size (i.e., decreasing V/S) as an accelerating factor, and to determine how small the samples can be and still produce reliable data. These results for Cs-137 and Sr-85 leaching from portland I cement waste forms containing 5 wt% sodium sulfate salt are shown in Figures 4.49 through 4.52.

The Cs-137 leaching results (Figure 4.49) indicate that leachability increases as V/S decreases sodium sulfate. The increase in Cs-137 leachability with decreasing V/S appears to saturate, or become ineffective, as V/S decreases below approximately 0.6, since there is no significant difference in Cs-137 leachability between the samples at V/S values of 0.61 and 0.42. However, this data may be misleading, because the specimens with V/S = 0.61 are disc-shaped as opposed to cylinders. Since the aspect ratio of height to diameter is not consistent with those of other V/S ratios, these specimens may become depleted too rapidly. Also, smaller specimens will require a sampling schedule that is more intensive in the early part of the experiment.

Figure 4.51 shows the results of changing the ratio of waste form volume to surface area (V/S) on Sr-85 leaching for the portland I cement waste forms containing 5 wt% sodium sulfate. There is an increase in leachability of Sr-85, which is clearer in the linear correlations plotted in Figure 4.52. These correlations show that decreasing V/S may be useful for accelerating Sr-85 leaching since the plots at V/S values of 1.85 remain linear over the course of the experiments, while those at V/S values of 0.61 and 0.42 remain linear until the samples begin to be affected by carbonation.

No measurable Co-57 activity above background was leached from the waste forms in any of these experiments.

4.2.8 Effect of Surface Condition and Porosity. No direct information on waste form porosity is available. This is not a factor one can alter to provide acceleration; it can only be observed. It is unclear to what extent surface coatings on cement waste forms significantly influence radionuclides releases. There is compelling evidence that under some conditions, there are controls on Sr-85 releases exerted by calcium carbonate coatings that form during leaching in seawater [66]. Other data are show that carbonate reaction rims, that form on portland cement in distilled water, have a greater capacity to sorb Cs-137 compared to solidified cement [62].

When sulfate waste is included in the cement, the surfaces that develop are structurally different, but there are no data to assess its effect on leaching. Preliminary analysis of cement containing 5 wt% Na_2SO_4 has been done and results provide some insight into the processes that occur in this material during immersion in water.

Before immersion, the surface of the cement waste form containing 5 wt% sodium sulfate salt looked similar to that of the baseline cement sample which contained no added salt (Figure 4.53). Even at high magnification, no discrete particles of salt were observed. Figure 4.54 shows the typical texture of cement, with intergrown fibrils that form the bonds that give cement its strength. Elemental analysis of the surface shows some enrichment of sulfur. A low intensity sodium peak also was observed in the salt-containing sample, whereas none was seen in the baseline sample. Before leaching, pores and bubbles in the salt-containing cement were empty or occasionally exhibited a few portlandite crystals, as was the case with unleached samples of plain cement.

After immersion for 55 days at 50°C a replicate of the sample discussed above was examined: slight cracking around the bottom of the sample was noted. Figure 4.55 shows the leached surface at a magnification of 400 times and Figure 4.56 at 1900 times. Before leaching, this surface was porous and open, now was covered by a profuse growth of crystals. Little porosity was evident.

Cut surfaces from inside this waste form also were examined. Figure 4.57 shows a sample of this material, taken about 2 mm from the surface. There is much cracking, apparently the result of swelling. No grains of salt were found. On examining this section at high magnification and using EDS, distinct chemical differences were found. Areas near the cracks were depleted of sulfur compared to spectra of the unleached cement/sulfate salt waste form, implying that there was significant mobility of sulfate in the cement after curing and during leaching.

Examination of larger bubbles, which were empty in the unleached sample, revealed that most were filled with crystals. Figure 4.58 shows a typical bubble at magnification of 400 times. The spectrum shown in Figure 4.60 is from an EDS analysis of a single crystal in this cavity. It is significantly different than the spectrum of the unleached waste form: no potassium or sodium are observed and the silicon peak is much reduced. The sulfur from the waste had apparently reacted with aluminum, silicon and calcium to form one or two phases that preferentially grew into the open cavities in the waste form.

Most of this growth may be ettringite and gypsum, but x-ray diffraction mineralogy of this material has not been performed.

Comparison of the bulk chemical composition of the leached surface (Figure 4.61) with a single crystal from inside an air bubble (Figure 4.60) showed essentially identical spectra. The surface is composed entirely of this crystalline mineral, with no other material observable by EDS. This surface, however, is chemically different than the bulk leached cement containing sodium sulfate. Figure 4.62 is an EDS spectrum of the center of the specimen from which the surface spectrum was obtained. There is much more silicon present and the mobile elements, sodium and potassium are also present. This spectrum is similar to that of unleached material.

The great diversity of chemistry from the outer surface to the interior of the same specimen and between leached and unleached specimens, compounded by structural differences, do not appear to cause any significant alteration of the leaching mechanism of Cs-137. Activation energies and leach rates are quite similar for Cs-137 from plain cement and from cement containing sodium sulfate (and the reaction products of the cement and the salt). More work is necessary to confirm this opinion.

Figure 4.1

Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.

Figure 4.2

Linear correlation plots for Cs-137 leaching from portland I cement containing 5 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.

Figure 4.3

Arrhenius plot of Cs-137 incremental leach rates from portland I cement containing 5 wt% sodium sulfate leached at 20, 40 and 50°C in deionized water.

Figure 4.4

Linear correlation plots for Cs-137 leaching from pure portland I cement at 20, 30, 40, 50 and 70°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.

Figure 4.5 Arrhenius plot of Cs-137 incremental leach rates from pure portland I cement leached at 20, 30, 40, 50 and 70°C in deionized water.

Figure 4.6 Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20, 40 and 50°C leached in deionized water.

Figure 4.7

Linear correlation plots for Sr-85 leaching from portland I cement containing 5 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.

Figure 4.8

Arrhenius plot of Sr-85 incremental leach rates from portland I cement containing 5 wt% sodium sulfate leached at 20, 40 and 50°C leached in deionized water.

Figure 4.9

Sodium cumulative amount (ppm) leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20 and 50°C. Samples were leached in deionized water.

Figure 4.10

Potassium cumulative amount (ppm) leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20 and 50°C. Samples were leached in deionized water.

Figure 4.11

Calcium cumulative amount (ppm) leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20 and 50°C. Samples were leached in deionized water.

Figure 4.12

Strontium cumulative amount (ppm) leached vs. time from portland I cement containing 5 wt% sodium sulfate at 20 and 50°C. Samples were leached in deionized water.

Figure 4.13 Linear correlation plot for sodium, potassium and Cs-137 leaching at 20 and 50°C from portland I cement containing 5 wt% sodium sulfate. Correlations are relative to the Cs-137 data. Samples were leached in deionized water.

Figure 4.14 Linear correlation plot for strontium and Sr-85 leaching at 20 and 50°C from portland I cement containing 5 wt% sodium sulfate. Correlations are relative to the Sr-85 data. Samples were leached in deionized water.

Figure 4.15

Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.

Figure 4.16

Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.

Figure 4.17

Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW, oxidic and anoxic ground waters at 20°C.

Figure 4.18

Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.

Figure 4.19

Linear correlation plots for Cs-137 leached from portland I cement containing 5 wt% sodium sulfate leached in DIW, oxic and anoxic ground waters at 20°C. Correlations are relative to the DIW data.

Figure 4.20

Linear correlation plots for Cs-137 leached from portland I cement containing 5 wt% sodium sulfate leached in DIW and DIW containing 100 ppm disodium EDTA at 20°C. Correlations are relative to the DIW data.

Figure 4.21

Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW, oxic and anoxic ground waters at 20°C.

Figure 4.22

Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.

Figure 4.23

Linear correlation plots for Sr-85 leached from portland I cement containing 5 wt% sodium sulfate in DIW, oxidic and anoxic ground waters. Correlations are relative to the DIW data. Samples were leached at 20°C.

Figure 4.24

Linear correlation plots for Sr-85 leached from portland I cement containing 5 wt% sodium sulfate in DIW and DIW containing 100 ppm disodium EDTA at 20°C. Correlations are relative to the DIW data.

Figure 4.25

Sodium cumulative amount leached (ppm) vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and oxic ground water at 20°C.

Figure 4.26

Potassium cumulative amount leached (ppm) vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and oxic ground water at 20°C.

Figure 4.27

Calcium cumulative amount leached (ppm) vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and oxic ground water at 20°C.

Figure 4.28

Strontium cumulative amount leached (ppm) vs. time from portland I cement containing 5 wt% sodium sulfate leached in DIW and oxic ground water at 20°C.

Figure 4.29

Linear correlation plots for Sodium leached from portland I cement containing 5 wt% sodium sulfate in DIW and oxic ground water at 20°C. Correlations are relative to the DIW data.

Figure 4.30

Linear correlation plots for Potassium leached from portland I cement containing 5 wt% sodium sulfate in DIW and oxic ground water at 20°C. Correlations are relative to the DIW data.

Figure 4.31

Linear correlation plots for calcium leached from portland I cement containing 5 wt% sodium sulfate in DIW and oxic ground water at 20°C. Correlations are relative to the DIW data.

Figure 4.32

Linear correlation plots for Strontium leached from portland I cement containing 5 wt% sodium sulfate in DIW and oxic ground water at 20°C. Correlations are relative to the DIW data.

Figure 4.33

Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.

Figure 4.34

Linear correlation plots for Cs-137 leached from portland I cement containing 5 wt% sodium sulfate in leachants with initial pH values of 3, 4, 5, 6 and 8. Correlations are relative to the pH 6 (DIW) data. Samples were leached at 20°C.

Figure 4.35

Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.

Figure 4.36

Linear correlation plots for Sr-85 leached from portland I cement containing 5 wt% sodium sulfate in leachants with initial pH values of 3, 4, 5, 6 and 8. Correlations are relative to the pH 6 (DIW) data. Samples were leached at 20°C.

Figure 4.37

Cs-137 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for portland I cement waste forms containing 5 wt% sodium sulfate leached at 20°C.

Figure 4.38

Linear correlation plots for Cs-137 leached at 20°C using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule for portland I cement waste forms containing 5 wt% sodium sulfate.

Figure 4.39

Sr-85 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for portland I cement waste forms containing 5 wt% sodium sulfate leached at 20°C.

Figure 4.40

Linear correlation plots for Sr-85 leached at 20°C using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule for portland I cement waste forms containing 5 wt% sodium sulfate. Correlations are relative to the ANS 16.1 data.

Figure 4.41

Portland I cement waste forms containing 5 wt % sodium sulfate. The one at left is as fabricated. The one at right was leached for 403 days in deionized water at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.

Figure 4.42

Cs-137 cumulative fraction leached vs. time from portland I cement waste forms containing 5 wt% sodium sulfate and from pure portland I cement at 20°C.

Figure 4.43

Linear correlation plots for Cs-137 leached at 20°C for portland I cement waste forms containing 5 wt% sodium sulfate and pure portland I cement. Correlations are relative to pure cement.

Figure 4.44

Sr-85 cumulative fraction leached vs. time from portland I cement waste forms containing 5 wt% sodium sulfate and from pure portland I cement at 20°C.

Figure 4.45

Linear correlation plots for Sr-85 leached at 20°C for portland I cement waste forms containing 5 wt% sodium sulfate and pure portland I cement. Correlations are relative to pure cement.

Figure 4.46

Linear correlation plot for Sr-85 versus Cs-137 leaching at 20°C for pure portland I cement.

Figure 4.47

Linear correlation plot for Sr-85 versus Cs-137 leaching at 20°C for portland I cement containing 5 wt% sodium sulfate.

Figure 4.48

Leaching curves of cumulative release (ppm) vs. time of sodium, potassium, calcium and strontium from portland I cement containing 5 wt% sodium sulfate. Samples were leached at 20°C in deionized water.

Figure 4.49

Cs-137 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.61, 0.85 and 1.85. Samples were leached in deionized water at 20°C.

Figure 4.50

Linear correlation plots for Cs-137 leached from portland I cement containing 5 wt% sodium sulfate at waste form volume to surface area ratios of 0.42, 0.61, 0.85 and 1.85. Correlations are relative to V/S = 0.85. Samples were leached in deionized water at 20°C.

Figure 4.51

Sr-85 cumulative fraction leached vs. time from portland I cement containing 5 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.61, 0.85 and 1.85. Samples were leached in deionized water at 20°C.

Figure 4.52

Linear correlation plots for Sr-85 leached from portland I cement containing 5 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.61, 0.85 and 1.85. Correlations are relative to V/S = 0.85. Samples were leached in deionized water at 20°C.

Figure 4.53

Outer surface of an unleached cement sample containing 5% sodium sulfate at a magnification of 400 times. This surface is indistinguishable from that of unleached pure cement.

Figure 4.54

Outer surface of an unleached cement sample containing 5% sodium sulfate at a magnification of 4700 times.

Figure 4.55

Outer surface of a cement sample containing 5% sodium sulfate after static leaching for 55 days at 50°C. Magnification is 400 times. Profuse crystal growth covers the surface.

Figure 4.56

Outer surface of a cement sample containing 5% sodium sulfate after static leaching for 55 days at 50°C. Magnification is 1900 times.

Figure 4.57

Interior of a cement sample containing 5% sodium sulfate after static leaching for 55 days at 50°C. This is a cut sample from 2 mm inside the outer edge. Note the many cracks.

Figure 4.58

A bubble, after leaching, was full of crystals. This was typical of voids in the sample.

Figure 4.59

EDS spectrum of the outer surface of unleached cement sample containing 5% sodium sulfate. Note that small sodium and potassium peaks are present and that sulfur is enriched compared to pure cement.

Figure 4.60

EDS spectrum of one of the crystals from Figure 4.58. This spectrum is significantly different from that of the unleached cement containing sodium sulfate shown in Figure 4.59. Sulfur and aluminum are enriched while silicon is depleted relative to the unleached composition.

Figure 4.61 EDS spectrum of the leached surface of cement containing 5% sodium sulfate using a large analytical area. This spectrum is identical to that in Figure 4.60 from a single crystal in a pore.

Figure 4.62 EDS spectrum of the center of the leached specimen. This more closely resembles the spectrum of the unleached material, Figure 4.59, than it does the leached surface, Figure 4.60.

5. PORTLAND I CEMENT CONTAINING INCINERATOR ASH AS SIMULATED WASTE

Portland cement, alone or blended with additives to enhance radionuclide retention, is the most commonly used solidification agent for low-level radwaste. Portland cement solidifies as the result of hydration reactions with water to form a porous, hydrophilic matrix of high surface area. The physical and chemical properties of portland cement have been well documented [45-50].

In general, portland cement shows a rapid release of cesium in leaching experiments while strontium and cobalt leach substantially less readily [1-3,10,11,29,51-58]. As a result, sorbents for cesium are commonly blended with cement to reduce its leachability [51-61]. These blended cement + sorbent mixtures often are formulated for specific waste streams.

This section presents data and results obtained from leaching studies investigating the factors deemed potentially important for LLW forms, as discussed in Section 2 of this report, for waste forms consisting of portland I cement containing 15 wt% incinerator ash as simulated waste.

5.1 Leaching Mechanisms

The overview presented in Section 4.1 summarizes the leaching mechanisms for cement, determined from the literature survey [1] and from the experimental work in this task.

5.2 Factors that Affect Leaching

Leaching results from experiments designed to investigate each of the factors listed in Table 2.1 for the cement waste forms containing incinerator ash are discussed in the following sections. The basis for evaluating the effect of each of the factors is a comparison with the results of tests on standard samples, i.e., 4.8 cm diameter by 6.4 cm high right cylinders, at 20°C in deionized water. Replicate tests, generally triplicates, provided a measure of the variability of the data.

5.2.1 Temperature. The effect of temperatures between 20 and 50°C on the leachability of portland I cement waste forms containing 15 wt% incinerator ash was investigated. Activation energies for cesium and strontium were calculated from the elevated temperature data, based on the assumption that diffusion is the leaching mechanism and the rate constant is proportional to the release rate. An activation energy of 4 to 6 kcal/mole would be expected for pure diffusion of simple ions in water solution. Temperature had no effect on cobalt leaching in these studies, in that cobalt was not observed in any of the leachates.

Figures 5.1, 5.2 and 5.3 summarize the effect of temperature on the leaching of Cs-137. Figure 5.1 presents the cumulative fraction leached (CFL) versus time for the triplicate samples at 20 and 50°C, and the duplicate samples at 40°C. Figure 5.2 plots linear correlations of these data versus

the 20° C data. Figure 5.3 is an Arrhenius plot of the incremental leach rates of these data.

Figure 5.1 shows that increasing temperature only slightly increases Cs-137 leachability. Also, the reproducibility, as indicated by the scatter of data at the same temperature, is decidedly better for the 20°C data than for the data at 40° and 50°C.

The correlation plots in Figure 5.2 indicate that the two 40°C data curves remain linear with respect to the 20°C data up to 0.3 CFL, while the 50°C data deviate from linearity beyond approximately 0.25 CFL. Since the 40°C data correlate with the 20°C data up to releases of approximately 0.3 CFL, depletion seems to be the cause of the deviation from linearity for the 50°C data. It has not been determined whether the deviation from linearity for the 40° and 50°C data results from a change in the leaching mechanism.

In the Arrhenius plots of Figure 5.3, least-squares lines were drawn through the 20, 40 and 50°C data for each leachant replacement interval. Since the leach rate generally decreases with time, the least-squares lines for each of the replacements proceed down the figure. Table 5.1 lists the apparent activation energies calculated from the slopes of these lines. The points for replacements 8 through 12 are not included. Scanning down the list in Table 5.1 suggests that the apparent activation energy, E_a , is near 4 to 6 kcal/mole through leachant replacement interval 7; a dashed line appears between the data for intervals 7 and 8. Starting with interval 8, the E_a values decrease and become erratic, indicating that factors other than the activated diffusion process are affecting the leach rates. Depletion of both the 40° and 50°C samples seems a most likely cause. Therefore, the E_a value for the process ($E_a = 4.9 \pm 1.5$ kcal/mole) is taken to be the average of the individual E_a values for replacement intervals 1 through 7 (Table 5.1). The activation energies for higher energy processes cannot be calculated because the exact form of the rate equation is not known. The average E_a of 4.7 ± 1.5 kcal/mole is consistent with that for diffusion of simple ions in water solution (4-6 kcal/mole).

