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Solidification/Stabilization of High Nitrate and Biodenitrified Heavy Metal Sludges with a Portland Cement/Flyash System

by

J. Scott Canonico

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Golden, Colorado

Date July 25, 1995

Signed: _____
J. Scott Canonico

Approved: _____
Dr. Nevis E. Cook, Jr.
Thesis Advisor

Golden, Colorado

Date July 26, 1995

_____
Dr. John A. Cordes
Division Director
Division of Environmental
Science and Engineering

ABSTRACT

Pond 207C at Rocky Flats Environmental Technology Site (RFETS) contains process wastewaters characterized by high levels of nitrates and other salts, heavy metal contamination, and low level alpha activity. The purpose of this research was to investigate the feasibility of treating a high-nitrate waste, contaminated with heavy metals, with a coupled dewatering and S/S process, as well as to investigate the effects of biodenitrification pretreatment on the S/S process. Pond 207C residuals served as the target waste. A bench-scale treatability study was conducted to demonstrate an S/S process that would minimize final product volume without a significant decrease in contaminant stabilization or loss of desirable physical characteristics.

The process formulation recommended as a result a previous S/S treatability study conducted on Pond 207C residuals was used as the baseline formulation for this research. Because the actual waste was unavailable due to difficulties associated with radioactive waste handling and storage, a surrogate waste, of known composition and representative of Pond 207C residuals, was used throughout this research. The contaminants of regulatory concern added to the surrogate were cadmium, chromium, nickel, and silver.

Product volume reduction was achieved by dewatering the waste prior to S/S treatment. The surrogate was dewatered by evaporation at 60 to 80 °C to total solids

contents from 43% to 78% by weight, and treated with Portland cement and fly ash. Two cement to flyash ratios were tested, 2:1 and 1:2, by weight. Contaminant leachability testing was conducted with a 0.5 water to pozzolan (the cement/flyash mixture) ratio and both cement to flyash ratios. Each product was tested for unconfined compressive strength (UCS) and for contaminant leachability by the Toxicity Characteristics Leaching Procedure (TCLP).

At the highest solids content achieved by dewatering, 78% solids by weight, the predicted final waste form volume for Pond 207C residuals after S/S processing was reduced by over 60% when compared to the baseline process. All tested process formulations produced final waste forms with an average UCS of 100 psi or greater. Percent fixation of Chrome (VI) increased at higher solids contents. Fixation of nickel varied from over 87% to 69%, and cadmium fixation was greater than 99% at every solids content tested. Silver TCLP extract concentrations were below detection limits in all cases except for one anomalous measurement.

Final product volume reduction was not achieved with coupled dewatering and S/S processing after biodenitrification pretreatment. The waste slurry became too viscous to mix with reagents after dewatering to approximately 55% solids. Fixation of contaminant constituents and final product UCSs were similar to the results of S/S processing without biodenitrification. Due to the lack of volume reduction, biodenitrification was not successful as a pretreatment for S/S processing under the test conditions of this research.

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Chapter 1

INTRODUCTION AND BACKGROUND

This research project was conducted to develop and demonstrate a cost-effective and appropriate treatment process for solar pond residuals present at the Department of Energy's Rocky Flats Environmental Technology Site (RFETS). The specific treatment investigated was dewatering, and subsequent solidification and stabilization (S/S) with a Portland Cement/Flyash system. The effects of biodenitrification pretreatment on S/S process performance were also investigated. Residuals from Pond 207C, one of five solar ponds at RFETS, were the target waste.

The objectives of the research were as follows:

- significantly reduce final product volume when compared to that of a previously developed process
- stabilize contaminant constituents to meet applicable land disposal restrictions
- produce a final product with desirable physical characteristics.

Knowledge of cement-based waste form chemistry has not progressed to the point where reliable design of S/S systems from theoretical principals is possible (Mattus and Gilliam, 1994 and Roy et al., 1991). Failure of a selected treatment process formulation to

sufficiently stabilize contaminant constituents in the waste to meet land disposal restrictions would necessitate additional treatment prior to off-site disposal. Therefore, a focused laboratory study was necessary to determine the feasibility of previously untested treatment process formulations.

Because the actual waste was unavailable due to difficulties associated with radioactive waste handling and storage, a surrogate waste of known composition was developed and used throughout this research. The surrogate formulation was based on characterization studies conducted by Halliburton NUS Environmental Corporation (1992) and Dames and Moore (1991). The surrogate was developed to be representative of the target waste. Contaminant constituents of concern were added to the surrogate waste in the form of soluble complexes at the highest concentrations reported in available waste characterization studies.

A related study is investigating the biodenitrification of the Pond 207C surrogate waste. The high concentration of nitrate salts in the waste could significantly interfere with the S/S reagents. Biodenitrification destroys nitrates and thus exhibited the potential to minimize nitrate interference. Therefore, another goal of this study was to investigate the feasibility of solidification and stabilization of the biodenitrification process residuals.

The biodenitrification research did not progress to the point where residuals were available in time for process integration with this study. Therefore, theoretical residuals

were used. The theoretical development of the biodenitrification process residuals is presented in Appendix I.

The research was conducted at bench-scale in the following three phases:

(I) Process Development and Solidification Assessment: During this phase, a coupled dewatering and S/S process was developed. The extent of waste dewatering that could be accomplished while maintaining mixability was determined. The volume reduction achieved through dewatering and the ability of potential process formulations to solidify the surrogate waste, without toxic constituents, were investigated.

(II) Process Assessment: The process formulations developed in Phase I were evaluated in terms of the three study objectives. For this phase, representative toxic constituents were added to the waste surrogate. In addition to the assessment of volume reduction and solidification, the stabilization of toxic constituents was measured.

(III) Investigation of the Effects of Biodenitrification Pretreatment: During the final phase of research, the effects of biodenitrification pretreatment on the performance of the processes developed in Phase I and assessed in Phase II were investigated. The pretreated waste was evaluated by the same testing methods as un-pretreated waste.

The following sections describe Pond 207C residuals, the target waste, and outline the relevant methodologies and results of a Pond 207C treatability study previously conducted by Halliburton NUS Environmental Corporation (hereafter, Halliburton). The results of the previously conducted treatability study are relevant to the present study

because the former was conducted with actual Pond 207C waste. Halliburton's process formulation was used as the baseline S/S treatment process in this research. The product volume resulting from the baseline process was the standard by which volume reduction results were judged, and baseline stabilization results were used to predict the performance of the process formulations developed in this study on Pond 207C waste.