Leaching at elevated temperature also was performed on portland type I cement samples containing radiotracers but NO simulated bulk waste. See Sections 4.2.1.1 and 4.2.1.2 for these data and accompanying discussions.

Figures 5.4, 5.5 and 5.6 summarize the effect of temperature on the leaching of Sr-85 from portland I cement waste forms containing 15 wt% incinerator ash. Figure 5.4 presents the cumulative fraction leached (CFL) versus time for the triplicate samples at 20 and 50°C and the duplicate samples at 40°C. Figure 5.5 plots linear correlations of these data versus the 20°C data. Figure 5.6 is an Arrhenius plot of the incremental leach rates.

Table 5.1

Apparent Activation Energies at each Leachant Replacement Interval for Sr-85
and Cs-137 From Portland I Cement Containing 15 Wt% Incinerator Ash

Interval	Time (d)	<u>E_a (Sr-85)</u>		<u>E_a (Cs-137)</u>	
		<u>kcal</u> <u>mole</u>	<u>J</u> <u>mol</u>	<u>kcal</u> <u>mole</u>	<u>J</u> <u>mol</u>
1	0.083	32.2	134.7	2.44	12.3
2	0.29	20.3	84.9	5.84	24.4
3	1	16.8	70.2	6.95	29.1
4	2	12.8	53.5	4.72	19.2
5	3	13.3	55.8	5.58	23.2
6	4	10.3	43.0	2.75	11.5
7	5	11.1	46.3	5.21	21.8

8	11	8.00	33.4	-17.9	-34.0
9	18	7.40	33.1	8.13	34.0
10	32	-0.09	-0.377	-7.85	-3.28
11	46	3.76	15.7	0.536	2.24
12	67	4.53	19.0	-2.22	-9.29
13	88	5.13	21.6	-14.8	-6.21
14	104	2.24	9.53	-2.59	-10.8

Figure 5.4 shows that increasing temperature increases the leachability of Sr-85. The reproducibility, is somewhat better for the 20 and 40°C data than for that at 50°C. Although temperature clearly accelerates leaching of Sr-85, the lack of reproducibility limits its value as an accelerating factor.

Although the initial portions of the 40 and 50°C data curves are linear with respect to the 20°C data, the correlation plots in Figure 5.5 show that they deviate from linearity as the replacement intervals become longer than a week (i.e., approximately at replacement interval 9). Depletion cannot be the cause of the deviation from linearity, as the CFL is less than 20%. It is probable that the deviation from linearity for these data results from carbonation of the surface of the waste form, which could reduce the solubility of strontium and thus reduce its leachability. This is a particularly likely mechanism since strontium is contained naturally in cement in amounts well above the trace levels of radiostrontium present in radwaste.

In the Arrhenius plots of Figure 5.6, least-squares lines were drawn through the 20, 40 and 50°C data at each replacement interval. Since the leach rate decreases with time, the least-squares line for each of the replacements proceed down the figure. Table 5.1 lists the apparent activation energies calculated from the slopes of these lines. These energies are not consistent with those expected for pure diffusion, but imply the existence of other mechanisms for the release of strontium. Since the mechanisms are unknown for strontium release, the proper form of the rate equation and the temperature dependence of the rate constant cannot be determined.

Cobalt-60, along with Cs-137 and Sr-90, is a radionuclide of concern in LLW. Co-57 was included as an analog of Co-60 in sample formulations for the test specimens containing radioactivity. No Co-57 activity above background was seen in any of the leachates for the cement samples containing sodium sulfate as simulated waste.

The leaching of sodium, potassium, calcium and strontium was measured from portland I cement waste forms containing 15 wt% incinerator ash but no radiotracers. These "Blanks" were otherwise nominally identical to the samples containing radiotracers. Previous results [2,3,29] showed that the first three elements listed above comprise the bulk of leachable cations from cement while the strontium that is in cement naturally may affect the leaching of radiostrontium. In the cement waste forms containing incinerator ash, the leached sodium comes from both the cement and from the ash.

Figures 5.7, 5.8, 5.9 and 5.10 show the cumulative amounts leached (ppm) versus time plots for, respectively, sodium, potassium, calcium and strontium from duplicate portland I cement blanks containing 15 wt% incinerator ash in deionized water at 50°C. The data for the experiments at 20°C are included for comparison. The sodium and potassium data are similar in that they all show "typical" leaching curves--i.e., monotonically increasing at a decreasing rate. However, calcium behaves differently. Specifically, calcium leaches at a linear release rate. Strontium leaches at a monotonically decreasing rate, but the shapes of the curves are clearly different from those of sodium and potassium. Possibly, strontium release can be separated into two rate

components, a monotonically decreasing component and a constant rate component.

Figure 5.11 is the correlation plot of sodium and potassium leaching from the blanks compared to the Cs-137 leaching from nominally identical portland I cement waste forms containing 15 wt% incinerator ash.

Figure 5.12 is the correlation plot for strontium leaching from the blanks compared to the Sr-85 leaching from the nominally identical waste forms containing 15 wt% incinerator ash doped with radiotracers.

5.2.2 Ratio of Waste Form Surface Area to Leachant Volume. The ANS 16.1 leach test procedure specifies that the ratio of the leachant volume (cubic cm) to the geometric surface area (square cm) of the specimen be 10 ± 0.2 (cm). To investigate the effect of increasing this ratio on leaching behavior, ratios of 20, 30 and 50 were compared with results from the usual ratio of 10 for cement incorporating sodium sulfate. These experiments were not performed for cement with incinerator ash.

5.2.3 Composition of the Leachant. Deionized water (DIW) was the standard leachant used in the ANS 16.1 Leach Test. Leachants used to examine the effect of its composition on the leaching of portland I cement waste forms containing 15 wt% incinerator ash were DIW and a simulated oxic groundwater from Oak Ridge National Lab (ORNL) [63]. The mineral content of the ORNL groundwater is listed in Table 3.3. The oxic groundwater contained soil-extracted humic and fulvic acids to make the compositions more realistic. Humic and fulvic acids have strong affinities for metal ions and can act as complexing and chelating agents.

Figure 5.13 shows the leaching curves for Cs-137 from portland I cement containing 15 wt% incinerator ash leached at 20°C in DIW, and oxic groundwaters. Figure 5.14 shows the correlation plot for these data, which is in accord with other groundwater leaching results [64,65] and is expected [3] because of the high ionic strength of the groundwater leachant. In sum, increasing the ionic strength of the leachant decreases Cs-137 leachability. Further, the presence of humic and fulvic acids and the oxic state of the leachant make little, if any, difference in Cs-137 leachability from these waste forms.

Figure 5.15 shows the corresponding leaching curves for Sr-85. Figure 5.16 shows the linear correlation plot for these data. The Sr-85 leachability is greatest in the oxic groundwater. This disagrees with other groundwater leaching results [64,65] and was not expected [3] because of the high ionic strength of the groundwater leachant. In sum, increasing the ionic strength of the leachant should decrease Sr-85 leachability, but the presence of humic and fulvic acids and the oxic state of the leachant enhanced the Sr-85 leachability.

No measurable Co-57 activity above background was leached from the waste forms containing incinerator ash in any of these experiments.

As described in Section 5.2.1, the leaching of sodium, potassium, calcium and strontium was measured from nonradioactive "Blank" portland I cement waste forms containing incinerator ash.

Figures 5.17, 5.18, 5.19 and 5.20 show the cumulative amounts leached (mg) versus time for, respectively, sodium, potassium, calcium and strontium from duplicate cement samples containing 15 wt% incinerator ash leached in oxic groundwater. Sodium and potassium continuously increase at a decreasing rate. Calcium and strontium leaching continuously increased up to the fifth day, after which the cumulative release was nearly constant. At this point, leaching may be limited by the formation of insoluble carbonates.

Figures 5.21, 5.22, 5.23 and 5.24 plot the linear correlations of the data shown in Figures 5.17-5.20, respectively.

5.2.4 pH of the Leachant. The pH of deionized water (DIW), the standard leachant in the ANS 16.1 leach test, is nominally 7 at 20°C but is actually about 6 due to dissolution of carbon dioxide from the air which makes the DIW slightly acidic. For cement waste forms, the initial pH of the leachant is not maintained since dissolution of soluble material from the cement matrix, primarily calcium hydroxide, shifts the pH higher. To investigate the effect of leachant pH, initial pH values of 4 and 8 were compared with the nominal leaching results obtained in DIW at pH 6. The results for Cs-137 and Sr-85 are shown in Figures 5.25 to 5.28.

Figure 5.25 indicates that the leachability of Cs-137 decreases as initial leachant pH values were made more acidic and more basic than the nominal pH of 6 for DIW. The apparent decrease in Cs-137 leachability with both decreased and increased leachant pH may be due to the increased ionic strength of the leachant solutions at pH values other than 6, as is clear in the linear correlation plot of Figure 5.26. Changing the leachant pH was not promising as an accelerating factor for Cs-137, so the experiments were not pursued.

Figure 5.27 shows the results of changing initial leachant pH on Sr-85 leaching for the portland I cement waste forms containing 15 wt% incinerator ash. There is an apparent decrease in leachability, which is clearer in the linear correlations plotted in Figure 5.28. These correlations show that acidic leachants are not useful for accelerating Sr-85. The alkaline solution (pH=8) severely decreases leaching of Sr-85, probably due to formation of carbonates.

No measurable Co-57 activity above background was leached from the waste forms containing incinerator ash in any of these experiments.

As described in Section 5.2.1, the leaching of sodium, potassium, calcium and strontium was measured from nonradioactive "Blank" portland I cement waste forms containing 15 wt% incinerator ash. However, since changing the initial leachant pH was not an accelerating factor for Cs-137 and had only marginal potential for Sr-85, no experiments varying the initial leachant pH were performed on this waste form.

5.2.5 Leachant Flow Rate or Replacement Frequency. If the buildup of material in the solution affects leachability, then the flow rate or replacement frequency of the leachant is a factor in accelerated test development. The ANS 16.1 leach test provides for daily leachant replacement through day five following replacements at 2 hours and 7 hours the first day. After day five the leachant replacement intervals are much longer. To investigate the effect of continuous leachant flow versus periodic replacement the portland I cement waste forms containing 15 wt% incinerator ash were leached using a flow experiment based on the MCC4S flow test, described in the Material and Methods section 2.3.3.

Figure 5.2 shows the release rates of Cs-137 leached from portland I cement containing 15 wt% incinerator ash versus time are shown in Figure 5.29. The release rates from cement containing incinerator ash from the modified ANS 16.1 testing procedure are shown for comparison. The release rates from both experiments were very similar, but there is greater scattering in the flow experiment data. No useful degree of acceleration in the leach rates were observed.

The release rates of Sr-85 leached from portland I cement containing 15 wt% incinerator ash versus time are shown in Figure 5.30. The release rate results from the modified ANS 16.1 procedure are also shown for comparison. The Sr-85 release rates are generally an order of magnitude lower than those for Cs-137. The Sr-85 results for the flow test and modified ANS 16.1 are very similar, with a greater degree of scattering in the flow test data. No useful degree of accelerated leaching was observed for Sr-85 by the flow test.

No measurable Co-57 activity above background was leached from the portland I cement waste forms containing 15 wt% incinerator ash. No experiments with continuously flowing leachant were performed to measure the release of nonradioactive elements.

5.2.6 Composition of the Waste Form. Incinerator ash forms voids on solidification of portland I cement waste forms [28] when the waste form cures by dehydration of the ash and water slurry during the solidification. Interaction of the ash and the cement does not appear to affect the leaching properties of the cement matrix at room temperature. No adverse effects on the physical integrity of the waste forms were observed after 320 days of leaching in deionized water. Figure 5.31 shows a waste form sample of portland I cement containing 15 wt% incinerator ash before and after 320 days of leaching in deionized water at 20°C: no changes were apparent, except for a darkening in color.

Radionuclide releases from cement containing 15 wt% incinerator ash are shown in Figure 5.32, for triplicate specimens. Variability between the samples was small (<5% at the 45 days). The leaching data for cement containing incinerator ash was compared to the results for neat cement. Up to 100 days the cement waste containing incinerator ash specimens leached faster. After 100 days Cs-137 leaching decreased for the samples containing incinerator ash waste. At 320 days the average ash sample CFL was 0.61 while that of pure cement was about 0.72. The scatter of the leaching data from samples with ash was small, with a 95% confidence interval of 3.4%.

To determine if the leaching mechanism of cement was altered by inclusion of ash waste, the CFL for Cs-137 from samples with waste was plotted against the CFL of samples without waste (Figure 5.33). The result is a continuously decreasing curve which is clearly nonlinear, implying that the leaching mechanism of cesium from cement samples containing ash differs from that of the neat cement samples. This difference may be attributed to two properties of the ash: (i) sorption of the radionuclide or (ii) pozzolanic reactions with the cement. The high release rates, compared to Cs-137 releases from neat cement, during the first few weeks of leaching followed by a rapid decrease in the release rate tend to favor the latter interpretation. The porosity of cement and ash specimens appears to be large before leaching as shown in Figure 5.31. How porosity is modified during leaching is under investigation.

The Sr-85 leaching results are shown in Figure 5.34 for triplicate specimens of cement containing 15 wt% incinerator ash. Radioactive decay limits the detection of this isotope to about 150 days from specimens without waste, whereas specimens with incinerator ash contained a larger source term and the Sr-85 remained detectable to over 300 days of leaching. Compared with the baseline samples of neat cement these data showed lower leaching with inclusion of the incinerator ash waste. Ideal behavior for waste form leaching controlled solely by diffusion of radionuclides from the matrix would show no difference in the leaching curves. Figure 5.35 is the linear correlation plot of the leaching results for Sr-85 from cement containing incinerator ash compared to the results for neat cement. The curvature of the data for cement containing incinerator ash indicates a departure from ideal behavior. Figure 5.36 shows a linear correlation plot of Sr-85 versus Cs-137 from portland I cement containing 15 wt% incinerator ash and neat cement. Why the Sr-85 release rate increased while the Cs-137 rate decreased is unclear.

No measurable Co-57 activity was leached from the cement waste forms containing incinerator ash in these experiments.

Figure 5.37 shows the leaching curves of cumulative release (ppm) vs. time for sodium, potassium, strontium and calcium from cement containing 15 wt% incinerator ash. The sodium and potassium data are similar, showing "typical" leaching curves, i.e., monotonically increasing at a decreasing rate. However, the calcium behaves differently, the releases increasing linearly with time to 320 days.

5.2.7 Ratio of Volume to Surface Area in the Waste Form (V/S). As reviewed in section 2.7, small-scale test specimens, under certain conditions, can be used to accelerate the leaching that would be expected from full-scale waste forms. There are data that support the use of small-scale test samples to accelerate leaching from cement waste forms containing various types of bulk waste, including incinerator ash [19,20,22]. The ANS 16.1 leach test specifies that the sample must have minimum dimensions of one cm. Experiments were performed using small-scale samples of various sizes to evaluate decreasing size (i.e., decreasing V/S) as an accelerating factor and to determine how

small the samples can be and still produce reliable data. These results for Cs-137 and Sr-85 leaching from portland I cement waste forms containing 15 wt% incinerator ash are shown in Figures 5.38 to 5.39.

The Cs-137 leaching results shown in Figure 5.38 indicate that leachability increases as V/S decreases. The increase in Cs-137 leachability with decreasing V/S appears to saturate, or become ineffective, as V/S falls below approximately 0.6, since there is no significant difference between the samples at V/S values of 0.61 and 0.42. Samples with a V/S ratio of 0.61 were disks that are expected to deplete more rapidly than right cylinders. However, the difference in aspect ratio of the disk may make this data misleading. The scattering in the data for the cylindrical samples with a V/S of 0.91 was appreciably better. A linear correlation plot is shown in Figure 5.39.

Figure 5.40 shows the results of changing the ratio of volume to surface area (V/S) on Sr-85 leaching for waste forms containing 15 wt% incinerator ash. There is an increase in leachability of Sr-85, which is more apparent in the linear correlations plotted in Figure 5.39. These correlations show that decreasing V/S may be useful for accelerating Sr-85 leaching, since the plots at V/S values of 0.91 remain linear over the course of the experiments while those at V/S values of 0.61 and 0.42 remain linear until the samples are affected by carbonation. A linear correlation plot for Sr-85 is shown in Figure 5.41.

No measurable Co-57 activity above background was leached from these cement waste forms in any of these experiments.

5.2.8 Surface Condition and Porosity. No quantitative information is available regarding porosity in cement specimens containing incinerator ash. However, one unleached specimen was sectioned and micrographs were made by SEM (Figures 5.42 and 5.43, magnification of 49-fold). Large voids are characteristic of this material. The ash itself is often a large sponge-like particle which is more porous than the cement. Voids seem to form around the edges of the ash, perhaps due to generation of gas or differential sorption of water during mixing. No EDS analysis was performed because of the heterogeneity of this material.

Figure 5.1

Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash at 20, 40 and 50°C in deionized water.

Figure 5.2

Linear correlation plots for Cs-137 leaching at 20, 40 and 50°C in deionized water from portland I cement containing 15 wt% incinerator ash. Correlations are relative to the 20°C data.

Figure 5.3 Arrhenius plot of Cs-137 incremental leach rates from portland I cement containing 15 wt% incinerator ash leached at 20, 40 and 50°C in deionized water.

Figure 5.4 Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash at 20, 40 and 50°C in deionized water.

Figure 5.5

Linear correlation plots for Sr-85 leaching at 20, 40 and 50°C in deionized water from portland I cement containing 15 wt% incinerator ash. Correlations are relative to the 20°C data.

Figure 5.6

Arrhenius plot of Sr-85 incremental leach rates from portland I cement containing 15 wt% incinerator ash leached at 20, 40 and 50°C in deionized water.

Figure 5.7 Sodium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash at 20 and 50°C in deionized water.

Figure 5.8 Potassium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash at 20 and 50°C in deionized water.