1.1. POND 207C WASTE CHARACTERISTICS

Pond 207C is one of five Solar Evaporation Ponds placed into service at RFETS in 1956. The ponds covered an area of approximately 6.5 acres. They were reportedly used to store and evaporate liquid process wastes having less than 100,000 picocuries per liter of total long-lived alpha activity (Bittner et al., 1993). Estimates of the solar pond waste volumes indicate that Pond 207C is one of the largest of the five ponds in terms of waste volume. Pond 207C also has the highest amount of dissolved solids of the five ponds (TDS >300,000 mg/L vs. TDS = 7,600 to 16,000 mg/L for Ponds 207A and 207B north, center, and south) (Halliburton, 1992 and Dames and Moore, 1991, as cited in Siegrist et al., 1994).

Pond 207C waste contains "high concentrations of nitrate and other salts." Trace metals that exceed land disposal restriction (LDR) limits in the waste are cadmium, chromium, lead, nickel, and silver (Halliburton, 1992).

In the mid-1980s, RFETS began treatment efforts on solar pond residuals. Treatment was terminated in 1990 because of poor S/S results and inability to dispose of the final waste form (Halliburton, 1992 and Siegrist et al., 1994). In 1994, the remaining solar pond residuals were removed from the ponds and placed in "numerous" 10,000 gal. tanks at RFETS (Siegrist et al., 1994).

Halliburton (1992) reported the following volumes of liquid and solid phases in Pond 207C:

Table 1.1: Pond 207C Phase Volumes

Phase	Volume (gallons)
Liquid	387,300
Crystal	61,100
Silt/Sludge	38,800
TOTAL	487,200

Detailed analyses of Pond 207C liquid and solid (sludge and crystal composite) phases compiled from the Halliburton (1992) and Dames and Moore (1991) reports (as cited in Siegrist et al., 1994) is presented in Tables 1.2 and 1.3.

Table 1.2: Pond 207C Liquid Analysis[a]

Analyte	Units	Detection Frequency	Concentration Range
Volatiles			
2-Butanone	µg/L	4/5	77-110
Methylene Chloride	µg/L	1/5	8
Pesticides			
Diazinon	µg/L	1/1	2.8
Simazine	µg/L	1/1	7.5
Inorganics			
Arsenic	µg/L	5/6	3350-4110
Barium	µg/L	5/6	110-150
Boron	µg/L	6/6	360,000-494,000
Cadmium	µg/L	6/6	312-560
Chromium	µg/L	6/6	2360-3940
Copper	µg/L	1/1	6790
Lead	µg/L	2/6	300
Magnesium	µg/L	5/6	1300-3870
Nickel	µg/L	6/6	2540-5090
Potassium	mg/L	6/6	54,500-78,700
Selenium	µg/L	2/6	600-3000
Silicon	µg/L	1/1	30,100
Sodium	mg/L	6/6	102,000-142,000
TCLP			
Arsenic	µg/L	5/5	4660-5510
Cadmium	µg/L	5/5	350-560
Chromium	µg/L	5/5	2240-9160
Nickel	µg/L	5/5	2330-4930
Silver	µg/L	5/5	150-430
Miscellaneous			
Gross Alpha	nCi/L	6/6	63-130
Gross Beta	nCi/L	6/6	170-230
pH	units	6/6	10.0-10.2
Alkalinity (methyl orange)	mg/L	6/6	45,000-63,000
Alkalinity (phenolphthalein)	mg/L	5/5	25,000-32,000
Ammonia	mg/L	5/6	1.8-6.4
Bicarbonate	mg/L	1/1	4000
Carbonate	mg/L	1/1	25,000
Conductivity at 25°C	µmhos	1/1	610,000
Chloride	mg/L	6/6	18,300-25,000
Cyanide - Total	mg/L	6/6	3.3-20

[a] Liquid analysis data from Halliburton NUS (1992) and Dames and Moore (1991) reports as cited in Siegrist et al. (1994). Concentration range applies to detected values only.

Table 1.2: Pond 207C Liquid Analysis (continued)[a]

Analyte	Units	Detection Frequency	Concentration Range
Miscellaneous (cont.)			
Nitrate	mg/L	5/5	57,000-66,000
Nitrate as N	mg/L	1/1	2600
Nitrite	mg/L	1/1	2500
Phosphorous - Total as P	mg/L	5/5	520-610
Specific Gravity	none	5/5	1.316-1.348
Sulfate	mg/L	6/6	12,200-18,000
Sulfide	mg/L	1/1	10
Total Dissolved Solids	mg/L	6/6	300,000-510,000
Total Organic Carbon	mg/L	6/6	54.9-1600
Total Suspended Solids	mg/L	6/6	76-1400

[a] Liquid analysis data from Halliburton NUS (1992) and Dames and Moore (1991) reports as cited in Siegrist et al. (1994). Concentration range applies to detected values only.

Table 1.3: Pond 207C Sludge Analysis[a]

Analyte	Units	Detection Frequency	Concentration Range
Volatiles			
2-Butanone	µg/kg	5/5	16-160
Benzene	µg/kg	2/5	7-31
Tetrachloroethene	µg/kg	5/5	8-73
Trichloroethene	µg/kg	2/5	5-7
1,1,2-Trichloro-1,2,2-triflouroethane	µg/kg	1/5	33
Semi-volatiles			
Pyrene	µg/kg	2/5	190-320
Inorganics			
Aluminum	mg/kg	5/5	69.5-1330
Antimony	mg/kg	1/5	13.8
Arsenic	mg/kg	7/10	2-37
Barium	mg/kg	5/5	13.2-61.4
Beryllium	mg/kg	2/5	1.1-17.6
Boron	mg/kg	10/10	78.9-1390
Cadmium	mg/kg	10/10	3.2-665
Calcium	mg/kg	1/5	1550
Chloride	mg/kg	5/5	2420-6890
Chromium	mg/kg	10/10	216-960
Copper	mg/kg	4/5	4.3-78
Cyanide - Total	mg/kg	10/10	1.6-170
Flouride	mg/kg	5/10	6,320-29,800
Iron	mg/kg	5/5	24.2-211
Lead	mg/kg	6/10	2-38.5
Lithium	mg/kg	5/5	24-108
Magnesium	mg/kg	5/10	1340-6250
Manganese	mg/kg	1/5	8.7
Mercury	mg/kg	8/10	0.11-1
Nickel	mg/kg	6/10	17.4-146
Nitrate as N	mg/kg	5/5	65,000-130,000
Nitrite	mg/kg	5/5	480-1000
Phosphate - Total	mg/kg	5/5	1300-3400
Potassium	mg/kg	10/10	16,900-365,000
Silicon	mg/kg	6/10	4.4-73.6
Sodium	mg/kg	10/10	45,800-378,000
Sulfate	mg/kg	5/5	28,800-141,00
Zinc	mg/kg	4/5	5.5-18.9

[a] Sludge data from Halliburton NUS (1992) and Dames and Moore (1991) reports as cited in Siegrist et al. (1994). Concentration range applies to detected values only. Samples include a composite berm sample.