Figure 5.9

Calcium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash at 20 and 50°C in deionized water.

Figure 5.10

Strontium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash at 20 and 50°C in deionized water.

Figure 5.11 Linear correlation plots for Sodium, Potassium and Cs-137 leaching at 20 and 50°C in deionized water from portland I cement containing 15 wt% incinerator ash. Correlations are relative to the Cs-137 data.

Figure 5.12 Linear correlation plots for Strontium and Sr-85 leaching at 20 and 50°C in deionized water from portland I cement containing 15 wt% incinerator ash. Correlations are relative to the Sr-85 data.

Figure 5.13

Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic ground water at 20°C.

Figure 5.14

Linear correlation plots for Cs-137 leached at 20°C from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic ground water. Correlations are relative to the DIW data.

Figure 5.15

Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxig ground water at 20°C.

Figure 5.16

Linear correlation plots for Sr-85 leached at 20°C from portland I cement containing 15 wt% incinerator ash in DIW and oxig ground water. Correlations are relative to the DIW data.

Figure 5.17

Sodium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic ground water at 20°C.

Figure 5.18

Potassium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic ground water at 20°C.

Figure 5.19

Calcium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic ground water at 20°C.

Figure 5.20

Strontium cumulative amount leached (ppm) vs. time from portland I cement containing 15 wt% incinerator ash leached in DIW and oxic ground water at 20°C.

Figure 5.21

Linear correlation plots for Sodium leached at 20°C from portland I cement containing 15 wt% incinerator ash in DIW and oxic ground water. Correlations are relative to the DIW data.

Figure 5.22

Linear correlation plots for Potassium leached at 20°C from portland I cement containing 15 wt% incinerator ash in DIW and oxic ground water. Correlations are relative to the DIW data.

Figure 5.23

Linear correlation plots for calcium leached at 20°C from portland I cement containing 15 wt% incinerator ash in DIW and oxic ground water.

Figure 5.24

Linear correlation plots for Strontium leached at 20°C from portland I cement containing 15 wt% incinerator ash in DIW and oxic ground water. Correlations are relative to the DIW data.

Figure 5.25

Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash leached at 20°C in leachants with initial pH values of 4, 6 and 8.

Figure 5.26

Linear correlation plots for Cs-137 leached at 20°C from portland I cement containing 15 wt% incinerator ash in leachants with initial pH values of 4, 6 and 8. Correlations are relative to the pH 6 (DIW) data.

Figure 5.27

Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash leached at 20°C in leachants with initial pH values of 4, 6 and 8.

Figure 5.28

Linear correlation plots for Sr-85 leached at 20°C from portland I cement containing 15 wt% incinerator ash in leachants with initial pH values of 4, 6 and 8. Correlations are relative to the pH 6 (DIW) data.

Figure 5.29

Cs-137 incremental leach rate vs. time from portland I cement containing 15 wt% incinerator ash comparing results of MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C.

Figure 5.30

Sr-85 incremental leach rate vs. time from portland I cement containing 15 wt% incinerator ash comparing results of MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C.

Figure 5.31

Portland I cement containing 15 wt% incinerator ash. The form at left is as fabricated. The one at right was leached for 403 days in deionized water at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.

Figure 5.32

Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash and from pure portland I cement at 20°C.

Figure 5.33

Linear correlation plots for Cs-137 leached at 20°C for portland I cement containing 15 wt% incinerator ash and pure portland I cement. Correlations are relative to pure cement.

Figure 5.34

Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash and from pure portland I cement leached in DIW at 20°C.

Figure 5.35

Linear correlation plots for Sr-85 leached from portland I cement containing 15 wt% incinerator ash and from pure portland I cement. Correlations are relative to pure cement. Samples were leached in deionized water at 20°C.

Figure 5.36

Linear correlation plot for Sr-85 versus Cs-137 leached from portland I cement containing 15 wt% incinerator ash in deionized water at 20°C.

Figure 5.37

Leaching curves of cumulative release (ppm) vs. time for sodium, potassium, calcium and strontium from portland I cement containing 15 wt% incinerator ash. Samples were leached at 20°C in deionized water.

Figure 5.38

Cs-137 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash at waste form volume to surface area (V/S) ratios of 0.42, 0.61 and 0.91. Samples were leached in deionized water at 20°C.

Figure 5.39

Linear correlation plots for Cs-137 leached from portland I cement containing 15 wt% incinerator ash at waste form volume to surface area (V/S) ratios of 0.42, 0.61 and 0.91. Correlations are relative to $V/S = 0.91$. Samples were leached in deionized water at 20°C.

Figure 5.40

Sr-85 cumulative fraction leached vs. time from portland I cement containing 15 wt% incinerator ash at waste form volume to surface area (V/S) ratios of 0.42, 0.61 and 0.91. Samples were leached in deionized water at 20°C.

Figure 5.41

Linear correlation plots for Sr-85 leached from portland I cement containing 15 wt% incinerator ash at waste form volume to surface area (V/S) ratios of 0.42, 0.61 and 0.91. Correlations are relative to V/S = 0.91. Samples were leached in deionized water at 20°C.

Figure 5.42

The ash itself is often more porous than the cement matrix in which it is solidified.

Figure 5.43

Large voids form possibly due to gas generation or differential water sorption between the cement and the ash.

6. VINYL ESTER-STYRENE (VES) EMULSION WITH AQUEOUS SODIUM SULFATE AS SIMULATED WASTE

The vinyl ester-styrene (VES) copolymer system can be used to solidify aqueous waste streams, such as sulfate salt evaporator bottoms. This is done using high-shear mixing to form an emulsion of the comonomer and aqueous waste solutions and then polymerizing the comonomer phase to solidify the emulsion. Polymerization is normally accomplished using a catalyst and promoter system that is added to the comonomer along with the waste solution. Since polymerization involves a chemical reaction initiated by the catalyst-promoter system, interactions with the waste can be detrimental to solidification of the emulsion.

Although the vinyl ester-styrene process for solidifying emulsified liquid wastes was considered promising and was developed commercially [67-69], it has not come into widespread use. Therefore, experimental work on the VES emulsion process was de-emphasized and efforts were directed toward the use of VES to solidify dry salts, presented later in section 7 of this report. This section presents the results obtained using the VES emulsion process for solidifying aqueous sodium sulfate solution as simulated waste.

6.1 Leaching Mechanisms

No completely defensible physicochemical model of the leaching behavior of VES-aqueous waste emulsion waste forms was developed from this work. In part this stemmed from the redirection of effort, as mentioned above, and in part from the fact that only waste loading appeared to have any consistent effect on the leaching behavior of the VES emulsion waste forms with aqueous sodium sulfate. Three pertinent observations from section 6.2 that address the question of the leaching mechanism for VES emulsion waste forms are listed below.

- (i) There is little difference in leachabilities of Cs-137, Sr-85 and Co-57 from VES emulsion waste forms. This finding suggests that there is little, if any, sorption of radionuclides by the solid polymer.
- (ii) The physical structure of the solidified polymer consists of a matrix in which larger pores appear to be connected by much smaller pores. However, the overall connectedness of the pore structure was not determined. The structure would also depend on the ratio of waste-to-binder, the duration of mixing and, possibly, the time that the polymerization reaction takes to solidify the form.
- (iii) Plots of radionuclide leaching releases often have a step-like appearance; this may indicate that small cells of the aqueous waste become accessible to leaching suddenly, such that a microburst of material is released.

These three observations suggest that the behavior of the polymer matrix is essentially inert toward the radionuclides investigated in this work, and that leaching is controlled by the physical structure of the emulsified form. The physical structure, in turn, is clearly a product of the thoroughness of the high-shear mixing. Item (iii) indicates that leaching may proceed as small bursts of release of waste material, perhaps driven by osmotic rupture of these regions. The leach rate then would slow as the tortuous ruptured-region layer increases in thickness and the diffusive path to the surface of the waste form lengthens. Under this scenario, the permeability of the polymer film itself would play only a minor role in the leachability of these waste forms.

6.2 Factors that Affect Leaching

This section presents our results on the effects that the factors listed in Table 2.1 have on the leaching behavior of vinyl ester-styrene (VES) emulsion waste forms containing aqueous sodium sulfate as simulated waste. Compositions of the test specimen are listed in Tables 3.1 and 3.2 for the VES emulsion with aqueous sodium sulfate solution and with DIW containing only radiotracers, respectively. The effects of each factor are based on comparison to the results from standard samples, i.e., 4.8 cm diameter by 6.4 cm tall right cylinders, leached at 20°C in DIW. Replicate tests, generally triplicates, provided a measure of the variability of the data.

6.2.1 Temperature. Investigations of the effect of temperature on the leachabilities of Cs-137, Sr-85 and Co-57 from VES emulsion with aqueous sodium sulfate solution showed that leachabilities of the three radionuclides differed substantially at 40 and 50°C compared to that at 20°C. Specifically, the relative leaching releases of the three radionuclides at 40 and 50°C paralleled that at 20°C for about 50 days and then increased rapidly. This occurred somewhat sooner at 50°C than that at 40°C. This behavior appears to result from relatively large and possibly constant leach rates developing following the initial (50 day) period of monotonically decreasing leach rates. Since the leach rates of the replicate 20°C data monotonically decreased to over 300 days it appears that the leaching mechanism may change at increased leaching temperature. Alternatively, the samples at 20°C may not have been leached long enough to unambiguously establish a constant leach rate, as may have happened for the samples at the higher temperatures. However, the long-term leaching releases at elevated temperature do not correlate with those at 20°C, so elevated temperature cannot be considered a valid accelerating factor until this anomaly between the 20°C data and the 40 and 50°C data is resolved.

Figure 6.1 shows Cs-137 CFL versus time from the VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. The 20°C data evidence a monotonically decreasing leach rate to over 300 days. The 40 and 50°C data show similar behavior through approximately 50 days, at which point the leachability appears to become constant. The constant rate established at 50°C data is substantially greater than that at 40°C data.

The linear correlations plotted in Figure 6.2 show that the differences in leaching behavior between the 20°C data and those at 40° and 50°C are significant. There are two regions of behavior:

- (i) The initial region in which Cs-137 leachabilities in the 40° and 50°C experiments are lower, but appear to correlate well with those from the 20°C experiments, and
- (ii) The long-term region in which the relative leachability at the higher temperatures increases rapidly compared to that at 20°C.

However, overall, the higher temperature experiments do not correlate with those at 20°C and increased temperature does not provide a valid accelerating factor for waste forms consisting of VES emulsion with aqueous sodium sulfate.

Leaching processes for VES emulsion appear to be the same for the three radionuclides used in these experiments. Consequently, the comments made on the Cs-137 leaching also apply to Sr-85 and Co-57. Figures 6.3 and 6.4 show CFL versus time and the linear correlations for Sr-85 leached at 20, 40 and 50°C. Figures 6.5 and 6.6 show the same types of plots, respectively, for Co-57.

Since temperature showed no clear promise as a potential accelerating factor, the leaching of non-radionuclides was not measured from the VES emulsion with aqueous sodium sulfate.

6.2.2 Ratio of Leachant Volume to Waste Form Surface Area. These experiments were not done for the VES emulsion waste forms with aqueous sodium sulfate as simulated waste: emphasis was placed on work with other materials.

6.2.3 Composition of the Leachant. The effect of the composition of the leachant on the leaching of Cs-137, Sr-85 and Co-57 from the VES emulsion with aqueous sodium sulfate was investigated, using the oxic ORNL-simulated ground water (described in Section 3). The leachabilities of all three radioisotopes were uniformly reduced approximately by a factor of two in the ground water compared to those in DIW. The fact that all three were reduced by the same factor indicates that solubility limits for Sr-85 and Co-57 did not significantly affect the leaching releases; otherwise the Sr-85 and/or Co-57 releases would be notably lower than the Cs-137 releases in the ground water. Figures 6.7, 6.8 and 6.9 are plots of CFL versus time for Cs-137, Sr-85 and Co-57 respectively.

No measurements were made of leaching of non-radionuclides from the VES emulsion since our emphasis shifted to VES-solidified dry salts.

6.2.4 pH of the Leachant. Leachants with initial pH values of 4 and 8 were compared with DIW, pH = 6. As mentioned previously, the nominal pH of DIW is 7 at 20°C, but dissolution of carbon dioxide from air reduces the pH to approximately 6. Leaching at pH values of 4 and 8 uniformly reduced the releases of Cs-137, Sr-85 and Co-57 by over half. Thus, adjusting the initial pH of the leachant away from neutral appears to substantially decelerate

leaching from VES emulsion with aqueous sodium sulfate. Figures 6.10, 6.11 and 6.12 are plots of CFL versus time for Cs-137, Sr-85 and Co-57, respectively, leaching in DIW (pH=6) and in leachants with initial pH values of 4 and 8.

No experiments were performed to measure leaching of non-radionuclides from the VES emulsion since our emphasis shifted to VES-solidified dry salts.

6.2.5 Effect of the Flow Rate or Replacement Frequency of the Leachant on VES Emulsion with Sodium Sulfate Solution. Leaching experiments using the MCC-4S flow test were performed for comparison to the results of the modified ANS 16.1 leach test used as the standard in this program. The nominal flow rates in these two tests are about the same for the first week (1.0 liter/day in the flow test compared to 1.3 liters/day in the modified ANS 16.1 test). As the ANS 16.1 test continued, sampling intervals increased to 21 days, giving an effective flow rate of 0.06 liters/day, while the flow test continued at 1.0 liters/day. In general, the flow test results paralleled those from the ANS 16.1 tests, but the former were less reproducible in that there was substantially greater scatter in the data. Therefore, the flow test was not a useful accelerating factor.

Figure 6.13 plots incremental leach rate versus time for Cs-137 leaching from the VES emulsion with the MCC-4S flow test and the modified ANS 16.1 test. During the first week, leach rates in the flow test were lower than those in the ANS 16.1 test, perhaps because of the lower rate of water exchange. After that time, the rates were essentially the same for the two tests. At about 70 days, a burst of activity was released from a specimen in the flow test, which increased the leach rate for approximately 14 days. Following this, the rate resumed its downward trend, with releases from the two tests being similar.

Figure 6.14 plots incremental leach rate versus time for Cs-137. Sr-85 leaching parallels that of Cs-137 very closely, with the same burst of activity being observed in the flow test at 70 days. Another burst was also observed for Sr-85 from the ANS 16.1 test after 300 days, but this is probably an artifact of an extremely low count rate due to radioactive decay of that radionuclide. This burst was not observed for Cs-137.

Figure 6.15 plots the incremental leach rate versus time for Co-60. Co-60 releases followed closely those of Cs-137 and Sr-85. The burst of activity at 70 days was observed in the flow test. Otherwise, results of the two tests were quite similar.

6.2.6 Composition of the Waste Form. The composition of the waste form was investigated by comparing the leaching of the VES emulsion with sulfate salt solution and with DIW. Both waste types consisted of approximately equal volumes of waste (i.e., sulfate salt solution or DIW) and VES comonomer solution. The density of the salt solution was greater than that for DIW so that the waste form compositions listed in Tables 3.1 and 3.2 for the VES emulsion with sodium sulfate solution and with DIW, respectively, are different on the weight % formulation basis used in the tables. The leachabilities of all three radionuclides (Cs-137, Sr-85 and Co-57) were much greater

from the VES emulsion waste forms containing the sodium sulfate solution than from those with DIW as simulated waste.

There was no visible change in the VES emulsion with sodium sulfate solution after leaching 340 days at 20°C compared to the as-fabricated form (Figure 6.16), neither was there any noticeable change in the VES emulsion with DIW leached for over 500 days at 20°C compared to the as-fabricated form (not shown). However, Figure 6.17 shows a surface layer delamination that occurred in the VES emulsion with sodium sulfate solution leached at 50°C for 100 days. Before sectioning, the leached form appeared to have blistered, but there was no visible cracking or other damage evident beyond the blistering. Further, blistering occurred only in the sample leached at 50°C and not in those leached at 40°C and 20°C, although it might be expected to occur in the 40°C sample, and possibly the 20°C sample, at longer times.

Since only one waste loading of the sulfate salt solution was tested, no evaluation of varying the ratio of the waste to binder of the VES emulsion waste form type is available.

Figures 6.18, 6.19 and 6.20 show the leaching of Cs-137, Sr-85 and Co-57, respectively, from VES emulsion waste forms containing sodium sulfate solution as simulated waste, compared to emulsions containing only DIW and radioactive tracers as simulated waste. The emulsion with the salt solution had large initial leach rates that decreased substantially after approximately 50 days.

Releases of Cs-137 showed a monotonically decreasing rate through 320 days leaching at 20°C. Releases of Sr-85 and Co-57 appear to increase at about 250 days; this is probably an artifact of the very low count rates observed for those radionuclides near the end of the experiment, resulting from their short half-lives.

6.2.7 Ratio of Volume to Surface Area of the Waste Form (V/S). As reviewed in section 2.7, small-scale test samples, under certain conditions, can be used to accelerate the leaching that would be expected from full-scale waste forms. However, for the VES emulsion waste forms containing sodium sulfate solution, size reduction was unsuccessful. The releases from the smaller samples did not correlate well with those from the standard 4.8 cm diameter by 6.4 cm tall samples ($V/S = 0.91$). In sum, the reproducibility of the data within each set of (V/S) replicates was marginal and the scatter in the data between sets of replicate samples suggests that the formation of the emulsion may control leachability to a greater extent than does any external factor.

Figures 6.21, 6.22 and 6.23 show Cs-137, Sr-85 and Co-57, respectively, leaching from VES emulsion waste forms containing sodium sulfate solution at waste form V/S ratios from 0.91, 0.62 and 0.42. Although the $V/S = 0.62$ samples leached faster than the standard ($V/S = 0.91$), the smallest samples ($V/S = 0.42$) leached slower initially and established a linear rate of release, rather than monotonically decreasing. The findings were inconsistent with the idea that smaller samples should leach relatively faster than larger ones. This tends to go against common sense, if nothing else, suggesting that

the details of sample fabrication may be the most important parameter affecting the leachability of the VES emulsion waste forms.