Table 1.3: Pond 207C Sludge Analysis (continued)[a]

Analyte	Units	Detection Frequency	Concentration Range
ASTM Leach[b]			
Chloride	mg/L	5/5	660-990
Nitrate	mg/L	5/5	8,900-11,000
Phosphorous - Total as P	mg/L	5/5	22/38
Sulfate	mg/L	5/5	810-1300
Total Dissolved Solids	mg/L	5/5	18,000-24,000
TCLP			
Arsenic	µg/L	5/5	447-538
Barium	µg/L	3/5	481-559
Cadmium	µg/L	5/5	342-5230
Chromium	µg/L	5/5	1840-3940
Lead	µg/L	2/5	33-52
Mercury	µg/L	1/5	0.4
Nickel	µg/L	5/5	563-2140
Silver	µg/L	5/5	9-23
Miscellaneous			
Gross Alpha	pCi/g	9/10	18-8700
Gross Beta	pCi/g	9/10	390-1200
pH	units	5/5	17,000-24,000
Alkalinity - Total	mg/kg	5/5	17,000-24,000
Ammonia	mg/kg	2/10	2.7-4.5
Moisture - Gravimetric	%	5/5	34.8-48.8
Swell Test	%	4/4	0-10
Total Organic Carbon	mg/kg	5/5	6400-9000
% Recovery of solids	%	5/5	9.2-18.8

[a] Sludge data from Halliburton NUS (1992) and Dames and Moore (1991) reports as cited in Siegrist et al. (1994). Concentration range applies to detected values only. Samples include a composite berm sample.

[b] ASTM leach analysis performed by analytical method ASTM D3987-85 (specifically EPA methods: 365.2 for phosphorous, 325.3 for chloride, 375.4 for sulfate, 352.2 for nitrate, and 160.1 for TDS)

1.2. PREVIOUS POND 207C TREATABILITY STUDY

Halliburton conducted an extensive treatability and process formulation study on S/S of Pond 207C residuals. As noted above, Halliburton's recommended process was used as the baseline process for this study and their results are used to evaluate the performance of the processes studied during this research.

Halliburton's stated main objective of preliminary process testing was "to determine if a cement/flyash system was capable of stabilizing the high-salt brine in Pond 207C (Halliburton, 1992)." Presumably based on industry experience and "the most closely related project" in the literature (S/S of a low-level alkaline waste at the Savannah River Plant as reported by Wilhite, undated), Halliburton proposed and evaluated a S/S system which utilized a pozzolanic mixture of Type V Portland Cement, Type C Flyash, and hydrated lime.

Halliburton used a water to pozzolan ratio (pozzolan was defined to be cement plus flyash, this definition is also applied throughout this thesis) of approximately 0.46, and a cement to flyash ratio of 1 to 2 for all preliminary testing. Tests performed on S/S waste specimens were unconfined compressive strength (UCS), the Toxicity Characteristic Leaching Procedure (TCLP), and freeze/thaw and wet/dry durability testing. UCS and the durability tests, "are not required for product certification. These tests were used as indicators to determine if a specified formula was of better quality than another formula with regard to strength and durability (Halliburton, 1992)."

The Treatability Study and Process Formulation Report (1992) explains Halliburton's methodology for development of an operating range for remediation as follows: "Once it was determined that a specified formulation resulted in an acceptable end product, testing was conducted to develop an operating range which could be used during remediation." During the final phase of testing, Halliburton varied the selected process formulation over a range which might be encountered during actual remedial operations at RFETS.

The following table is a summary of Halliburton's recommended operating range for S/S of the Pond 207C waste:

Table 1.4: Pond 207C S/S Process
Recommended Operating Range

Cement/Flyash/Lime Ratio	1/1.2/0.05 to 1/3.34/0.09
Water to Pozzolan Ratio	0.34 to 0.50
Total Suspended Solids (%)	0 to 17.2
Total Dissolved Solids (%)	0 to 40.4

(Source: Halliburton, 1992)

Halliburton used Type V Portland Cement because of its resistance to sulfate attack, and Type C Flyash. Halliburton also recommended the addition of a proprietary additive, Latex 2000, which "appears to produce a final product which has better resistance to the wet/dry and freeze/thaw durability testing (Halliburton, 1992)."

With few exceptions, the test specimens that Halliburton analyzed passed every category of every test. The exceptions were two batches prepared with proprietary

retarder additive dosages that were "apparently too high," and an anomalous TCLP failure. According to the Process Formulation Report, "The operating range was developed to be conservative enough to ensure that all samples passed the required criteria. Because of schedule constraints, the operating range was not pushed to greater limits which would determine the points of failure (Halliburton, 1992)."

The fact that virtually all test specimens met all testing criteria indicated that there possibly existed a significant margin for process improvement. It was reasonable to expect that the performance (as measured by the tests noted above) of Halliburton's recommended S/S process formulation on dewatered Pond 207C waste would be degraded at the higher solids contents (solids content is defined as percent total solids, by weight), but possibly not to the point of regulatory failure. Thus, significant final product volume reduction could be achieved.

Halliburton noted that, "[T]wo parameters appear to be the most significant regarding process control. The first is the blending of the pozzolanic mixture, and the second is the ratio of water to pozzolans in the process stream (Halliburton, 1992)." Here again was evidence of the potential for process improvement. If the pozzolan blend and water to pozzolan ratio were held constant, the process appeared to have the potential for successful S/S of dewatered Pond 207C waste.

Chapter 2

RESEARCH OBJECTIVES

This chapter explains the previously stated research objectives in detail. Research objectives were formulated based on Pond 207C waste characteristics and the results reported in the previous studies.

2.1. FINAL PRODUCT VOLUME REDUCTION

The first objective of this research was to significantly reduce final product volume when compared to that of a previously demonstrated process. Reduction of the final product volume, or waste minimization, could have significant economic impact if the final disposition of treated waste is off-site disposal, as explained below.