6.2.8 Porosity and Surface Condition of the Waste Form. The VES emulsion waste forms are fabricated using high-shear mixing of the comonomer and aqueous waste solutions. Since these solutions are not soluble in each other, the waste is a two-phase system. The waste forms fabricated for our experiments were approximately 50% by volume VES polymer (after solidification) and 50% by volume sodium sulfate solution.

Electron microscope images were obtained with blank samples, before and after leaching. Figure 6.24 shows the outer surface of a VES waste form magnified 400 times. Pores at the surface of the sample typically range from 12 μm to about 30 μm . Inside the surficial pores, there are other openings that are much smaller, less than 1 μm in diameter. Figure 6.25 shows the interior of the same sample: the structure is much like that of the surface. Figure 6.26 is an 1800-fold magnification of the VES surface and shows many small pores inside the larger pores and in the polymer, forming the network around the larger pores. Another view, taken of a cut section at the interior of the waste form, is shown in Figure 6.27. There is a large amount of cutting debris present because the polymer is somewhat elastic and tears rather than cuts cleanly. The interior contains pores of the same size range and configuration as the surface. Often polymers that form emulsions with water form a skin around the cast form that is less porous than the bulk of the material. In the VES emulsion, there does not appear to be any skin formation.

No physical changes were observed in polymer samples that had leached for 471 days. These organic materials released less than 2 g/ml total organic carbon in leaching intervals that typically show high releases for soluble components. Therefore, it is not surprising that there was no change in physical form.

Figure 6.1

Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.

Figure 6.2

Linear correlation plots for Cs-137 leaching from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.

Figure 6.3

Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.

Figure 6.4

Linear correlation plots for Sr-85 leaching from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.

Figure 6.5

Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.

Figure 6.6

Linear correlation plots for Co-57 leaching from VES emulsion with aqueous sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.

Figure 6.7 Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached in DIW and oxic ground water at 20°C.

Figure 6.8 Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached in DIW and oxic ground water at 20°C.

Figure 6.9

Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached in DIW and oxic ground water at 20°C.

Figure 6.10

Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached at 20°C in leachants with initial pH values of 4, 6 and 8.

Figure 6.11

Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached at 20°C in leachants with initial pH values of 4, 6 and 8.

Figure 6.12

Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate leached at 20°C in leachants with initial pH values of 4, 6 and 8.

Figure 6.13

Cs-137 incremental leach rate vs. time from VES emulsion with sodium sulfate comparing results from MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C in deionized water.

Figure 6.14

Sr-85 incremental leach rate vs. time from VES emulsion with sodium sulfate comparing results from MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C in deionized water.

Figure 6.15

Co-57 incremental leach rate vs. time from VES emulsion with sodium sulfate comparing results from MCC-4S flow test to modified ANS 16.1 leachant replacement schedule. Samples were leached at 20°C in deionized water.

Figure 6.16

VES emulsion with aqueous sodium sulfate. The form at left is as fabricated. The one at right was leached for 403 days in deionized water at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.

Figure 6.17

Sectioned specimen of VES emulsion with sodium sulfate solution that was leached for 100 days at 50°C showing delamination of surface.

Figure 6.18

Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate and from VES emulsion with DIW. Samples were leached at 20°C in deionized water.

Figure 6.19

Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate and from VES emulsion with DIW. Samples were leached at 20°C in deionized water.

Figure 6.20

Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate and from VES emulsion with DIW. Samples were leached at 20°C in deionized water.

Figure 6.21

Cs-137 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.

Figure 6.22

Sr-85 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leach in deionized water at 20°C.

Figure 6.23

Co-57 cumulative fraction leached vs. time from VES emulsion with aqueous sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.

Figure 6.24

Surface of a VES emulsion sample at a magnification of 400 times. Most pores are approximately 5-10 microns in diameter.

Figure 6.25 Interior section of a VES emulsion sample at a magnification of 400 times. The interior structure appears similar to that of the surface shown in Figure 6.24.

Figure 6.26 Surface of a VES emulsion sample at a magnification of 1900 times. Much smaller pores are visible with diameters less than one micron.

Figure 6.27

Interior section of a VES emulsion sample at a magnification of 1900 times. There is considerable saw debris, but the pores are in the same size range as those at the surface, shown in Figure 6.26.

7. VINYL ESTER-STYRENE (VES) CONTAINING SULFATE SALT AS SIMULATED WASTE

The use of polymeric solidification agents for the disposal of low-level radioactive waste is of interest to the nuclear industry. A major benefit from these materials is the high waste loading that can be achieved when they are coupled to an advanced volume reduction system, such as an evaporator/drier.

Application of thermosetting polymers for the solidification of dry waste is based on the physical encapsulation of the waste stream. Polymerization of the liquid monomer takes place when a catalyst and promoter are added, yielding a continuous matrix of cured polymer with small waste particles dispersed throughout. The polymer matrix is structurally rigid and of very limited permeability to water: this implies that the pore structure of the polymer matrix remains intact even though the waste may dissolve out of or otherwise be removed from the waste form. The impermeability of the polymer matrix to water means that mass transport of waste substances occurs through, and is constrained by, the pore structure of the matrix. The only other interaction between the polymer matrix and the waste that may affect leaching is sorption or ion exchange capacity. In our experiments these mechanisms were below detectable levels for the radionuclides of interest. There is little, if any, chemical reaction between the waste and the matrix. This discussion is predicated on the assumption that the waste has not interfered with the polymerization process itself.

This section presents data from studies investigating potential leach rate acceleration factors for waste forms consisting of vinyl ester-styrene copolymer and anhydrous sodium sulfate salt as simulated waste.

7.1 Mechanisms of Leaching

Vinyl ester-styrene specimens containing only radioactive tracers leached so slowly that no statistically significant activity was detected in the leachate [3]. Addition of 40 wt% dry salt increased leaching by a factor of 200 to 300 times, apparently by producing a network of interconnected pores that allowed water to enter and dissolved salt to leave the specimen.

Waste loading is a major determinant of leaching behavior in VES waste forms incorporating soluble salts. Such behavior is not explainable by assuming that the waste form approximates to a homogeneous medium. Instead, the two-phase nature of the waste form must be explicitly recognized as being a major factor that determines leaching behavior in this and similar systems.

The data presented in this section suggests a two-part leaching process for this material. In several experiments, leaching behavior during the first week was characterized by low scatter in the data and a positive response to acceleration factors. After this initial period, leaching became much more variable. This change may be the result of the structure of the specimens. Electron microscope images, presented in section 7.2.8, show that a coating of polymer (without salt particles) surrounds the main body of the waste/polymer composite. As a result, leaching may proceed in two steps:

1. diffusion of water through the outer coating,
2. dissolution and transport of waste through the tortuous porosity which develop as leaching proceeds.

7.2 Factors that Affect Leaching

Leaching results from experiments designed to investigate each of the factors listed in Table 2.1 for vinyl ester-styrene waste forms containing sodium sulfate are discussed in the following sections. Each acceleration factor is evaluated by comparing results for that factor with those from a set of baseline leaching experiments on standard specimens (i.e., 4.8 cm diameter by 6.4 cm high right cylinders, at 20°C in 1.3 liter of deionized water). Replicate tests, generally triplicates, provided a measure of the variability of the data.

7.2.1 Temperature. The ability of increased temperature to accelerate leaching of VES waste forms containing sodium sulfate was investigated at 40 and 50°C. Releases of Cs-137 at these temperatures and at 20°C are shown in Figure 7.1. Releases below 0.2 CFL and prior to 7 days leaching had little scatter and a general trend of increased leaching with temperature (Figure 7.2). With longer leaching times, the scatter among samples increased to the point where this trend was not observable. Releases stop at about 0.8 CFL. Assuming this is not a source term problem, the implication is that 20% of the waste is held in unconnected pores or has been permeated with VES. In either case, the waste is unavailable for leaching. This phenomenon was also observed for Sr-85 and Co-57 at the same CFL values, as shown in Figures 7.3 and 7.4, respectively.

Linear correlations for Cs-137 CFL at different temperatures are shown in Figure 7.5. During the first week of the test, leaching at elevated temperatures resulted in non-linear releases compared to releases at 20°C. Figures 7.6 and 7.7 give correlation plots for Sr-85 and Co-57, which appear more linear in this early stage of leaching than does the data for Cs-137.

The increase in leachability and scatter with the longer leaching intervals could be the effect of a change in properties of the polymer itself. More likely, it is caused by increasing porosity as salt dissolves. However, this is unknown as are the basic responses of the material to the effects of dissolution of salt and elevated temperature. Continued efforts with solid phase analysis will be needed to understand these processes.

7.2.2 Ratio of Waste Form Surface Area to Leachant Volume. To maximize release rates, the concentration gradient of any dissolved species, between the pore water of the waste form and the leachant, should be as large as possible. This effect can most easily be observed by increasing the volume of leachant. Typically for the sample size used for these tests the leachant volume was 1300 ml (a surface area to leachant volume ratio of 10:1) but tests were also run at 2600 ml (20:1), 3900 ml (30:1) and 6500 ml (50:1).

Results for the four ratios tested are shown in Figure 7.8 for Cs-137 and in Figures 7.9 and 7.10 for Sr-85 and Co-57, respectively. In all cases release rates of specimens leached at ratios of 20, 30 and 50 are not statistically different than the release rates in the reference ratio of 10. This is reasonable, since the solubility of the hydrated sodium sulfate salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) is 143 g in 1300 ml of cold water. Each waste form contained approximately 44 g of anhydrous sodium sulfate (which weighed about 100g when fully hydrated). Therefore each volume of leachant could have dissolved the total load of salt that was present in any waste form. Therefore, increasing the volume of the leachant is not a useful acceleration factor for VES containing dry sodium sulfate salt.

7.2.3 Composition of the Leachant. While deionized water was the standard leachant used, others were investigated for their potential as accelerating factors. These were:

- 1) a simulated ground water from Oak Ridge National Laboratory [63], under oxidizing and reducing conditions
- 2) a solution of 100 ppm disodium EDTA

Figure 7.11 shows CFL for Cs-137 for anoxic and oxic groundwater and, as a basis for comparison, deionized water. Anoxic ground water leached Cs-137 at a slower rate than did oxic ground water, probably because of the higher ionic strength of the anoxic solution. However, the two groundwaters are not statistically different than deionized water. Similar results were obtained for Sr-85 and Co-57, as shown in Figures 7.12 and 7.13 respectively. Co-57 is the only multivalent radionuclide that was investigated and here some effect of reducing conditions may be expected. In power-reactor waste the Co-60 is primarily associated with particulates and is not readily soluble under oxidizing conditions. In the simulated waste used in this study, the Co-57 already was in solution. Therefore, exposure to reducing conditions (which converts cobalt to a more soluble low valence state) would not alter leachability of cobalt in solution, but could strongly enhance the leaching of cobalt that was in the solid phase. Therefore, some enhanced releases of Co-60 could be expected from real waste under reducing conditions.

There was no discernable effect on the leaching of VES specimens in 100 ppm disodium EDTA, as shown in Figures 7.14, 7.15 and 7.16 for Cs-137, Sr-85 and Co-57, respectively. Again, some increase in Co-60 leaching from real reactor waste may be expected due to increased solubility of complexed cobalt.

7.2.4 pH of the Leachant. The effects of leachant pH were investigated at solution pH values of 8, 6, 5, 4 and 3. The pH of the deionized water used in this study is nominally 7 at 20°C, but dissolution of carbon dioxide from the air moves this value to around 6. In fact, pH measurements of deionized water are difficult due to the very low ionic strength of the water.

Releases of Cs-137 from VES samples containing 40 wt% sodium sulfate are shown in Figure 7.17. During the first ten days the test pH had a positive effect on leaching. Later, increased scatter in the data masked any acceleration (Figure 7.18). Releases of Sr-85 and Co-57 are shown in Figures 7.19 and

7.20. Acceleration is less evident, although leaching at pH 8 shows a slight positive effect early in the experiments.

The linear correlation plot for Cs-137, Figure 7.21, indicates that acceleration occurred at pH = 8 but it was not linear. This may indicate that the matrix material was changing, or that there was an effect of the length of sampling interval.

7.2.5 Flow Rate or Replacement Frequency of the Leachant. The effects of increased exposure to water, to maximize the concentration gradient across the waste form, can be accomplished by increasing the volume of the leachant as discussed in section 7.2.2. It can also be done by increasing the frequency with which the leachant is replaced or by using a continuous flow-through leach test, such as the MCC-4s procedure.

Figures 7.22, 7.23 and 7.24 show Cs-137, Sr-85 and Co-57 data from triplicate experiments with daily sampling intervals as well as for the ANS 16.1 tests. Daily samplings give results similar to those of the ANS 16.1 tests. While Sr-85 and Co-57 releases from the daily intervals appear lower than Cs-137, the difference is not statistically significant.

Similarly, results from continuous flow-through tests show little difference from the ANS 16.1 test. Figures 7.25, 7.26 and 7.27 present the flow-through and ANS 16.1 results as rates (fraction release/second) because data from the flow-through test is not readily calculated as cumulative fraction leached. Again, the two tests are not discernibly different. The data for the ANS 16.1 test falls to low rates, but this fall occurs at times longer than the flow-through data was taken.

7.2.6 Composition of the Waste Form. Composition of the waste form, in the case of waste loading, could be a useful acceleration factor if a systematic increase in leaching is a function of waste content. This concept was explored for VES containing sodium sulfate at loadings of 20, 30 and 40 wt%. Leachabilities at these loadings are shown in Figures 7.28, 7.29 and 7.30 for Cs-137, Sr-85 and Co-57. After 30 days of leaching, Cs-137 releases were related to the amount of loading, with the 20 wt% loading having the lowest CFL and the 40 wt% loading the highest. Earlier in the experiment, this was not so. Strontium-85 data shows no difference in leaching between the 20 and 30 wt% specimens. Only single specimens were used for the 20 and 30 wt% loadings, and the variability between samples makes it difficult to draw conclusions. It is unclear if this factor is a useful means of acceleration. From theoretical considerations, discussed earlier in this report, loading should accelerate leaching. More experimental work is needed in this area.

7.2.7 Waste Form Volume to Surface Area Ratio. By altering the size and shape of leaching specimens and by meeting required conditions of the leaching mechanism (e.g., control by diffusion) it is possible, on theoretical grounds, to accelerate leaching as discussed in section 2.7. Consequently tests were run with varying ratios of volume to surface area (V/S).

Several specimens were made of two sizes other than the standard 6.4 x 4.8 cylinder (V/S = 0.91). The dimensions, volumes and surface areas of each

sample are given in Appendix A. The specimens with $V/S = 0.62$ were cylindrical disks measuring 1.6 cm in height and 13.8 cm in diameter. These were leached in 3650 ml of water to maintain the surface area to leachant volume of 10. Specimens with $V/S = 0.41$ were cylinders measuring 2.6 cm height by 2.4 cm in diameter, which were leached in 300 ml of water.

Results are shown in Figures 7.31, 7.32 and 7.33 for Cs-137, Sr-85 and Co-57 respectively. Similar trends were observed for all isotopes. The small cylinders ($V/S = 0.41$) had greater releases than did the disks ($V/S = 0.62$). For the first week of leaching, the small specimens also leached significantly faster than the standard sized specimen. This was up to a CFL of about 0.40. At this point depletion and scatter in the data from standard sized specimens make analysis difficult. Releases from the disk-shaped specimens were not significantly different than those from the standard leach rates for Cs-137. Leach rates for specimens of $V/S = 0.42$ were substantially greater than the others for the first 6 days. Results from the disk-shaped specimens may not be useful because the difference in aspect ratio of the disk versus the cylinders could give misleading results.

7.2.8 Porosity and Surface of the Waste Form. Little work was done to characterize solid phase controls on leachability of this material. The physical appearance of leached specimens as shown in Figure 7.34 was much like that of unleached replicates. To date there have been no studies conducted to determine how the VES matrix responds to leaching of soluble components from the waste form.

Figure 7.35 is an SEM micrograph, at 60 fold magnification, of the interior of an unleached VES specimen containing 40% sodium sulfate salt. Individual salt grains were surrounded by the polymer matrix. At this waste loading there is little contact between grains. There were several air bubbles with diameters of about 50-75 μ m. When the surface of this specimen was observed by SEM (Figure 7.36), no salt was visible and the x-ray spectrum showed very little sodium or sulfur. Apparently a coating of polymer that contained no salt formed around the specimen. Some small pores leading through the coating are visible on this surface.

SEM examination of a leached specimen showed no physical difference from an unleached sample. The boundary between the polymer and salt grains was intact and the salt showed no signs of dissolution. This is shown in Figure 7.37 where the polymer matrix is visible, at the center of the photograph, between two salt grains. Energy-dispersive spectroscopy suggested that no sodium or sulfur was present in the matrix next to salt grains, even after leaching. The surface of the leached specimen was similar in appearance to the unleached surface, although more pores may have been present. A more detailed study of this material is necessary to relate the structure of the solid phase to its leaching behavior.

Figure 7.1

Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C. Samples were leached in deionized water.

Figure 7.2

Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C leached in deionized water. Data shown is for initial 35 days of the experiment.

Figure 7.3

Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C in deionized water.

Figure 7.4

Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C leached in deionized water.

Figure 7.5

Linear correlation plots for Cs-137 leaching from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data.

Figure 7.6

Linear correlation plots for Sr-85 leaching from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.

Figure 7.7

Linear correlation plots for Co-57 leaching from VES containing 40 wt% sodium sulfate at 20, 40 and 50°C. Correlations are relative to the 20°C data. Samples were leached in deionized water.

Figure 7.8

Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.

Figure 7.9

Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.

Figure 7.10

Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at leachant volume to waste form surface area ratios of 10, 20, 30 and 50:1. Samples were leached in deionized water at 20°C.

Figure 7.11

Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW, oxic and anoxic ground waters at 20°C.

Figure 7.12

Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW, oxic and anoxic ground waters at 20°C.

Figure 7.13

Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW, oxidic and anoxic ground waters at 20°C.

Figure 7.14

Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.

Figure 7.15

Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.

Figure 7.16

Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.

Figure 7.17

Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.

Figure 7.18

Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8. First twenty days.

Figure 7.19

Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.

Figure 7.20

Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate leached at 20°C in leachants with initial pH values of 3, 4, 5, 6 and 8.

Figure 7.21

Linear correlation plots for Cs-137 leached from VES containing 40 wt% sodium sulfate in leachants with initial pH values of 3, 4, 5, 6 and 8 at 20°C. Correlations are relative to the pH 6 (DIW) data.

Figure 7.22

Cs-137 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for VES waste forms containing 40 wt% sodium sulfate leached at 20°C.

Figure 7.23

Sr-85 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for VES waste forms containing 40 wt% sodium sulfate leached at 20°C.

Figure 7.24

Co-57 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for VES waste forms containing 40 wt% sodium sulfate leached at 20°C.

Figure 7.25

Cs-137 incremental leach rate vs. time from VES containing 40 wt% sodium sulfate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.

Figure 7.26

Sr-85 incremental leach rate vs. time from VES containing 40 wt% sodium sulfate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.

Figure 7.27

Co-57 incremental leach rate vs. time from VES containing 40 wt% sodium sulfate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.

Figure 7.28

Cs-137 cumulative fraction leached vs. time from VES containing 20, 30 and 40 wt% sodium sulfate. Samples were leached in deionized water at 20°C.

Figure 7.29 Sr-85 cumulative fraction leached vs. time from VES containing 20, 30 and 40 wt% sodium sulfate. Samples were leached in deionized water at 20°C.

Figure 7.30 Co-57 cumulative fraction leached vs. time from VES containing 20, 30 and 40 wt% sodium sulfate. Samples were leached in deionized water at 20°C.

Figure 7.31

Cs-137 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.

Figure 7.32

Sr-85 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.

Figure 7.33

Co-57 cumulative fraction leached vs. time from VES containing 40 wt% sodium sulfate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.

Figure 7.34

Vinyl ester-styrene forms containing 40 wt% sodium sulfate. The one at left is as fabricated. The one at right was leached for 403 days in deionized water at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.

Figure 7.35

Interior of a sectioned, unleached VES specimen containing 40 wt% sodium sulfate. There appears to be little contact between grains of salt.

Figure 7.36

Unleached surface of a VES specimen containing 40 wt% sodium sulfate. No salt grains are visible but several open pores are evident. A leached surface is similar in appearance. Magnification is 400 times.

Figure 7.37

Two grains of salt separated by VES polymer. This specimen had been leached but no obvious effect from the leaching was noted. No sodium or sulfur was detected by EDS in the polymer between the grains.

8. BITUMEN CONTAINING SODIUM TETRABORATE AS SIMULATED WASTE

Bitumen is any of several various mixtures of hydrocarbons and other substances, occurring naturally or obtained by distillation from coal or petroleum. Bitumen is found in asphalt and tar and used for surfacing roads and for water proofing. Asphalt, also called mineral pitch, is a brownish-black semisolid mixture of bitumens containing much mineral matter. The term bitumen refers to asphalt free of mineral matter. Tar, however, is a dark, oily, viscous mixture, consisting mainly of hydrocarbons, produced by the destructive distillation of organic substances such as wood, coal, or peat. Coal tar, for example, is a black liquid [70,71].

Various types of bitumen have been used as solidification agents for LLW. Bitumens and asphalts are generally characterized by their softening point temperatures [72] and the process by which they were prepared [73]. An oxidized bitumen, Pioneer 321, which has been used for rad-waste processing, was used to prepare the waste forms for this experimental work.

This section presents results obtained from leaching studies investigating the factors deemed potentially important for LLW forms, as discussed in Section 2 of this report, consisting of bitumen incorporating sodium tetraborate.

8.1 Leaching Mechanisms

The following overview summarizes the leaching mechanisms for bitumen as determined from the literature survey [1] and the experimental work in this task.

The function of bitumen in the solidification of LLW is generally considered to be that of an adhesive coating. As such, the waste content of bituminized waste does not significantly change the mechanical properties of the solidified form until the waste loading exceeds approximately 60 weight% [74,75]. Conversely, the strength of a cement form depends on waste loading and reportedly decreases substantially at salt loadings greater than 130 g per Kg of cement product (i.e., 13 wt% of waste form) [76]. The leaching data have been analyzed based on two postulated mechanisms [74,77]. In one, diffusion was presumed to be the mass transport process [77], whereas in the other [74], the solubility of the activity was presumed to control the leaching. Functionally, the diffusion-mechanism would result in a release rate proportional to $t^{-1/2}$, while the solubility-controlled mechanism would give a constant rate of release of activity from the waste form. These different analyses may not be incompatible since the bitumens used for solidification, the waste and the process used to incorporate the wastes all differed.

Although bitumen is generally considered to be hydrophobic, it has a small, but definite, permeability to water. It is a viscoelastic material which has little mechanical strength at ordinary temperatures and creeps readily under the loads that are typical of shallow land burial. Because it forms an adhesive coating and is only slowly permeable to water, bitumen waste forms typically have low short-term leachabilities. However, bitumen wastes

forms incorporating soluble wastes often swell at longer times during leaching and then the leach rate increases substantially. The onset of swelling is also a function of waste loading, as further discussed in section 8.2.6.

The results of the leach tests shown in this report for bitumen waste forms together with those referenced in the literature survey [1] showed that the leaching of bitumen waste forms incorporating soluble wastes generally had two distinct regions of behavior. There was an initial region of low rates normally associated with short-term leach tests on bitumen waste forms. The water uptake within the waste form is not sufficient to initiate swelling. However, as water uptake becomes sufficient to start the swelling and, as swelling progresses, the leach rate increases substantially. Severe swelling has been reported with waste forms incorporating salts and ion exchange resins [78]. With sodium sulfate, at loadings greater than approximately 17 wt%, the waste form cracks open and falls apart during immersion and leaching in deionized water. Bitumen waste incorporating insoluble wastes and wastes that do not swell should exhibit low leach rates, even at long immersion times. To summarize, the leaching mechanisms for bitumen must account for:

- (i) Diffusion of radionuclides at low waste loadings and relatively short leaching times.
- (ii) Water permeation and swelling, with its effect on leaching.
- (iii) The rapid increase in leaching at longer leaching times and especially at waste loadings greater than approximately 20 wt%.

8.2 Factors that Affect Leaching

Leaching results from experiments designed to investigate each of the factors listed in Table 2.1 for the bitumen (Pioneer 321 Asphalt) waste forms containing anhydrous sodium tetraborate are discussed in the following sections. The basis for evaluating the effect of each of the factors is a comparison with the results of tests on standard samples, i.e., 4.8 cm diameter by 6.4 cm high right cylinders, at 20°C in deionized water. Replicate tests, generally triplicates, provided a measure of the variability of the data.

8.2.1 Temperature. The effect of temperatures between 20 and 50°C on the leachability of bitumen waste forms containing 40 wt% sodium tetraborate was investigated. Oxidized bitumen (Pioneer 321) softens between 70 and 140°C and has "good adhesive and self-healing properties" [73].

Figures 8.1 through 8.6 summarize the effect of temperature on the leaching of radionuclides from this form. Figures 8.1, 8.3 and 8.5 present the cumulative fraction leached (CFL) versus time for Cs-137, Sr-85 and Co-57, respectively, at 20, 40 and 50°C. Figures 8.2, 8.4 and 8.6 show linear correlations of these data versus the 20°C data.

Elevated temperatures do not accelerate leaching from bitumen for any of the radionuclides investigated. The statistical scattering in the data is large but it seems that at 50°C, leaching is actually reduced relative to that

at 20°C. This could be caused by a "self-healing" process in which bitumen would flow into pores that form as the salt begins to swell.

Since the leaching of radionuclides at elevated temperature is only marginally useful, the leaching of non-radionuclide elements from bitumen containing 40 wt% sodium tetraborate was not presented.

8.2.2 The Surface Area of the Waste Form to Leachant Volume. The ANS 16.1 leach test specifies that the ratio of the leachant volume (cubic cm) to the geometric surface area (square cm) of the test specimen should be 10 ± 0.2 (cm). To investigate the effect of increasing this ratio on leaching behavior, ratios of 30, and 50 were used. The results for Cs-137, Sr-85 and Co-57 from bitumen containing 40 wt% sodium tetraborate are shown in Figures 8.7, 8.8, and 8.9.

No apparent increase in the leaching of Cs-137, Sr-85 or Co-57 was observed (Figures 8.7, 8.8, and 8.9) due to an increase in the leachant volume to sample surface area ratio. The apparent decrease in the observed leaching (CFL) is probably an artifact: specifically, although all of the samples in these experiments were nominally identical, only the two sets at the larger volumes were replicates, whereas the samples at 1300 ml (i.e., ratio of 10:1) were fabricated at a different time. Therefore, increasing the leachant volume to surface ratio was not promising as an accelerating factor for Cs-137, Sr-85 or Co-57. Further experiments to measure the release of non-radionuclide elements were not pursued.

8.2.3 Leachant Composition. Deionized water (DIW) was the standard leachant used in the ANS 16.1 leach test. Leachants used to examine the effect of leachant composition on the leaching of bitumen waste forms containing 40 wt% sodium tetraborate included DIW, simulated groundwater of an Oak Ridge National Lab (ORNL) well water [33] and DIW containing 100 ppm EDTA. The mineral content of the ORNL groundwater is listed in Table 3.3. In addition, we used two variations of the ORNL simulated groundwater:

- (i) in a well-oxygenated state (i.e., oxic groundwater), and
- (ii) in a solution depleted of oxygen (i.e., anoxic groundwater).

Both oxic and anoxic groundwaters contained soil-extracted humic acids to make the compositions more realistic. Humic acids have strong affinities for metal ions and can act as complexing and chelating agents [79]. The experiments with 100 ppm EDTA in the leachant were used to examine the effect of a very strong chelating agent, the disodium ethylenediaminetetraacetate (EDTA) hexahydrate salt.

Figure 8.10 shows the leaching curves for Cs-137 from bitumen containing 40 wt% sodium tetraborate leached at 20°C in DIW, oxic and anoxic groundwaters. Figure 8.11 shows leaching curves for Cs-137 leached from bitumen in DIW, and in a solution of DIW with 100 ppm EDTA. The greatest leachability was observed in DIW. Suppression of Cs-137 leaching might be expected because of the relatively higher ionic strength of the groundwater leachant [3] and is corroborated by other reports [64,65]. Since the EDTA would not affect the

solubility of Cs-137, the increase in ionic strength of the leachant is the only obvious effect that it would have. Likewise, anoxic groundwater has a substantially greater ionic strength than does oxic groundwater, as shown in Table 3.3. In sum, the presence of chelating agents and the oxic or anoxic state of the leachant make little difference in the Cs-137 leachability from the bitumen waste forms, and increasing the ionic strength of the leachant decreases the Cs-137 leachability.

Figure 8.12 shows the comparable leaching curves for Sr-85. Figure 8.13 shows the leaching curves for Sr-85 leached in DIW and a 100 ppm solution of EDTA. In all cases Sr-85 is more leachable in DIW. For either the oxic or anoxic groundwater the high carbonate content and the high ionic strength of the leachant would explain the reduced leachability of Sr-85. The presence of natural chelating agents, i.e., the humic acids or the synthetic chelating agent EDTA make little, if any, difference in the Sr-85 leachability from these solutions. In fact, the relative increase in the ionic strength of the EDTA solution only decreases the Sr-85 leachability.

Figure 8.14 shows the leaching curves for Co-57 from bitumen containing 40 wt% sodium tetraborate at 20°C in DIW, oxic and anoxic groundwaters. Figure 8.15 shows the leaching curves for Co-57 in DIW and a 100 ppm solution of EDTA. The Co-57 leachability was enhanced in both the oxic groundwater and the 100 ppm solution of EDTA. However, the Co-57 leachability in the anoxic groundwater was lower than that of the DIW. The oxic groundwater, anoxic groundwater and the 100 ppm solution all have ionic strengths that are greater than that of the DIW and would be expected to suppress leaching to some extent as was observed for both Cs-137 and Sr-85 (discussed in Section 8.2.3). Cobalt(II) is the only stable oxidation state in aqueous solutions at room temperatures (20°C) containing no complexing agents. In basic solution, cobaltous hydroxide is rather insoluble ($K_{sp}=1E-16$) [80,81]. However cobalt ions are strongly complexed in aqueous solutions, especially by EDTA. The presence of Co (III) in solution is not favored. But in the presence of complexing agents, such as humic acids or EDTA, and slightly basic conditions, the stability of Co(III) is greatly improved. The groundwater solutions are slightly basic and contain natural humic acids, which are known complexing agents [80]. Formation of a complex of Co(III) could possibly account for the increased leachability of Co-57 both in the oxic groundwater and the 100 ppm solution of EDTA. The correlation diagrams in Figures 8.16 and 8.17 clearly show the increased leachability in oxic groundwater and the 100 ppm EDTA solution, respectively.

The leaching of sodium and boron from bitumen containing 40 wt% sodium tetraborate at 20°C in DIW and oxic groundwater is shown in Figure 8.18: Figure 8.19 shows the linear correlation plots for sodium, boron and Cs-137. Considerable leaching of sodium tetraborate was observed.

8.2.4 pH of the Leachant. The pH of deionized water (DIW), which is the standard leachant in the ANS 16.1 leach test, is nominally 7 at 20°C but is actually slightly acidic (about 6) due to dissolution of carbon dioxide from the air. Initial leachant pH values of 4, 6 and 8 were used in the investigations. Increasing the acidity of the leaching solution would be expected to increase the leach rate of most constituents: conversely,

decreased leachability of many constituents would be expected in basic solutions.

The results shown in Figure 8.20 for bitumen containing 40 wt% sodium tetraborate leached at 20°C indicated that the leachability of Cs-137 was not affected by the initial pH of the leachant over a range of 4 to 8. Further experiments were not pursued since pH was not an accelerating factor for Cs-137. Similarly, the initial pH of the leachant solution also did not affect the leachability of Sr-85 (Figure 8.21).

Leaching of Co-57, however, was different. Figure 8.22 shows the leaching data for Co-57 from bitumen containing 40 wt% sodium tetraborate. Figure 8.23 shows a correlation plot of these data. The leaching of Co-57 is enhanced in the alkaline (pH=8) solution. This effect is consistent with the observations made for oxic groundwater and the 100 ppm solution of EDTA reported in section 8.2.3 for Co-57 leaching, namely that oxygen saturated, somewhat alkaline solutions that contain small amounts of complexing agents (natural or synthetic) may show enhanced leachability of Co-57 from these bitumen waste forms. Cobaltous hydroxide is rather insoluble in alkaline solutions and would not be expected to dissolve. Cobalt (II) is the only stable oxidation state of cobalt in aqueous solution at room temperature in the absence of complexing agents. However Co(III) existence is enhanced in slightly alkaline aqueous solutions containing complexing agents. Complexes of Co(III) are exceedingly numerous and have been extensively studied. Bitumen itself is a mixture of organic substances that could possibly act as chelating agents for Co(III). But more importantly, the borate ion of the waste itself could possibly act as a chelating ligand [82].

8.2.5 Flow and Replacement Frequency of the Leachant. The flow or replacement frequency of the leachant may affect leachability because of the buildup of materials in the leachant. The ANS 16.1 leach test provides for daily replacements through day five following replacements at 2 hours and 7 hours and the first day. Following day five, the replacement intervals are much longer, up to three weeks in duration. The effect of changing the leaching period from daily to longer periods was investigated by conducting a leaching experiment in which the sampling intervals, after the first three short intervals, were one day. Daily leachant replacements continued until the end of the experiment (34 days). To investigate the effect of continuous replacement (flow) versus periodic replacement, bitumen waste forms containing 40 wt% sodium tetraborate were leached in a flow experiment based on the MCC4S flow test (Materials and Method section 2.3.3).

Figure 8.24 shows the CFL of Cs-137 from bitumen wastes for triplicate samples using the modified ANS 16.1 test and changing daily. Figure 8.25 shows the correlation diagram for the same data. There appears to be no useful acceleration due to maintaining the leaching interval at one day. Two experimental artifacts are worth noting. First, the final CFLs for Cs-137 from the modified ANS 16.1 test were considerably different from sample to sample, approximately 0.75 to 1.2. Second, one of the samples used in the daily test showed a large initial rise in the Cs-137 leaching. Both of these effects probably reflect the difficulty in preparing entirely uniform samples

of the waste form which are essentially heterogeneous mixtures of dry solids in a viscid liquid.

The Cs-137 release rate versus in the flow test with duplicate bitumen waste forms are shown in Figure 8.26 where the time is shown because one cannot directly calculate the CFL from the MCC4S flow test data. For comparison, Figure 8.26 also shows the release rate of Cs-137 for the modified ANS 16.1 test. No observable increase in the release rate was found in the flowing leachate.

Figure 8.27 shows the leaching results for Sr-85 from the bitumen waste with 40 wt% sodium tetraborate using the modified ANS 16.1 sampling schedule and sampling daily. Figure 8.28 shows the linear correlation diagram for this data. No apparent increase in the leaching was observed for changing the sampling periods to a daily basis. Figure 8.29 shows the leach rates for triplicate samples during the modified ANS 16.1 tests, and duplicate samples during the MCC4S flow test. No apparent difference in the rate of leaching was observed in this experiment.

The CFL of Co-57 from the bitumen waste observed during the modified ANS 16.1 test and the daily sampling test, using triplicate samples in both cases, are shown in Figure 8.30. Figure 8.31 shows the linear correlation for the same data. One sample in the daily sampling experiment exhibited enhanced leaching of Co-57. The other two waste forms did not. It is believed that this difference, for samples that are nominally identical, reflects the difficulty of preparing entirely uniform waste forms.

Figure 8.32 shows the release rates of Co-57 observed for triplicate samples during the modified ANS 16.1 test and duplicate samples used for the MCC4S flow test. No apparent difference in the leach rates were observed.

8.2.6 Composition of the Waste Form. The composition of the waste form is a major determinant in the leaching behavior of bitumen waste forms containing soluble salts. Bitumen has a small but definite permeability to water. The osmotic pressure gradient inside the waste form is between the soluble salt through the water-permeable bitumen membrane and the external leachate solution. This osmotic pressure causes the elastic bitumen binder to swell and the waste form to crack. The effect is strongly controlled by the amount of waste in the waste form. For sodium tetraborate, the swelling becomes noticeably rapid at waste loadings greater than 20 wt%. Figure 8.33 shows the severe swelling and cracking of bitumen waste forms containing 40 wt% sodium tetraborate before and after 403 days in DIW at 20°C. To demonstrate these effects, experiments were conducted with neat bitumen and bitumen containing 20, 30 and 40 wt% sodium tetraborate in DIW at 20°C.