As of September 1994, final disposition of treated Pond 207C residuals had not been determined (Siegrist et al., 1994). "Possible scenarios include both on-site disposal or off-site disposal at either the Department of Energy Nevada Test Site or Envirocare of Utah (ICF Kaiser Engineers, 1993; Sams, Jones and Sams, 1994, and Los Alamos Technology Office, 1994; as cited in Siegrist et al., 1994) An evaluation of disposal options for treated pond sludges from RFETS determined the most likely option for off-site disposal is land burial at Envirocare of Utah, Inc. (Siegrist et al., 1994). Envirocare's

1994 price for disposal of wastes of less than 15,000 cubic yards total volume was greater than $1500 per cubic yard (Siegrist et al., 1994). Transportation costs from RFETS to the Envirocare facility in Clive, Utah will also be significant. Therefore, in an off-site disposal scenario, waste minimization is of critical economic importance.

Maximizing the amount of the contaminants of concern per unit weight of final S/S waste form will result in less volume to be landfilled (assuming reasonably consistent waste form specific gravities). One way to express the amount of waste constituents contained in a given S/S process waste form is waste loading. Waste loading can be defined as follows:

$$Waste\ Loading = \frac{Weight\ of\ Waste\ Solids}{Final\ Product\ Weight} \tag{2.1}$$

where: $$Final\ Product\ Weight = Weight\ of\ Waste\ Solids + Weight\ of\ Water + Weight\ of\ Reagents \tag{2.2}$$

As defined in Equation 2.1, waste solids consist of all dissolved and suspended solids in a given waste. Water is not considered in the weight of waste to be treated because the water content of the waste that is not required for S/S reagent hydration is assumed to be removable by a dewatering process. A waste loading of 1.0 would imply a dried mass of waste solids with no water content or reagents.

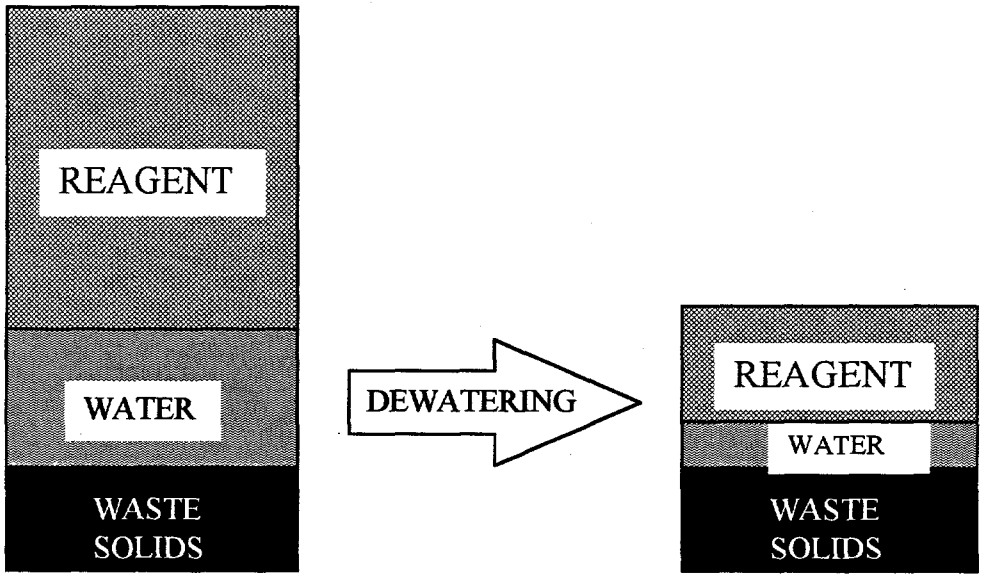
Dried Pond 207C solids would probably not meet land disposal restrictions (Halliburton, 1992). Therefore, S/S reagents, pozzolans in the case of this research, must be added. Sufficient water must be present to hydrate the pozzolans for them to be effective. The final waste form will therefore consist of waste solids, water, and pozzolanic reagents.

Dewatering of Pond 207C residuals was not a part of Halliburton's recommended S/S treatment process. Pozzolanic reagents were added in proportion to the amount of water originally present in the residuals. Pond 207C residuals have a solids content of approximately 42% by weight, and are therefore 58% water. With a water to pozzolan ratio of 0.5 (the water to pozzolan ratio is addressed in detail in Chapter 3), this yields a waste loading of 19% (i.e., $\textit{Waste Loading} = \frac{0.42}{0.42 + 0.58 + 1.16} = 0.19$). Dewatering the residuals to a solids content of 62% and keeping the water to pozzolan ratio constant at 0.5 would yield a waste loading of 36% (i.e., $\textit{Waste Loading} = \frac{0.62}{0.62 + 0.38 + 0.76} = 0.36$). A graphic representation of the effects of dewatering is presented in Figure 2.1.

The reader will note how dewatering yields a final product with a much greater percentage of waste solids (higher waste loading) and reduced volume. At a constant water to pozzolan ratio of 0.5, removal of a given weight of water from the waste eliminates the need for addition of twice that weight in reagents. For example, removal of

one kilogram of water eliminates the need for addition of two kilograms of reagent, for a total weight reduction of three kilograms. Thus the potential exists for savings in the cost of S/S reagents, as well as transportation and disposal costs.

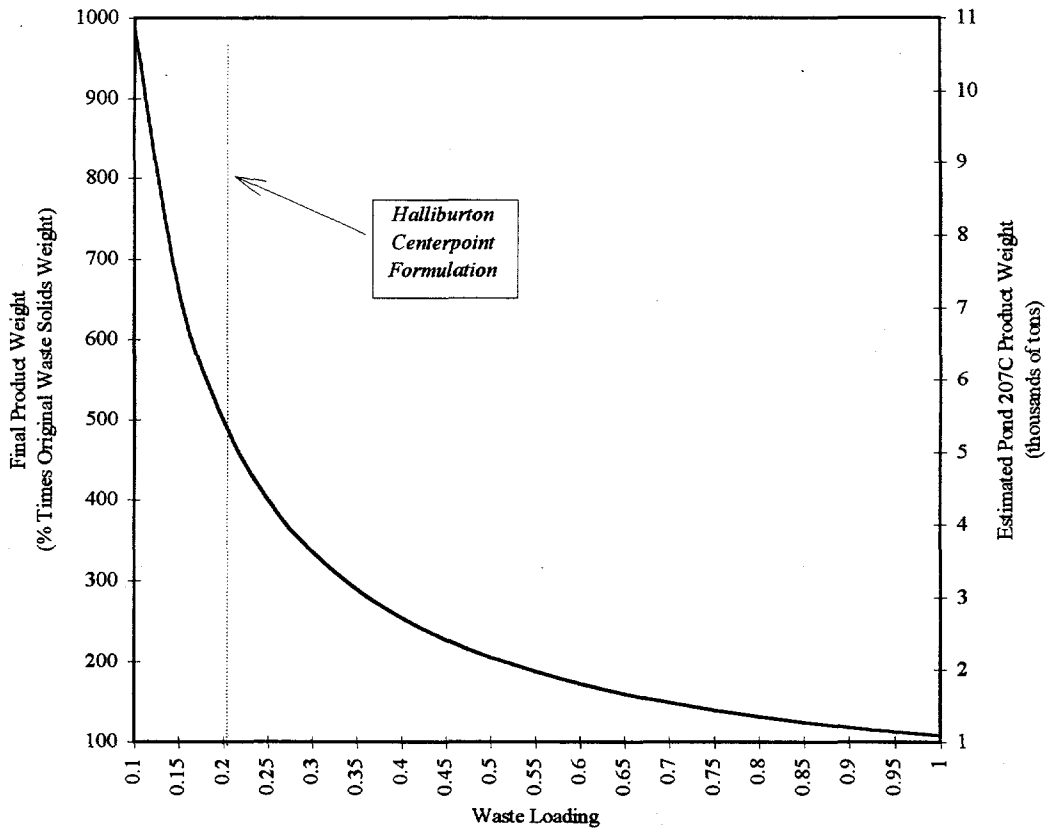
Figure 2.1:
Effects of Dewatering on Final Product Volume