Figure 8.34 shows the Cs-137 CFL data from triplicate samples in these experiments. All four sets of leaching curves are characterized by an initial period of relatively low leach rates. The neat bitumen continues to leach at a low rate for over 500 days. For the waste forms containing sodium tetraborate, the initial slow leaching period was followed by a rapid rise in the CFL of Cs-137. Although there is significant statistical scattering in the leaching curves, the behavior of the sets of leaching curves for each waste

form waste loading can be distinguished clearly. The increase in the CFL corresponded to the waste form loading, that is, minimal leaching was observed for neat bitumen (0 wt%) and maximal for bitumen containing 40 wt% sodium tetraborate. The approximate time at which the leach rate increased was 100 days for 20 wt%, 5 days for 30 wt% and 2 days for 40 wt%. This change corresponded to the start of swelling of the waste form and, presumably, to the permeation of water from the leachant.

The leaching behavior of Cs-137 for bitumen waste forms containing sodium tetraborate cannot be accounted for by diffusion alone since it appears to be dependent on the rate of permeation of water into the waste form.

The leaching data for Sr-85 from triplicate samples of bitumen waste forms containing 0, 20, 30 and 40 wt% are shown in Figure 8.35. The data on Sr-85 is quite similar to that of Cs-137. However, the statistical scattering the 20 and 30 wt% waste loadings, after 5 days of leaching, falls into a broad band between the neat bitumen (0 wt%) samples and those containing 40 wt% sodium tetraborate. In sum, the CFL from bitumen is characterized by an initial slow rate of release, followed by a rapid rise in the CFL; at any time after the initial period this rate depends on the waste form loading, such that the greatest leaching was observed for the highest waste loading.

Figure 8.36 shows the leaching data for Co-57 from triplicate samples of these bitumen waste forms. Co-57 leaching is generally an order of magnitude lower than that of Cs-137 and Sr-85. Still, the leaching behavior of Co-57 is quite similar to that of Sr-85. The major difference is that the relative rise in the leach rate is not as great but still clearly apparent for the samples containing sodium tetraborate. The statistical scattering in the leaching data for the samples containing 20 and 30 wt% sodium tetraborate is relatively large but falls into a broad band between that observed for neat bitumen (0 wt%) and the samples containing 40 wt% sodium tetraborate.

Leaching of sodium and boron from bitumen waste forms containing 40 wt% sodium tetraborate are shown in Figure 8.18. Complete leaching of the sodium tetraborate waste was observed.

8.2.7 Ratio of Surface to Volume (V/S) in the Waste Form. Sample scale is a major accelerating factor for predicting the behavior of full-scale waste forms. For leaching behavior that can be accounted for by diffusion theory, the waste form volume to surface area ratio (V/S) can be theoretically correlated with the CFL of a radionuclide. To examine the scaling behavior of small laboratory specimens, waste forms of bitumen containing 40 wt% sodium tetraborate of three different sizes were leached with DIW at 20°C.

Figure 8.37 shows the Cs-137 leaching data for triplicate samples of each size. There was no apparent acceleration for diminishing waste form volume to surface area (V/S) ratio. The rapid rise in the Cs-137 leach rate apparently overwhelms any observable differences due to scale. The large scattering in the final CFL data reflects the difficulty of preparing uniform samples, which were nominally identical.

The Sr-85 leaching data for triplicate samples of each sample size is shown in Figure 8.38. The increase in leaching of Sr-85 appears to correlate with the ratio of volume to surface area (V/S) before depletion of the sample occurs. The broad statistical scattering of the final CFL data again reflects the problem of uniformity. Figure 8.39 shows the correlation diagram for the same data. The precision in the leaching data appears to be relatively good below 0.4 CFL, but deteriorates very significantly above this value. The scaling data for Sr-85 appears to be of limited usefulness.

Figure 8.40 shows that leaching data for Co-57. The statistical scattering for the small sample was quite appreciable above about 0.1 CFL. The leaching behavior appears to increase with decreasing ratio of waste form volume to surface area (V/S). This is further illustrated in the correlation diagram Figure 8.41. At about 0.025 CFL, the leaching behavior of each sample size falls into three broad but separate bands. The statistical uncertainties in the Co-57 CFL data may limit the usefulness of these results.

8.2.8 Porosity and Surface Condition of the Waste Form. The porosity of bitumen waste forms is known to be very small, but the swelling of waste forms containing 40 wt% sodium tetraborate indicates that water permeability is a critical factor in the performance of the waste form.

Figure 8.1 Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C leached in deionized water.

Figure 8.2 Linear correlation plots for Cs-137 leaching from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C. Correlations are relative to the 20°C data.

Figure 8.3 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C leached in DIW.

Figure 8.4 Linear correlation plots for Sr-85 leaching from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C. Correlations are relative to the 20°C data.

Figure 8.5 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C leached in DIW.

Figure 8.6 Linear correlation plots for Co-57 leaching from bitumen containing 40 wt% sodium tetraborate at 20, 40 and 50°C. Correlations are relative to the 20°C data.

Figure 8.7

Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at leachant volume to waste form surface area ratios of 10, 30 and 50:1. Samples were leached in DIW at 20°C.

Figure 8.8

Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at leachant volume to waste form surface area ratios of 10, 30 and 50:1. Samples were leached in DIW at 20°C.

Figure 8.9 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at leachant volume to waste form surface area ratios of 10, 30 and 50:1. Samples were leached in DIW at 20°C.

Figure 8.10 Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW, oxic and anoxic ground waters at 20°C.

Figure 8.11

Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.

Figure 8.12

Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW, oxidic and anoxic ground waters at 20°C.

Figure 8.13 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.

Figure 8.14 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW, oxic and anoxic ground waters at 20°C.

Figure 8.15

Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in DIW and in DIW containing 100 ppm disodium EDTA at 20°C.

Figure 8.16

Linear correlation plots for Co-57 leached from bitumen containing 40 wt% sodium tetraborate in DIW, oxidic and anoxic ground waters. Correlations are relative to the DIW data.

Figure 8.17

Linear correlation plots for Co-57 leached from bitumen containing 40 wt% sodium tetraborate in DIW and DIW containing 100 ppm disodium EDTA. Correlations are relative to the DIW data.

Figure 8.18

Cumulative fraction leached of sodium and boron versus time from bitumen containing 40 wt% sodium tetraborate leached in DIW and oxic ground water at 20°C.

Figure 8.19

Linear correlation plots for sodium, boron and Cs-137 leached from bitumen containing 40 wt% sodium tetraborate in DIW and oxic ground water at 20°C. Correlations are relative to the data for Cs-137 leached in DIW.

Figure 8.20

Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in leachants with initial pH values of 4, 6 and 8 at 20°C.

Figure 8.21 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate leached in leachants with initial pH values of 4, 6 and 8 at 20°C.

Figure 8.22 Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate in leachants with initial pH values of 4, 6 and 8 at 20°C.

Figure 8.23

Linear correlation plots for Co-57 leached from bitumen containing 40 wt% sodium tetraborate in leachants with initial pH values of 4, 6 and 8. Correlations are relative to the pH 6 (DIW) data.

Figure 8.24

Cs-137 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for bitumen waste forms containing 40 wt% sodium tetraborate leached at 20°C.

Figure 8.25

Linear correlation plots for Cs-137 leached from bitumen waste forms containing 40 wt% sodium tetraborate using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule. Correlations are relative to the ANS 16.1 data.

Figure 8.26

Cs-137 incremental leach rate vs. time from bitumen waste forms containing 40 wt% sodium tetraborate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.

Figure 8.27

Sr-85 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for bitumen waste forms containing 40 wt% sodium tetraborate leached at 20°C.

Figure 8.28

Linear correlation plots for Sr-85 leached from bitumen waste forms containing 40 wt% sodium tetraborate using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule. Correlations are relative to the ANS 16.1 data.

Figure 8.29

Sr-85 incremental leach rate vs. time from bitumen waste forms containing 40 wt% sodium tetraborate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.

Figure 8.30

Co-57 cumulative fraction leached vs. time from daily leachant replacement and from modified ANS 16.1 leachant replacement schedule for bitumen waste forms containing 40 wt% sodium tetraborate leached at 20°C.

Figure 8.31

Linear correlation plots for Co-57 leached from bitumen waste forms containing 40 wt% sodium tetraborate using daily leachant replacement and the modified ANS 16.1 leachant replacement schedule. Correlations are relative to the ANS 16.1 data.

Figure 8.32

Co-57 incremental leach rate vs. time from bitumen containing 40 wt% sodium tetraborate comparing results of MCC-4S Flow test to modified ANS 16.1 leachant replacement schedule at 20°C.

Figure 8.33

Bitumen forms containing 40 wt% sodium tetraborate. The one at left is as fabricated. The one at right was leached for 320 days in deionized water at 20°C. Samples were 4.8 cm diameter by 6.4 cm high right cylinders.

Figure 8.34

Cs-137 cumulative fraction leached vs. time from bitumen containing 0, 20, 30 and 40 wt% sodium tetraborate. Samples were leached in DIW at 20°C.

Figure 8.35

Sr-85 cumulative fraction leached vs. time from bitumen containing 0, 20, 30 and 40 wt% sodium tetraborate. Samples were leached in DIW at 20°C.

Figure 8.36

Co-57 cumulative fraction leached vs. time from bitumen containing 0, 20, 30 and 40 wt% sodium tetraborate. Samples were leached in DIW at 20°C.

Figure 8.37 Cs-137 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.

Figure 8.38 Sr-85 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.

Figure 8.39

Linear correlation plots for Sr-85 leached from bitumen waste forms containing 40 wt% sodium tetraborate at waste form volume to surface area ratios (V/S) of 0.42, 0.62 and 0.91. Correlations are relative to the V/S = 0.91 data.

Figure 8.40

Co-57 cumulative fraction leached vs. time from bitumen containing 40 wt% sodium tetraborate at waste form volume to surface area (V/S) ratios of 0.42, 0.62 and 0.91. Samples were leached in deionized water at 20°C.

Figure 8.41

Linear correlation plots for Co-57 leached from bitumen waste forms containing 40 wt% sodium tetraborate at waste form volume to surface area ratios (V/S) of 0.42, 0.62 and 0.91. Correlations are relative to the V/S = 0.91 data.

9. SODA-LIME GLASS INCORPORATING INCINERATOR ASH AS SIMULATED WASTE

The glass waste form samples that we investigated were produced by Mound Laboratory [4]. Mound Laboratory investigated the glass solidification of LLW using a process in which combustible LLW was fed into an electrically heated glass furnace for incineration. Solid residue from the incineration either dissolves in the glass or is suspended in the glass as ash particulates. The volume fraction of ash is typically small and the porosity due to the ash inclusions is unconnected.

The samples provided were not ideal because of their low radio-nuclide activity levels (c.f., Table 3.1). This, plus the inherently low leachability of glass, resulted in unmeasurably low releases in the leach tests. Three leach tests were performed:

- (i) ANS 16.1 Leach Test in deionized water at 50°C for 67 days. Sample was a right cylinder, 1 cm diameter by 1 cm high.
- (ii) 28-day static leach test at 90°C in deionized water. Sample was a right cylinder 1 cm diameter by 1 cm high.
- (iii) MCC3 Agitated Powder Leach Test.

No activity above background was detected in any of the leachates, precluding any evaluation of factors that affect leachability.

10. SUMMARY AND CONCLUSIONS

This experimental investigation of the factors that affect leaching was specifically directed toward finding those that accelerate the leach rate without changing the leaching mechanisms of solidified low-level waste forms. Each of these sought-for factors is summarized in this section, while the complete results for these potential accelerating factors is contained in sections 4 through 8 of this report along with the information obtained on those factors that showed no acceleration and/or changed the leaching mechanism.

Tables 10.1, 10.2 and 10.3 summarize the results of the leaching studies for each acceleration factors of Cs-137, Sr-85 and Co-57, respectively. Positive acceleration which did not alter leaching mechanisms is shown as a "yes." Clearly negative results, either slowed leaching, statistically insignificant changes in leaching or changes in mechanisms are indicated by a "no." Results that are promising but unclear are marked by an "mixed." For example, releases from VES containing sodium sulfate salt appear to be accelerated by temperature during the first week of leaching. Later, however, the data becomes scattered, making any final conclusion uncertain. This factor may still be useful as one of several combined factors. In general, a better understanding of release mechanisms is also necessary for materials in the "mixed" category.

Results of these leaching studies on single acceleration factors will be used in the next stage of this program to determine what combinations of individual factors will be tested. In general, the most effective acceleration factors were:

- temperature
- composition of the waste form
- size

Often some of the materials investigated responded in very different ways to various acceleration factors and these reactions are not well understood. Indeed, the leaching mechanisms for some are not conclusively defined. Some have been observed to change with time, even when no acceleration factors were applied.

A brief review of the acceleration factors that proved to be positive follows.

Temperature - Perhaps the single most clear-cut acceleration factor for cement waste forms is temperature. Temperature substantially accelerated Cs-137 leaching from plain cement, from cement with sodium sulfate salt and from cement with incinerator ash. Leach rates may be increased by more than twenty-fold, giving the equivalent of one year of data in 18 days. This is particularly important since cement materials are the most commonly used

solidification agents and the most likely materials to be used for engineered barriers.

Strontium release from cement materials is not accelerated very well by temperature. This finding is not unreasonable because, as cement ages, carbonation of its surface inhibits strontium leaching. This topic requires more study, particularly regarding the rate changes of carbonate formation and its relationship to strontium uptake.

Cobalt is not generally released from cement (unless complexed in real waste) and it is not released from experiments using temperature as an acceleration factor. So this is a case where "no" for acceleration is required.

Accelerated leach tests of other materials using temperature had less conclusive results. At 40°C bitumen specimens may show some increased leaching; however, at 50°C leaching decreased, apparently because heated bitumen can flow and heal itself. Moreover, the statistical scatter is greater at elevated temperatures than at 20°C.

Releases from VES with sodium sulfate salt increased with temperature during the first week of leaching. After that the scatter in the data obscured any trends. This effect may be related to the leaching mechanism, as discussed in Section 7. Nevertheless, temperature may be a useful acceleration factor for VES.

Composition of the Waste Form - Increasing waste loading tends to increase releases. Whether the increase in leachability is a reproducible function of loading is not clear, but there is some evidence that it may be for borate salts in bitumen. If this is so, testing waste forms with greater salt loadings may give accelerated results for specimens with lower loadings. It also will give information about the integrity of the waste form since increased leaching and degradation of the waste are associated phenomena.

Size - A theoretical discussion of the effect of waste form size on leaching is given in Section 2.7. Reduction in size for portland cement materials accelerates leaching of Cs-137 and Sr-85, as long as size changes keep the same aspect ratio. A particular problem with this concept is maintaining homogeneous and representative specimens at small sizes. Nevertheless, for the cement-based waste forms tested in this program, it is a useful acceleration factor.

The releases from VES specimens of different sizes containing dry sulfate salt were mixed. For the first 6 days leach rates were higher from the small specimens than from those of standard size. After reaching a CFL of 0.40, increased scatter and depletion masked any trends. If the early portion of leaching is representative of long-term releases from this material, then size could be used as an acceleration factor.

Other Factors - Other factors had positive results that influenced only certain radionuclides from specific solidification agents. The best example is leaching of Co-57 from bitumen, which were accelerated by in oxic groundwater,

100 ppm EDTA solution and in buffered solutions at pH 8. Cobalt is the only multivalent isotope used in this study, and was expected to behave differently under various conditions.

10.1 Prelude to Future Works

Combining some acceleration factors may not only be expected to result in faster leaching, but also in some marginal cases, more consistent results. In exploring the effects of combined factors it will be important to more fully understand the physical and chemical controls on leaching. For most materials tested it has become clear that responses to leaching (either with or without acceleration factors) change with time; carbonate layers grow on cement, bitumen heals developing pores at 50°C, VES may have a two-step leaching mechanism related to a skin of clean polymer at its surface. These observations coming from this program have impacts not only on work to develop an accelerated leach test, but also on understanding the long-term durability of these materials.

Table 10.1

Summary of Acceleration Factor Effects for Cs-137

Acceleration Factors	Portland Cement + Na_2SO_4	Portland Cement + Incinerator Ash	VES Emulsion + Na_2SO_4 Sol.	VES + Na_2SO_4 Salt	Bitumen + $\text{Na}_2\text{B}_4\text{O}_7$
Temperature °C					
40	yes	yes	no	mixed	mixed
50	yes	yes	no	mixed	no
Leachant Volume to Surface Area of the Waste Form	no	ND	ND	no	no
Leachant Composition					
Oxic GW	no	no	no	no	no
Anoxic GW	no	ND	ND	no	no
100 ppm EDTA	no	ND	ND	mixed	no
Leachant pH	no	no	no	no	no
Leachant Replacement					
Flow Test	no	no	mixed	no	no
Daily	no	ND	ND	no	no
Waste Form Composition	mixed	mixed	yes	mixed	yes
Size (V/S)	yes	yes	mixed	yes	yes

Yes - definite acceleration with consistent mechanism.

No - no acceleration or change in mechanism.

Mixed - unclear results, but some positive potential.

ND - not done.

Table 10.2

Summary of Acceleration Factor Effects for Sr-85

Acceleration Factors	Portland Cement + Na ₂ SO ₄	Portland Cement + Incinerator Ash	VES Emulsion + Na ₂ SO ₄ Sol.	VES + Na ₂ SO ₄ Salt	Bitumen + Na ₂ B ₄ O ₇
Temperature °C					
40	yes	yes	no	mixed	mixed
50	yes	yes	no	mixed	no
Leachant Volume to Waste Form Surface Area	no	ND	ND	no	no
Leachant Composition					
Oxic GW	no	yes	no	no	no
Anoxic GW	no	ND	ND	no	no
100 ppm EDTA	yes	ND	ND	no	no
Leachant pH	yes	no	no	no	no
Leachant Replacement					
Flow Test	no	no	no	no	no
Daily	yes	ND	ND	no	no
Waste Form Composition	no	no	yes	yes	yes
Size (V/S)	yes	yes	yes	yes	yes

Yes - definite acceleration with consistent mechanism.