The relationship between waste loading, and the product weight is illustrated in Figure 2.2. The figure was constructed using Equation 2.1 and a water to pozzolan ratio of 0.5. Product weight increase is defined in terms of the weight of waste solids, where a waste loading of 1.0 will yield a product with the weight of the solids alone (100%). A waste loading of 50% will yield a product with 50% waste solids by weight, or, stated

differently, the final waste form weight will be twice the weight of waste solids alone (200%).

Figure 2.2:
Product Weight vs. Waste Loading



The right hand abscissa presents estimates of total product weight for S/S treatment of Pond 207C based on the average percent total solids of 42% (by weight) and

a 487,000 gallon waste volume with a specific gravity of 1.244 (Halliburton, 1992). In order to estimate weights, it was assumed that dry waste solids and final products have specific gravities of 2.0 (the solids in the Pond 207C surrogate waste used in this study had a specific gravity of approximately 2.2 and the final products had specific gravities of approximately 1.9).

By inspection of Figure 2.2, it is evident that relatively small increases in waste loading can result in significant S/S product weight reductions. For example, in order to reduce the product weight from five times (500%) the weight of waste solids (the approximate result of the "centerpoint" process recommended by Halliburton) to three times (300%) waste solids weight, or, in other words, to reduce the weight of the S/S product by 40%, would require increasing the waste loading to about 0.36. Holding the water to pozzolan ratio constant at 0.5, a waste loading of 0.36 could be achieved by increasing percent solids in the process feed waste stream to approximately 62%.

Using the same assumption of specific gravities of 2.0 for all final products as used in construction of Figure 2.2, final product volume estimates can be made. At Halliburton's centerpoint formulation, total S/S product volume will be about 3,200 cubic yards (5,500 tons). At a waste loading of 0.36, product volume will be about 1,800 cubic yards (3,000 tons). Obviously, such reductions in volume and weight will result in considerable savings in transportation and disposal costs.

Given the demonstrated importance of waste loading in terms of waste minimization, the primary objective of this research effort was to examine the effects of increased waste loadings on product characteristics with the goal of developing and demonstrating a viable S/S process formulation with minimized final product volume.

2.2. STABILIZATION

The second project objective was to stabilize contaminant constituents to meet applicable land disposal restrictions. The U.S. EPA has defined stabilization as those techniques "which have their beneficial action primarily by limiting the solubility or by detoxifying the waste contaminants even though the physical characteristics of the waste may or may not be changed or improved (U.S. EPA, 1982)."

The EPA promulgated the TCLP as a laboratory method to "determine the mobility [solubility] of both organic and inorganic analytes present in . . . wastes (40 CFR 261)." The TCLP requires that a sample of a solid waste be agitated in an acidic extraction fluid twenty times the weight of the solid sample (a 20:1 dilution). The concentrations of contaminants in the extraction fluid are measured after agitation to determine regulatory compliance (40 CFR 261). The land disposal restrictions (LDRs) for contaminant concentrations in TCLP waste extracts were promulgated by the EPA in 40 CFR 268.

The final waste product must meet land disposal restrictions to be certifiable for off-site land disposal. Stabilization of the toxic constituents of Pond 207C residuals is addressed in three separate sections--inorganics, volatile organics and cyanide--below.

2.2.1. Inorganics: The following table provides an analysis of the relative importance of inorganic Pond 207C contaminants of regulatory concern. Maximum concentrations are for Pond 207C waste taken from the data presented in Tables 1.2 and 1.3. LDRs are taken from 40 CFR 268.41, Table CCWE (Constituent Concentrations in Waste Extract).

Table 2.1: Inorganic Contaminant Evaluation

Constituent	LDR (CCWE) (mg/L)	Max Reported Concentration (mg/kg)	Calculated Max TCLP Extract (mg/L)	Ratio (Max Leach/LDR)	% Fixation Req'd	Selected Spike Conc. (mg/kg)
Antimony	0.23	13.8	0.7	3.0	66.7	0
Arsenic	5.0	40.2	2.0	0.4	0.0	0
Barium	52	61.4	3.0	0.06	0.0	0
Cadmium	0.066	665	33.3	503.8	99.8	**700**
Chromium	5.0	960	48.0	9.6	89.6	**1000**
Lead	0.51	38.5	1.9	3.8	73.5	0
Mercury	0.025	4.4	0.2	8.8	88.6	0
Nickel	0.32	146	7.3	22.8	95.6	**150**
Selenium	5.7	NR	0	0	0.0	0
Silver	0.072	73.6	3.7	51.1	98.0	**200**

Notes:
1. NR = Not Reported
2. All LDR's are reported for F039 wastes except chromium which has a lower standard (5.0 vs. 5.2) as a characteristic (D077) waste.
3. CCWE = Constituent Concentration in Waste Extract

The maximum possible TCLP extract concentration in Table 2.1 is based on the 20:1 dilution required by the procedure. This concentration represents the worst case scenario, where all the contaminant in the sample ("Calculated Max TCLP Extract" in Table 2.1) is leached into the extraction fluid. The additional "dilution" which results from S/S reagent addition is not considered. Inspection of the table reveals three contaminants which have a relatively high potential for leaching above the LDR standard (i.e., greater than 95% fixation required); cadmium, nickel, and silver.

According to a previous S/S study, no metals of regulatory concern show potential for leaching above the LDR standards after S/S processing (Halliburton, 1992). A possible exception is cadmium, about which it was noted, "The limited . . . data seem to indicate that if the TCLP extract pH falls below 6 (approximate), then the LDR standard of 0.066 mg/L might be exceeded (Halliburton, 1992)."

Considering the above assessment of the leaching potential of cadmium, as well as the high degree of fixation required to meet regulatory limits, the ability of the S/S process to stabilize cadmium is of critical importance.

Conner (1990) writes with respect to the potential for leaching of nickel, "Additives used in certain [electroplating] baths may form stable, soluble nickel complexes that do not precipitate with the usual CFS reagents and additives." In contrast, Conner notes, "fixation of silver in CFS [chemical fixation and stabilization] systems is rarely, if

ever, a problem." However, since silver requires the second highest degree of fixation, its behavior in the S/S process was investigated.

In its higher valence state (Cr^{6+}), chromium is highly soluble and often not stabilized in conventional S/S systems (Conner, 1990 and Kindness, Macias, and Glasser, 1994). The speciation of chromium, and thus its valence state, in Pond 207C residuals was unknown. Although the higher concentrations of chromium reported in semi-solid phases of Pond 207C residuals (see Tables 1.2 and 1.3) indicated that chromium was probably in its less soluble 3+ valence state, a conservative assumption was that chromium was present as Cr^{6+}. Stabilization of chromium was therefore investigated in this study. The contaminant requiring the next highest degree of fixation, mercury, is generally stabilized in most S/S systems (Conner, 1990), and was not investigated.

Based on previous study results and the observations cited, and the tabulated analysis of inorganic contaminants, the surrogate sludge was spiked to the concentrations presented in bold numbers in Table 2.1 for cadmium, chromium, nickel, and silver. In order to evaluate stabilization of a "worst case" waste, contaminant constituents were added as dissolved complexes at the given concentrations. The degree of stabilization achieved was determined by TCLP extraction.

2.2.2. Volatile Organics: A previous study noted that no volatile organics "are present in concentrations to be of regulatory concern (Halliburton, 1992)." As a confirmation,

TCLP Zero Headspace Extractions (ZHE) were performed on the "centerpoint mixes" in that study. All of the resulting ZHE analyses were below the detection limit of 50 μg/L (Halliburton, 1992).

Based on previous negative results, and the added costs, both in time and additional equipment, of performing ZHE analyses, volatile organic contaminants were not investigated.

2.2.3. Cyanide: Halliburton measured the effects of their recommended S/S process on cyanide by TCLP. There is no LDR for cyanide, and "all values [were] less than the Maximum Contaminant Limit (MCL) for cyanide (50 μg/L) in drinking waters (Halliburton, 1992)." Therefore, cyanide leaching did not merit further investigation.

In summary, stabilization of the contaminants cadmium, chromium, nickel, and silver was measured by TCLP extraction. The extract concentration of the contaminants of concern were compared to LDRs to determine the degree of success. Because this study was conducted with a surrogate waste, stabilization results were interpreted directly and relative to previous results with the actual Pond 207C waste.

2.3. SOLIDIFICATION

The third objective of this research was to produce a final product with desirable physical characteristics. This requires solidification of the liquid and semi-liquid phases of Pond 207C waste.

The EPA defines solidification as, "the production of a monolithic block of treated waste with a high structural integrity (U.S. EPA, 1982)." The EPA describes the ideal solidified waste form as a, "monolithic mass that has good dimensional stability, freeze-thaw resistance, low permeability, a high bearing capacity, and resistance to attack by biological agents." Standard tests of the success of a solidification process include bulk and dry unit weight, unconfined compressive strength, permeability, wet/dry durability, and freeze/thaw durability (U.S. EPA, 1982).

A previous treatability study devoted, "considerable effort . . . to wet/dry and freeze/thaw durability testing because of the likelihood that the stabilized waste may be stored at Rocky Flats for an extended period of time until ultimate disposal . . . (Halliburton, 1992)." All test specimens, with one exception, passed all wet/dry and freeze/thaw durability tests.

This research was conducted under the assumption that, through proper scheduling and waste handling, treated Pond 207C waste will not be subject to numerous wet/dry or freeze/thaw cycles at RFETS. With respect to the exposure of hazardous waste to such cycling at a hazardous waste landfill, Conner (1990) writes, "Properly designed and located landfills are subjected to such cycling only for a limited period during the filling of the cell, if at all." Therefore, wet/dry and freeze/thaw durability were not seen as critical physical characteristics of the final waste form. These properties were not evaluated.

Unconfined compressive strength (UCS) testing is not required for product certification at Envirocare (Halliburton, 1992; Siegrist et al., 1994). However, for the purposes of comparison, UCS provides an important indicator as to the quality of given waste form. A general guideline is a UCS of ≥50 psi, which is required to support the overburden pressures and operating equipment loads in a landfill (LaGrega, Buckingham, and Evans, 1994).

Bulk density, expressed as specific gravity, of waste products was also assessed. No specific gravity requirements exist; however, maximizing specific gravity will help to minimize product volume.

A UCS of ≥50 psi was adopted as the standard for successful stabilization. No minimum standard for final product specific gravity was adopted. However, higher final product specific gravities were viewed as a superior characteristic for the purpose of process comparison.

Chapter 3

THEORY OF CEMENT-BASED WASTE FORMS

The following chapter presents a brief overview of theoretical cement-based S/S concepts central to this research project.

3.1. THE CEMENT MATRIX

The principal reaction which imparts strength and durability to Portland cement after it is mixed with water and allowed to set is the hydration of aluminosilicate to form a silica gel, generally designated as C-S-H in the literature. C-S-H is shorthand for Ca, Si, and H_2O, the constituents of hydrated calcium silicate, or silica gel. A general, unbalanced reaction which describes silica gel formation in concrete is:

$$Ca(OH)_2 + Al_2Si_2O_7 + H_2O \rightarrow C\text{-}S\text{-}H \quad \text{(Glasser, 1993).}$$

Although technically correct, the term "gel" is somewhat misleading. The gel-like mass which results from the hydration reaction has a very high cohesiveness and tensile strength (Czernin, 1980). The resulting product is "tolerant of wet material . . . not flammable and is durable in the natural environment (Glasser, 1993)."

In addition to its physical characteristics, cement has several chemical characteristics which make it well suited for the solidification and stabilization of wastes.