No - no acceleration or change in mechanism.

Mixed - unclear results, but some positive potential.

ND - not done.

Table 10.3

Summary of Acceleration Factor Effects for Co-57

Acceleration Factors	Portland Cement + Na ₂ SO ₄	Portland Cement + Incinerator Ash	VES Emulsion + Na ₂ SO ₄ Sol.	VES + Na ₂ SO ₄ Salt	Bitumen + Na ₂ B ₄ O ₇
Temperature °C					
40	NRO	NRO	no	mixed	no
50	NRO	NRO	no	mixed	no
Leachant Volume to Waste Form Surface Area	NRO	ND	ND	no	no
Leachant Composition					
Oxic GW	NRO	NRO	no	no	yes
Anoxic GW	NRO	ND	ND	no	no
100 ppm EDTA	NRO	ND	ND	no	yes
Leachant pH	NRO	NRO	no	no	yes
Leachant Replacement					
Flow Test	NRO	NRO	no	no	no
Daily	NRO	ND	ND	no	no
Waste Form Composition	NRO	NRO	yes	mixed	yes
Size (V/S)	NRO	NRO	yes	yes	yes

Yes - definite acceleration with consistent mechanism.

No - no acceleration or change in mechanism.

Mixed - unclear results, but some positive potential.

ND - not done.

NRO - no release observed.

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APPENDIX A

Appendix A contains ten tables that list the sample parameters (weight, height, diameter, volume and surface area), leachant type and volume and the leaching temperature ($\pm 2^{\circ}\text{C}$) for each of the samples containing radiotracers (Cs-137, Sr-85 and Co-60 or Co-57) fabricated and tested in this task. Each sample has been assigned a TESTID and a SAMPLEID for identification in the text and in the figures. Each table contains the parameters for a single sample type (i.e., composition), as follows:

- Table A1: Portland type I cement containing 5 wt% sodium sulfate salt as simulated waste
- Table A2: Portland type I cement containing 15 wt% incinerator ash as simulated waste
- Table A3: Vinyl ester-styrene emulsion with aqueous sodium sulfate solution as simulated waste
- Table A4: Vinyl ester-styrene containing 20 wt% sodium sulfate salt as simulated waste
- Table A5: Vinyl ester-styrene containing 30 wt% sodium sulfate simulated waste
- Table A6: Vinyl ester-styrene containing 40 wt% sodium sulfate salt as simulated waste
- Table A7: Bitumen containing 20 wt% sodium tetraborate salt as simulated waste
- Table A8: Bitumen containing 30 wt% sodium tetraborate salt as simulated waste
- Table A9: Bitumen containing 40 wt% sodium tetraborate salt as simulated waste
- Table A10: Portland type I cement containing only radiotracers of Cs, Sr and Co as simulated waste

Table A1

Test and Sample Parameters for Portland I Cement With Sodium Sulfate (5 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 0.54¹. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1111	PS1A	208.9	6.25	4.70	108	127	DIW ²	1300	20
1112	PS1B	206.3	6.20	4.60	103	123	DIW	1300	20
1113	PS1C	208.5	6.30	4.60	105	124	DIW	1300	20
1116	PS1F	21.9	2.50	2.50	12.3	29.4	DIW	300	20
1117	PS1G	23.4	2.60	2.50	12.8	30.2	DIW	300	20
1118	PS1H	21.8	2.40	2.50	11.8	28.7	DIW	300	20
1119	PS1I	412.9	1.50	13.9	228	369	DIW	3650	20
1120	PS1J	420.8	1.50	13.9	228	369	DIW	3650	20
1121	PS1K	413.9	1.50	13.9	228	369	DIW	3650	20
1122	PS2L	216.3	6.70	4.70	116	134	DIW	1300	40
1123	PS2M	202.3	6.20	4.70	108	126	DIW	1300	40
1124	PS3A	204.4	6.20	4.70	111	129	DIW	1300	50
1125	PS3B	196.6	6.20	4.70	108	126	DIW	1300	50
1126	PS3C	210.0	6.50	4.70	113	131	DIW	1300	50

Table A1 (cont.)

Test and Sample Parameters for Portland I Cement With Sodium Sulfate (5 wt%) Type Waste
Waste-to-Binder Ratio (w/w) = 0.54¹. Samples Contain Co-57, Sr-85 and Cs-137.

-A2-	Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
	1129	PS4A	211.8	6.50	4.60	108	127	GW ³	1300	20
	1130	PS4B	205.6	6.40	4.60	106	126	GW	1300	20
	1131	PS4C	209.2	6.50	4.60	108	127	GW	1300	20
	1135	PS7B	205.6	6.30	4.70	109	128	DIW ⁴	1000	20
	1136	PS7C	198.9	6.10	4.60	101	121	DIW	1000	20
	1137	PS6A	211.4	6.50	4.60	108	127	DIW	2600	20
	1138	PS6B	190.0	5.80	4.70	100	120	DIW	3900	20
	1139	PS10A	204.6	6.40	4.60	101	126	pH3 ⁵	1300	20
	1140	PS10B	209.3	6.40	4.60	106	126	pH4 ⁵	1300	20
	1141	PS10C	208.4	6.40	4.60	106	126	pH5 ⁵	1300	20
	1142	PS10D	215.0	6.60	4.60	110	129	pH8 ⁶	1300	20

Table A1 (cont.)

Test and Sample Parameters for Portland I Cement With Sodium Sulfate (5 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 0.54¹. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1150	7-PS2A	203.5	6.20	4.70	108	126	ANOXIC	1300	20
1151	7-PS2B	217.7	6.60	4.80	119	136	ANOXIC	1300	20
1152	7-PS2C	209.1	6.40	4.70	111	129	ANOXIC	1300	20
1160	7-PS5A	210.3	6.40	4.60	106	126	DIW	1300	20
1161	7-PS5B	211.7	6.30	4.60	105	124	DIW	1300	20
1162	7-PS5C	202.9	6.20	4.60	103	123	DIW	1300	20
1163	7-PS7A	2234	14.2	10.0	112	603	DIW	6000	20
1164	7-PS7B	2220	14.0	10.1	112	604	DIW	6000	20
1165	7-PS7C	2238	14.0	10.0	110	597	DIW	6000	20
1168	7-PS8A	206.4	6.20	4.70	108	126	DIW	3900	20
1169	7-PS8B	215.9	6.50	4.70	113	131	DIW	3900	20
1170	7-PS8C	223.9	6.90	4.70	120	137	DIW	3900	20
1171	7-PS9A	211.3	6.40	4.60	106	126	DIW	6500	20
1172	7-PS9B	202.9	6.20	4.60	103	123	DIW	6500	20
1173	7-PS9C	223.5	6.70	4.60	111	130	DIW	6500	20

Table A1 (cont.)

Test and Sample Parameters for Portland I Cement With Sodium Sulfate (5 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 0.54¹. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1174	7-PS11A	213.7	6.40	4.60	106	126	EDTA ⁸	1300	20
1175	7-PS11B	215.6	6.50	4.60	108	127	EDTA	1300	20
1176	7-PS11C	212.1	6.50	4.60	108	127	EDTA	1300	20
1177	7-PS12A	24.4	2.70	2.40	12.2	29.4	DIW	300	50
1178	7-PS12B	25.4	2.70	2.40	12.2	29.4	DIW	300	50
1179	7-PS12C	27.1	3.00	2.40	13.8	31.7	DIW	300	50

1. A 14.3 wt% solution of Na₂SO₄ in water was used as the waste simulant.

2. DIW = deionized water.

3. GW = simulated groundwater.

4. Flow Test MCC4S, 1L/day.

5. HNO₃ solution.

6. NaHCO₃ solution (0.5g/L).

7. Anoxic = simulated anoxic groundwater.

8. EDTA - 100 ppm solution of disodium ethylenediamine tetraacetate dihydrate.

Table A2

Sample and Test Parameters for Portland Type I Cement With Incinerator Ash (60 wt% cement, 15 wt% ash, 30 wt% water).
Waste-to-Binder Ratio (w/w) = 0.58¹. Samples Contain Co-57, Sr-85 and Cs-137.

-A5-	Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
	1211	PA1A	216.6	6.80	4.70	118	135	DIW ²	1300	20
	1212	PA1B	207.2	6.45	4.70	112	130	DIW	1300	20
	1213	PA1C	214.8	6.50	4.60	108	127	DIW	1300	20
	1216	PA1F	22.9	2.60	2.50	12.8	30.2	DIW	300	20
	1217	PA1G	23.3	2.60	2.50	12.8	30.2	DIW	300	20
	1218	PA1H	24.0	2.70	2.50	13.2	31.0	DIW	300	20
	1219	PA1I	423.3	1.50	13.9	227	369	DIW	3650	20
	1220	PA1J	397.3	1.50	13.9	227	369	DIW	3650	20
	1221	PA1K	426.0	1.50	13.9	227	369	DIW	3650	20
	1222	PA2L	210.9	6.50	4.70	113	131	DIW	1300	40
	1223	PA2M	203.6	6.40	4.70	111	129	DIW	1300	40
	1224	PA3A	213.4	6.50	4.70	113	131	DIW	1300	50
	1225	PA3B	221.9	6.30	4.70	109	128	DIW	1300	50
	1226	PA3C	207.4	6.40	4.70	111	129	DIW	1300	50

Table A2 (cont.)

Sample and Test Parameters for Portland Type I Cement With Incinerator Ash (60 wt% cement, 15 wt% ash, 30 wt% water).
Waste-to-Binder Ratio (w/w) = 0.58¹. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1229	PA4A	210.1	6.70	4.70	116	134	GW ³	1300	20
1230	PA4B	200.9	6.40	4.70	111	129	GW	1300	20
1231	PA4C	199.6	6.50	4.70	113	131	GW	1300	20
1235	PA7B	205.7	6.50	4.60	108	127	DIW	1000	20
1236	PA7C	209.3	6.60	4.60	110	129	DIW	1000	20
1240	PA10B	200.1	6.30	4.60	105	124	pH4 ⁵	1300	20
1242	PA10D	217.0	7.00	4.60	116	134	pH8 ⁶	1300	20

1. Ratio ash plus water to cement.

2. DIW - deionized water.

3. GW - simulated groundwater.

4. Flow Test MCC4S, 1L/day.

5. HNO₃ solution.

6. NaHCO₃ solution (0.5 g/L).

Table A3

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) Emulsion With Sodium Sulfate (15 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 1.5¹. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1311	VS1A	126.5	6.40	4.65	109	128	DIW	1300	20
1312	VS1B	126.1	6.35	4.70	110	128	DIW	1300	20
1313	VS1C	125.9	6.25	4.70	108	127	DIW	1300	20
1316	VS1F	132.0	2.40	2.50	11.8	28.7	DIW	300	20
1317	VS1G	138.2	2.60	2.50	12.8	30.2	DIW	300	20
1318	VS1H	136.9	2.60	2.50	12.8	30.2	DIW	300	20
1319	VS1I	262.2	1.50	1.39	228	369	DIW	3650	20
1320	VS1J	252.2	1.50	1.39	228	369	DIW	3650	20
1321	VS1K	240.4	1.30	1.39	197	360	DIW	3650	20
1322	VS2L	123.9	6.40	4.70	111	129	DIW	1300	40
1323	VS2M	126.2	6.50	4.70	113	131	DIW	1300	40
1324	VS3A	125.8	6.50	4.70	113	131	DIW	1300	50
1325	VS3B	123.5	6.30	4.70	109	128	DIW	1300	50
1326	VS3C	124.4	6.40	4.70	111	129	DIW	1300	50

Table A3 (cont.)

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) Emulsion With Sodium Sulfate (15 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 1.5¹. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1329	VS4A	125.7	6.40	4.70	111	129	GW ³	1300	20
1330	VS4B	127.0	6.40	4.70	111	129	GW	1300	20
1331	VS4C	130.0	6.60	4.70	114	132	GW	1300	20
1335	VS7B	124.5	6.20	4.70	108	126	DIW ⁴	1000	20
1336	VS7C	124.4	6.20	4.70	108	126	DIW	1000	20
1340	VS10B	124.6	6.30	4.60	105	124	pH4 ⁵	1300	20
1342	VS10D	125.3	6.30	4.60	105	124	pH8 ⁶	1300	20

1. Prepared using a 25 wt% solution of sodium sulfate.

2. DIW = deionized water.

3. GW = simulated groundwater.

4. Flow Test MCC4S, 1L/day.

5. HNO₃ solution.

6. NaHCO₃ solution (0.5 g/L).

Table A4

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) With Sodium Sulfate (20 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.25. Samples Contain Co-57, Sr-85, Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1451	V2S1A	124.7	6.20	4.50	98.6	120	DIW ²	1300	20
1452	V2S3A	124.7	6.30	4.60	105	124	DIW	1300	50
1454	V2S7A	16.8	3.00	2.40	13.6	31.7	DIW	300	20
1455	V2S12A	20.3	3.60	2.40	16.3	36.2	DIW	300	50

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1. Anhydrous salt.

2. DIW = deionized water.

Table A5

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) and Sodium Sulfate (30 wt%) Type Waste.¹
 Waste-to-Binder Ratio (w/w) = 0.43. Samples Contain Co-57, Sr-85, Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1551	V3S1A	127	6.25	4.50	99.4	120	DIW ²	1300	20
1552	V3S3B	124	6.20	4.60	103	123	DIW	1300	50
1554	V3S7A	18.2	3.10	2.40	14.2	32.4	DIW	300	20
1555	V3S12A	17.5	3.10	2.40	14.2	32.4	DIW	300	50

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1. Anhydrous salt.

2. DIW = deionized water.

Table A6

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) With Sodium Sulfate (40 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 0.67. Samples Contain Co-57, Sr-85 and Cs-137.¹

-ALL-	Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
	1611	VDS1A	145.5	6.40	4.50	102	122	DIW ²	1300	20
	1612	VDS1B	144.4	6.30	4.60	105	124	DIW	1300	20
	1613	VDS1C	146.6	6.50	4.60	108	127	DIW	1300	20
	1616	VDS1F	16.5	2.70	2.30	11.2	27.8	DIW	300	20
	1617	VDS1G	15.8	2.60	2.40	11.7	28.6	DIW	300	20
	1618	VDS1H	15.7	2.60	2.40	11.7	28.6	DIW	300	20
	1619	VDS1I	289.8	1.60	13.8	239	369	DIW	3650	20
	1620	VDS1J	292.3	1.70	13.8	254	373	DIW	3650	20
	1621	VDS1K	263.1	1.40	13.8	200	346	DIW	3650	20
	1622	VDS2L	145.2	6.20	4.50	98.6	120	DIW	1300	40
	1623	VDS2M	142.0	6.40	4.50	102	122	DIW	1300	40
	1624	VDS3A	145.2	6.40	4.50	102	122	DIW	1300	50
	1625	VDS3B	142.4	6.60	4.50	105	125	DIW	1300	50
	1626	VDS3C	148.5	6.50	4.50	103	124	DIW	1300	50

Table A6 (cont.)

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) With Sodium Sulfate (40 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 0.67. Samples Contain Co-57, Sr-85 and Cs-137.¹

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1629	VDS4A	143.0	6.20	4.60	103	123	GW ³	1300	20
1630	VDS4B	146.1	6.40	4.60	106	126	GW	1300	20
1631	VDS4C	146.4	6.40	4.60	106	126	GW	1300	20
1634	VDS7A	141.9	6.30	4.50	100	121	DIW ⁴	1000	20
1635	VDS7B	145.9	6.40	4.50	102	122	DIW	1000	20
1636	VDS7C	148.1	6.50	4.50	103	124	DIW	1000	20
1637	VDS6A	148.0	6.50	4.60	108	127	DIW	2600	20
1638	VDS6B	145.4	6.30	4.70	109	128	DIW	3900	20
1639	VDS10A	145.5	6.30	4.60	105	124	pH3 ⁵	1300	20
1640	VDS10B	146.2	6.30	4.50	100	121	pH4 ⁵	1300	20
1641	VDS10C	147.7	6.30	4.50	100	121	pH5 ⁵	1300	20
1642	VDS10D	143.0	6.30	4.60	105	124	pH10 ⁶	1300	20

Table A6 (cont.)

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) With Sodium Sulfate (40 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 0.67. Samples Contain Co-57, Sr-85 and Cs-137.¹

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1650	V4S2A	138.2	6.20	4.60	103	123	ANOXIC ⁷	1300	20
1651	V4S2B	143.9	6.30	4.70	109	128	ANOXIC	1300	20
1652	V4S2C	145.0	6.30	4.70	109	128	ANOXIC	1300	20
1660	V4S5A	144.9	6.30	4.50	100	121	DIW	1300	20
1661	V4S5B	141.6	6.20	4.50	98.6	120	DIW	1300	20
1662	V4S5C	146.6	6.30	4.50	100	121	DIW	1300	20
1663	V4S8A	144.3	6.20	4.70	108	126	DIW	3900	20
1664	V4S8B	141.8	6.40	4.60	106	126	DIW	3900	20
1665	V4S8C	139.7	6.10	4.60	101	121	DIW	3900	20
1666	V4S9A	147.6	6.30	4.60	105	124	DIW	6500	20
1667	V4S9B	144.8	6.20	4.50	98.6	120	DIW	6500	20
1668	V4S9C	148.3	6.40	4.60	106	126	DIW	6500	20

Table A6 (cont.)

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) With Sodium Sulfate (40 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 0.67. Samples Contain Co-57, Sr-85 and Cs-137.¹

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1669	V4S11A	139.8	6.00	4.60	99.7	120	EDTA ⁸	1300	20
1670	V4S11B	147.9	6.30	4.60	105	124	EDTA	1300	20
1671	V4S11C	144.2	6.10	4.60	101	121	EDTA	1300	20
1672	V4S12A	16.7	2.70	2.40	12.2	29.4	DIW	300	20
1673	V4S12B	16.0	2.60	2.40	11.8	28.6	DIW	300	20
1674	V4S12C	15.4	2.40	2.40	10.9	27.1	DIW	300	20

1. Anhydrous salt.
2. DIW = deionized water.
3. GW = groundwater.
4. Flow Test MCC4S, 1L/day.
5. HNO₃ solution.
6. NaHCO₃ solution (0.5 g/L).
7. Anoxic = simulated anoxic groundwater.
8. EDTA = 100 ppm solution of disodium ethylenediamine tetraacetate dihydrate.