Table 3.1 lists some physical and chemical mechanisms by which cement can stabilize waste constituents. The reader will note that several of the examples of stabilization mechanisms in Table 3.1 involve contaminants of concern in the present study (specifically, cadmium, chromium, and nickel).

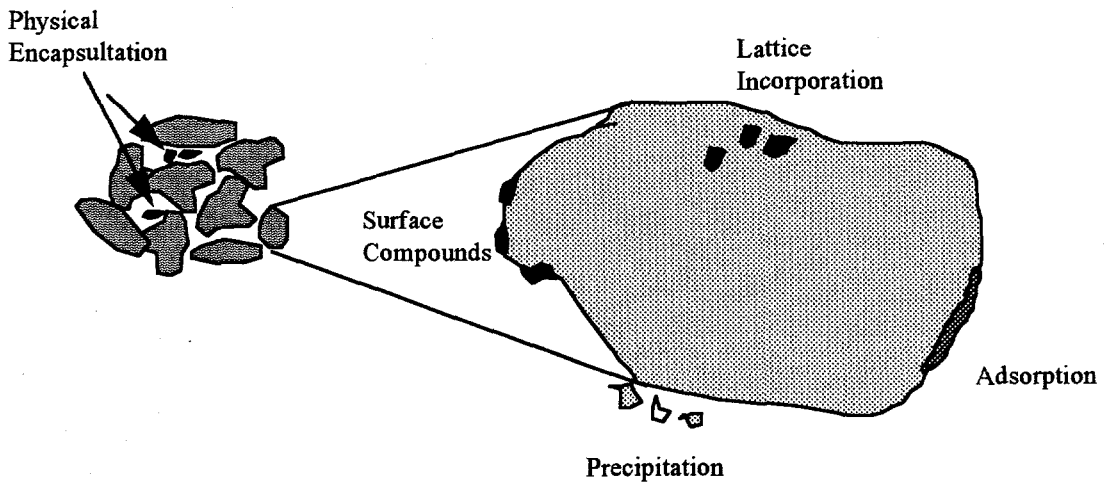
Table 3.1: Cement Stabilization Mechanisms[a]

Mechanism	Example
Sorption into/onto high surface area C-S-H	Pb^{2+} adsorption
Precipitation of metal hydroxides	$Cd(OH)_2$ precipitation
Formation of surface compounds	$Ca[Cd(OH)_4]$ formation
Lattice incorporation in the cement matrix	Cr^{6+} incorporation
Development of solubility limiting hydrous silicates and calcium salts	CuSi formation
Physical encapsulation	Ni^{2+} encapsulation

[a] Sources: Conner, 1990; Bishop, 1988; Butler et al., 1993; Cocke and Mollah, 1993; Glasser, 1993; and Roy et al., 1993.

The stabilization mechanisms outlined in Table 3.1 are graphically depicted in Figure 3.1.

Figure 3.1:
Graphical Representation of Stabilization
Mechanisms Active in the Cement Matrix



(Adapted from Cocke and Mollah, 1993)

The left side of Figure 3.1 represents several cement grains with contaminant constituents physically encapsulated within the cement matrix. This is also known as micro-encapsulation. Roy and others (1993) suggest that "physical encapsulation is the principal mechanism of solidification/stabilization."

The right side of Figure 3.1 represents a single cement grain. Several different stabilization mechanisms which are potentially active in cement-based S/S systems are depicted. Of particular note are precipitation, believed to be active in the stabilization of cadmium, chromium, and silver (Conner, 1990 and Kindness, Macias, and Glasser, 1994), and lattice incorporation, postulated as active in the stabilization of chromium (Bishop, 1988).

The primary objective of cement-based S/S process formulation is the maximization of stabilization mechanisms such as those listed in Table 3.1 and depicted in Figure 3.1, while minimizing associated losses of desirable physical characteristics. By maximizing the stabilization effectiveness per unit weight of reagents used in S/S processing, it may be possible to reduce the amount of reagent used without a critical loss of treatment effect. Final waste form weight and volume could thereby be significantly reduced.

3.2. WATER TO CEMENT RATIO

One of the most important factors affecting the quality of the final cementitious product is the water-to-cement (W/C) ratio. "Minimization of the amount of mixing water is exponentially related to [a] decrease in porosity and an increase in strength (Roy and Scheetz, 1993)."

To achieve complete hydration, cement must react with a quantity of water roughly equal to 25% of its weight (the water required for hydration is frequently called the "water demand" of the cement). However, "the cement paste requires a substantial excess of mixing water, which should . . . amount to about 35-40 per cent of the weight of cement (Czernin, 1980)." Because cement pastes with low W/C ratios do not flow plastically, a W/C ratio of 0.50 is "typically used in practice for making a good quality (high strength) structural concrete (Czernin, 1980)." Thus, a significant chemical excess

of mixing water exists within the cement matrix in many concrete and cement-based S/S applications.

The presence of soluble waste constituents, which may "bind" water in chemical reactions, may increase the water demand of the wet mix. The associated effects of increased water demand on rheology may limit the operational window of an S/S process (Glasser, 1993), making W/C ratio an even more critical parameter.

In the present study, final product volume reduction was achieved through dewatering by evaporation. Dewatering reduced the water content of the surrogate waste and thereby effectively increased the proportion of soluble waste constituents in the waste. The relative water demand of soluble waste constituents was thus increased.

3.3. CEMENT REPLACEMENT WITH FLYASH

A pozzolan is a material "that does not exhibit cementing ability when used by itself, but in combination with other materials, such as Portland Cement or lime, will interact with these agents resulting in a cementitious reaction (Conner, 1990)." Flyash is such a pozzolan, and, as mentioned above, is a constituent of both Halliburton's recommended pozzolanic mixture (Halliburton, 1992) and the pozzolanic mixtures used in this research.

Partial replacement of cement with flyash may result in a product of reduced strength and delayed strength development (Inst for Mat'l and Env Research, 1992).

However, it has several advantages for S/S systems, not the least of which is the fact that flyash is a waste itself. It also reduces the heat of the hydration reaction. Additionally, the potential reduction in product strength is partly or totally compensated for by:

- lowered water demand
- improved particle packing, and associated reduction in permeability
- improved workability due to the spherical shape of flyash particles
- the pozzolanic reaction
- an improved interface between aggregates (or waste solids) and the cementitious matrix
- a possible reduction in the tendency to form bleed water (Inst for Mat'l and Env Research, 1992)
- possible increased reduction of Cr^{6+} to Cr^{3+} (Kindness et al. 1994)
- lower reagent costs (Conner, 1990).