Table A7

Sample and Test Parameters for Bitumen With Sodium Tetraborate (20 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.25. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1711	B2B1A	110.3	6.10	4.80	110	128	DIW ²	1300	20
1712	B2B1B	110.1	6.10	4.60	101	121	DIW	1300	20
1713	B2B1C	110.0	6.10	4.70	106	125	DIW	1300	20
1716	B2B1F	12.0	2.60	2.40	11.8	28.6	DIW	300	20
1717	B2B1G	12.8	2.60	2.40	11.8	28.6	DIW	300	20
1718	B2B1H	14.1	2.90	2.40	13.1	30.9	DIW	300	20
1719	B2B1I	127.9	2.00	10.8	183	251	DIW	2725	20
1720	B2B1J	140.6	2.00	11.0	190	259	DIW	2725	20
1721	B2B1K	175.3	2.50	11.5	260	298	DIW	2725	20
1722	B2B2L	114.3	6.10	4.60	101	121	DIW	1300	40
1723	B2B2M	112.9	6.10	4.60	101	121	DIW	1300	40
1724	B2B3A	113.3	6.20	4.70	108	126	DIW	1300	50
1725	B2B3B	115.1	6.10	4.50	90.7	118	DIW	1300	50
1726	B2B3C	110.3	6.00	4.50	95.3	117	DIW	1300	50

Table A7 (cont.)

Sample and Test Parameters for Bitumen With Sodium Tetraborate (20 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.25. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1729	B2B4A	111.8	6.10	4.60	101	121	GW ³	1300	20
1730	B2B4B	111.4	6.10	4.60	101	121	GW	1300	20
1731	B2B4C	110.9	6.10	4.60	101	121	GW	1300	20
1734	B2B7A	115.9	6.30	4.50	100	121	DIW ⁴	1000	20
1735	B2B7B	113.9	6.10	4.50	97.0	118	DIW	1000	20
1736	B2B7C	109.7	6.00	4.40	91.2	113	DIW	1000	20
1740	B2B10B	111.7	6.20	4.50	98.6	120	pH4 ⁵	1300	20
1742	B2B10D	111.6	6.20	4.50	98.6	120	pH8 ⁶	1300	20
1750	B2B2A	120.1	6.50	4.70	113	131	ANOXIC ⁷	1300	20
1751	B2B2B	114.2	6.40	4.60	106	126	ANOXIC	1300	20
1752	B2B2C	114.8	6.40	4.60	106	126	ANOXIC	1300	20
1755	B2B11A	120.4	6.10	4.60	101	121	EDTA ⁸	1300	20
1756	B2B11B	124.5	6.30	4.60	105	124	EDTA	1300	20
1757	B2B11C	115.5	6.20	4.60	103	123	EDTA	1300	20

Table A7 (cont.)

Sample and Test Parameters for Bitumen With Sodium Tetraborate (20 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.25. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1758	B2B12A	16.6	3.10	2.40	14.2	32.4	DIW	300	50
1759	B2B12B	12.8	2.40	2.40	10.9	27.1	DIW	300	50
1760	B2B12C	14.7	2.80	2.40	12.7	30.2	DIW	300	50

-A17-

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1. Anhydrous salt.
  2. DIW = deionized water.
  3. GW = simulated groundwater.
  4. Flow Test MCC4S, 1L/day.
  5. HNO₃ solution.
  6. NaHCO₃ solution (0.5 g/L).
  7. Anoxic = simulated anoxic groundwater.
  8. EDTA = 100 ppm solution of disodium ethylenediamine tetraacetate dihydrate.

Table A8

Sample and Test Parameters for Bitumen With Sodium Tetraborate (30 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.43. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1851	B3B1A	124.6	6.10	4.50	97.0	118	DIW ²	1300	20
1852	B3B1B	129.4	6.30	4.50	100	121	DIW	1300	20
1853	B3B1C	138.1	6.70	4.50	107	126	DIW	1300	20
1854	B3B3A	132.4	6.60	4.60	110	129	DIW	1300	50
1855	B3B3B	128.8	6.30	4.60	105	124	DIW	1300	50
1856	B3B3C	131.7	6.50	4.60	108	127	DIW	1300	50
1857	B3B7A	14.0	2.30	2.40	10.4	26.4	DIW	300	20
1858	B3B7B	14.4	2.50	2.40	11.3	27.9	DIW	300	20
1859	B3B7C	13.3	2.40	2.40	10.9	27.1	DIW	300	20
1860	B3B12A	13.3	2.40	2.40	10.9	27.1	DIW	300	50
1861	B3B12B	14.9	2.60	2.40	11.8	28.6	DIW	300	50
1862	B3B12C	14.1	2.50	2.40	11.3	27.9	DIW	300	50

1. Anhydrous.

2. DIW = deionized water.

Table A9

Sample and Test Parameters for Bitumen With Sodium Tetraborate (40 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.67. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1911	BB1A	127.3	6.00	4.65	102	122	DIW ²	1300	20
1912	BB1B	129.0	6.25	4.70	108	127	DIW	1300	20
1913	BB1C	130.8	6.25	4.60	104	124	DIW	1300	20
1916	BB1F	13.5	2.60	2.50	12.8	30.2	DIW	300	20
1917	BB1G	12.7	2.60	2.50	12.8	30.2	DIW	300	20
1918	BB1H	14.2	2.70	2.50	13.2	31.0	DIW	300	20
1919	BB1I	188.2	1.50	118	164	274	DIW	2725	20
1920	BB1J	190.8	1.60	117	172	274	DIW	2725	20
1921	BB1K	188.6	1.60	116	169	270	DIW	2725	20
1922	BB2L	129.1	6.20	4.70	108	126	DIW	1300	40
1923	BB2M	126.5	6.30	4.70	109	128	DIW	1300	40

Table A9 (cont.)

Sample and Test Parameters for Bitumen With Sodium Tetraborate (40 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.67. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1924	BB3A	132.6	6.30	4.70	109	128	DIW	1300	50
1925	BB3B	130.4	6.30	4.70	109	128	DIW	1300	50
1926	BB3C	131.9	6.40	4.70	111	129	DIW	1300	50
1929	BB4A	132.2	6.10	4.60	101	121	GW ³	1300	20
1930	BB4B	132.6	6.20	4.60	103	123	GW	1300	20
1931	BB4C	127.1	6.10	4.60	101	121	GW	1300	20
1935	BB7B	131.6	6.20	4.70	108	126	DIW ⁴	1000	20
1936	BB7C	128.7	6.00	4.60	99.7	120	DIW	1000	20
1940	BB10B	124.8	6.00	4.50	95.4	117	pH4 ⁵	1300	20
1942	BB10D	128.2	6.10	4.60	101	121	pH8 ⁶	1300	20
1950	B4B2A	127.3	6.00	4.50	95.4	111	ANOXIC ⁷	1300	20
1951	B4B2B	134.1	6.30	4.60	105	124	ANOXIC	1300	20
1952	B4B2C	141.4	6.60	4.60	110	129	ANOXIC	1300	20

Table A9 (cont.)

Sample and Test Parameters for Bitumen With Sodium Tetraborate (40 wt%) Type Waste¹.
 Waste-to-Binder Ratio (w/w) = 0.67. Samples Contain Co-57, Sr-85 and Cs-137.

-A21-	Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
	1960	B4B5A	137.6	6.10	4.50	97.0	118	DIW	1300	20
	1961	B4B5B	138.1	6.20	4.50	98.6	120	DIW	1300	20
	1962	B4B5C	137.4	6.10	4.50	97.0	118	DIW	1300	20
	1963	B4B8A	139.1	6.40	4.70	111	129	DIW	3900	20
	1964	B4B8B	139.8	6.20	4.70	108	126	DIW	3900	20
	1965	B4B8C	136.7	6.40	4.70	111	129	DIW	3900	20
	1966	B4B9A	130.5	5.90	4.60	102	118	DIW	6500	20
	1967	B4B9B	134.9	6.10	4.60	106	121	DIW	6500	20
	1968	B4B9C	138.8	6.20	4.60	108	123	DIW	6500	20

Table A9 (cont.)

Sample and Test Parameters for Bitumen With Sodium Tetraborate (40 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.67. Samples Contain Co-57, Sr-85 and Cs-137.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	(°C)
1969	B4B11A	139.5	6.40	4.50	102	122	EDTA ⁸	1300	20
1970	B4B11B	138.8	6.40	4.60	106	126	EDTA	1300	20
1971	B4B11C	142.8	6.50	4.60	108	127	EDTA	1300	20

1. Anhydrous salt.
2. DIW = deionized water.
3. gw = simulated groundwater.
4. Flow Test MCC4S, 1L/day.
5. HNO₃ solution.
6. NaHCO₃ solution (0.5 g/L).
7. Anoxic = simulated anoxic groundwater.
8. 100 ppm solution of disodium ethylenediamine tetraacetate dehydrate.

Table A10

Sample and Test Parameters for Solidification Agents for Baseline Leaching Tests¹

-A23-	Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachant Volume (cm ³)	Temperature (°C)
	1001	PC-A ²	199.5	6.30	4.80	114	131	DIW ³	1300	20
	1002	PC-B	198.6	6.30	4.80	114	131	DIW	1300	20
	1003	PC-C	198.6	6.30	4.80	114	131	DIW	1300	20
	1004	BIT-A ⁴	111.0	6.40	4.70	111	129	DIW	1300	20
	1005	BIT-B	107.2	6.40	4.70	111	129	DIW	1300	20
	1006	BIT-C	108.7	6.40	4.70	111	129	DIW	1300	20
	1007	VES-A ⁵	98.1	6.00	4.80	109	127	DIW	1300	20
	1008	VES-B	102.7	6.00	4.80	109	127	DIW	1300	20
	1009	VES-C	99.0	6.00	4.80	109	127	DIW	1300	20

1. Replicates A, B and C contain Co-57, Sr-85 and Cs-137.

2. Portland Type I Cement.

3. DIW = deionized water.

4. Bitumen.

5. Vinyl Ester-Styrene Emulsion.

APPENDIX B

Appendix B contains seven tables that list the sample parameters (weight, height, diameter, volume and surface area), leachant type and volume and the leaching temperature ($\pm 2^{\circ}\text{C}$) for each of the BLANK samples (i.e., those not containing radiotracers) fabricated and tested in this task. Each sample has been assigned a TESTID and a SAMPLEID for identification in the text and in the figures. Each table contains the parameters for a single sample type (i.e., composition), as follows:

- Table B1: Portland type I cement containing 5 wt% sodium sulfate salt as simulated waste
- Table B2: Portland type I cement containing 15 wt% incinerator ash as simulated waste
- Table B3: Vinyl ester-styrene emulsion with aqueous sodium sulfate solution as simulated waste
- Table B4: Vinyl ester-styrene containing 40 wt% sodium sulfate salt as simulated waste
- Table B5: Bitumen containing 20 wt% sodium tetraborate salt as simulated waste
- Table B6: Bitumen containing 40 wt% sodium tetraborate salt as simulated waste
- Table B7: Portland type I cement (neat), pure bitumen and vinyl ester-styrene emulsion with deionized water

Table B1

Sample and Test Parameters for Portland I Cement With Sodium Sulfate (5 wt%) Type Waste.
Waste-to-Binder (w/w) = 0.54¹. Blank Specimens.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachant Volume (cm ³)	Temperature (°C)
1114	PS1D	195.9	6.20	4.70	108	126	DIW ²	1300	20
1115	PS1E	192.8	6.20	4.70	108	126	DIW	1300	20
1127	PS3D	193.5	6.10	4.70	106	125	DIW	1300	50
1128	PS3E	205.3	6.50	4.70	113	130	DIW	1300	50
1132	PS4D	195.5	6.20	4.60	103	123	GW ³	1300	20
1133	PS4E	201.8	6.40	4.50	102	122	GW	1300	20
1153	7-PS2D	194.5	6.20	4.70	108	126	ANOXIC ⁴	1300	20
1154	7-PS2E	186.0	6.00	4.70	104	123	ANOXIC	1300	20
1166	7-PS7D	1992.4	12.90	10.10	1034	570	DIW	6000	20
1167	7-PS7E	1955.1	12.40	10.10	994	554	DIW	6000	20

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1. A 14.3 wt% solution.

2. DIW - deionized water.

3. GW - simulated groundwater.

4. Anoxic - simulated anoxic groundwater.

Table B2

Sample and Test Parameters for Portland Type I Cement With Incinerator Ash (60 wt% cement, 15 wt% incinerator ash, 30 wt% water). Waste-to-Binder (w/w) = 0.58.¹ Blank Specimens.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachant Volume (cm ³)	Temperature (°C)
1214	PA1D	205.4	6.90	4.70	120	137	DIW ²	1300	20
1215	PA1E	211.9	7.20	4.70	125	141	DIW	1300	20
1227	PA3D	201.6	6.90	4.65	118	135	DIW	1300	50
1228	PA3E	205.7	7.00	4.70	121	138	DIW	1300	50
1232	PA4D	202.7	6.60	4.50	105	125	GW	1300	20
1233	PA4E	203.8	6.60	4.70	114	132	GW	1300	20

1. Ratio of ash plus water to cement.

2. DIW = deionized water.

3. GW = simulated groundwater.

Table B3

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) Emulsion With Sodium Sulfate (15 wt%) Type Waste.
Waste-to-Binder Ratio (w/w) = 1.5. Blank Specimens.¹

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1314	VS1D	122.9	6.10	4.65	104	123	DIW ²	1300	20
1315	VS1E	127.2	6.40	4.65	109	128	DIW	1300	20
1327	VS3D	125.5	6.40	4.65	109	128	DIW	1300	50
1328	VS3E	125.8	6.40	4.60	106	126	DIW	1300	50
1332	VS4D	121.1	6.10	4.60	101	121	GW ³	1300	20
1333	VS4E	120.1	6.10	4.60	101	121	GW	1300	20

1. Prepared using a 25 wt% solution of sodium sulfate.

2. DIW = deionized water.

3. GW = simulated groundwater.

Table B4

Sample and Test Parameters for Vinyl Ester-Styrene (DOW) With Sodium Sulfate (40 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.67. Blank Specimens.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1615	VDS1D	148.2	6.40	4.60	106	126	DIW ²	1300	20
1616	VDS1E	149.1	6.40	4.60	106	126	DIW	1300	20
1627	VDS3D	149.4	6.40	4.60	106	126	DIW	1300	50
1628	VDS3E	154.5	6.60	4.60	110	129	DIW	1300	50
1632	VDS4D	147.7	6.20	4.50	98.6	120	GW ³	1300	20
1633	VDS4E	149.7	6.40	4.60	106	126	GW	1300	20
1653	V4S2D	148.5	6.40	4.60	106	126	ANOXIC ⁴	1300	20
1654	V4S2E	147.1	6.40	4.60	106	126	ANOXIC	1300	20

1. Anhydrous salt.

2. DIW = deionized water.

3. GW = simulated groundwater.

4. Anoxic = simulated anoxic groundwater.

Table B5

Sample and Test Parameters for Bitumen With Sodium Tetraborate (20 wt%) Type Waste.¹
Waste-to-Binder Ratio (w/w) = 0.25. Blank Specimens.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1714	B2B1D	115.2	6.20	4.60	103	123	DIW ²	1300	20
1715	B2B1E	114.6	6.10	4.60	101	121	DIW	1300	20
1727	B2B3D	113.1	6.00	4.50	95.4	117	DIW	1300	50
1728	B2B3E	111.7	6.00	4.50	95.4	117	DIW	1300	50
1732	B2B4D	114.1	6.00	4.70	104	123	GW ³	1300	20
1733	B2B4E	120.5	6.20	4.60	103	123	GW	1300	20
1753	B2B2D	109.6	5.80	4.60	93.4	117	ANOXIC ⁴	1300	20
1754	B2B2E	110.5	6.00	4.50	95.4	117	ANOXIC	1300	20

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1. Anhydrous salt.

2. DIW = deionized water.

3. GW = simulated groundwater.

4. Anoxic = simulated anoxic groundwater.

Table B6

Sample and Test Parameters for Bitumen With Sodium Tetraborate (40 wt%) Type Waste¹.
Waste-to-Binder Ratio (w/w) = 0.67. Blank Specimens.

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachate Volume (cm ³)	Temperature (°C)
1914	BB1D	131.4	6.30	4.60	105	124	DIW ²	1300	20
1915	BB1E	126.4	6.20	4.60	103	123	DIW	1300	20
1927	BB3D	120.2	6.10	4.70	106	125	DIW	1300	50
1928	BB3E	118.4	6.00	4.65	102	122	DIW	1300	50
1932	BB4D	131.0	6.20	4.70	108	126	GW ³	1300	20
1933	BB4E	132.5	6.30	4.70	109	128	GW	1300	20
1953	B4B2D	124.3	6.00	4.50	95.4	117	ANOXIC ⁴	1300	20
1954	B4B2E	133.3	6.30	4.60	105	124	ANOXIC	1300	20

1. Anhydrous salt.

2. DIW = deionized water.

3. GW = simulated groundwater.

4. Anoxic = simulated anoxic groundwater.

Table B7

Sample and Test Parameters for Solidification Agents for Baseline Leaching Tests¹

Sample ID	Test ID	Weight (g)	Height (cm)	Diameter (cm)	Sample Volume (cm ³)	Surface Area (cm ²)	Leachant Type	Leachant Volume (cm ³)	Temperature (°C)
1011	PC-Blank	198.8	6.30	4.80	114	131	DIW	1300	20
1012	BIT-Blank	110.2	6.40	4.70	111	129	DIW	1300	20
1013	VES-Blank	108.5	6.10	4.80	110	128	DIW	1300	20

1. PC-Blank is Portland Type I Cement neat.

2. Bitumen

3. Vinyl Ester-Styrene Emulsion (DOW)