The maximum replacement ratio of flyash to cement recommended for use in mass concrete applications, such as highway construction, is 20-25% (i.e., 20-25% of the cement, by weight, is replaced by an equal weight of flyash). Mixtures with up to 50% cement replacement with flyash are sometimes used where heat buildup is a concern and early strength development is not important (Halstead, 1986).

Disadvantages of the use of flyash in S/S systems include the previously mentioned potential loss of structural strength and, even more importantly, increased product weight

and volume. Conner notes that use of cement-flyash systems "results in a larger volume and weight increase than with Portland cement alone, and thus is usually only justified where low handling, transportation, and disposal costs are encountered (Conner, 1990)." Another disadvantage of the use of flyash as a reagent is that it may have a significant metal content. Thus the potential exists for metal leaching from the flyash itself (Conner, 1990).

Several of the characteristics of flyash and pozzolan mixtures incorporating flyash are of particular importance to the current research. The lowered water demand effects the amount of excess water in the final waste form. Both the lowered water demand and the improved workability due to the spherical shape of flyash particles can improve the waste-S/S reagent slurry rheology. An improved interface between the pozzolanic mixture and waste constituents may improve stabilization of some contaminants. Increased reduction of Cr^{6+} to Cr^{3+} is a potentially important improvement in the stabilization of chromium.

With respect to the S/S of Pond 207C residuals, this study's target waste, the lower cost for flyash is of reduced importance since the cost of reagents is relatively low when compared to total handling and disposal costs. The formation of bleed water is difficult to definitively detect at the scale of this experiment, but the low effective water to pozzolan ratio of high waste loadings make its formation unlikely. Reduced strength of a final waste form could result in its failure to meet this study's criteria of ≥50 psi UCS and

therefore the reduction in strength resulting from the use of flyash may prove to be important.

As noted in Chapter 2, transportation and disposal costs will be considerable if the final disposition of the waste is off-site disposal. Thus, the reported potential for increased volume (or lowered specific gravity) of treated waste may have a significant impact on the primary objective of this research. Finally, leaching of metals from the flyash reagent may cause a treated waste that would have otherwise passed LDRs to fail to meet land disposal acceptance criteria.

Chapter 4

METHODS AND MATERIALS

This research was divided into the following three phases as first outlined in Chapter 1:

I. Process Development and Solidification Assessment

II. Process Assessment

III. Investigation of the Effects of Biodenitrification Pretreatment

Each phase will be addressed separately below. Appendix II contains sample calculations to help illustrate how the protocols for each phase were carried out in the laboratory. These sample calculations represent a single sample as it goes through the entire laboratory protocol, from surrogate waste preparation through the testing protocols.

For the sake of brevity, the coupled evaporation and S/S process, without biodenitrification pretreatment, is hereafter referred to as the S/S process. The process with biodenitrification pretreatment is referred to as the bio-S/S process.

4.1. PHASE I: PROCESS DEVELOPMENT AND SOLIDIFICATION ASSESSMENT

The protocol followed for Phase I was developed by Dr. Nevis Cook, Colorado School of Mines. The objective of Phase I was to investigate the feasibility of an

alternative to the S/S process recommended by Halliburton. The alternative involves thermal dewatering (evaporation) of varying percentages of the Pond 207C surrogate waste water content. The goal of dewatering is to produce a final waste form of reduced weight and volume (or increased waste loading, as presented earlier). The protocol followed in Phase I is explained below.

4.1.1 Surrogate Waste Preparation and Lime Addition: A brine with concentrations of salts representative of the major dissolved salts present in Pond 207C residuals was prepared according to the formulation outlined in Table 4.1 (here "brine" refers to the soluble waste constituents dissolved in deionized water). The formulation was developed by Dr. JoAnn Silverstein, University of Colorado, Boulder, for a biodenitrification study on the same Pond 207C waste.

Table 4.1: Brine Constituents

Constituent	Concentration (g/L)
KNO_3	98.1
K_2SO_4	22.7
KCl	30.6
NaCl	11.7
$NaHCO_3$	79.0
NaOH	166.4

The brine had total dissolved solids (TDS) of approximately 30% by weight and a specific gravity of 1.24.

According to a characterization study, Pond 207C waste contained an insoluble fraction of "silt-like material" (Halliburton, 1992). In order to replicate the insoluble fraction, a fine grain soil material, collected from a site near the RFETS, was added in an amount equal to 0.14 × TDS, or 42 grams per 1000 g brine. The added insoluble mineral fraction was sized by passing it through a 100 mesh sieve. This sieve nominally passes all solids 149 μm and smaller in diameter. Therefore, the added insoluble solids were not truly silt in the strict definition based on a particle size range for silt of 0.002 to 0.06 mm. For the sake of brevity, however, the added insoluble solids will hereafter be called "silt." The added silt had a water content of 4.1% and volatile solids content of 7.0% by weight. The water and organic carbon contents were measured by drying samples to constant weight at 105°C and then oxidizing volatiles at 550°C for two hours.

Hydrated lime [$Ca(OH)_2$], a S/S reagent, was also added during surrogate waste preparation. In addition to facilitating silica gel formation after pozzolan addition, lime addition aids in the fixation of cadmium through CdOH formation and buffers the waste/acetic acid mixture during TCLP testing. Lime was added in a proportion equal to 0.05 × TDS (15 grams per 1000 g brine). Lime was added during waste preparation to ensure its uniform distribution throughout the waste prior to pozzolan addition.

The amount of waste prepared for each sample was adjusted to yield approximately 450 ml after sample evaporation . This ensured that at least two duplicate 210 ml curing cylinders could be filled.

4.1.2. Surrogate Waste Dewatering: Dewatering of prepared wastes was accomplished by evaporation in a water bath at 60 to 80 °C. Because a film of precipitate developed on top of the sludge during evaporation, it was necessary to stir the mixture continuously during evaporation. This was accomplished with acrylic impellers powered by 300 rpm, 12 watt electric motors, one per each evaporating sample.

The water content of wastes was evaporated to achieve solids contents (percent solids, by weight) ranging from 43% solids (the baseline formulation) to over 80%. In order to calculate percent solids, all mass losses during evaporation were assumed to be the result of evaporating water. When percent of waste solids remaining after evaporation was calculated, the weight of reagent lime was not included in the weight of solids.

4.1.3. S/S Reagent Addition: The S/S reagents Type V Portland cement and Type C flyash were added in two weight to weight ratios (PC/FA), 2:1 and 1:2. The 1:2 mixture was the pozzolan formulation recommended by Halliburton (1992). The 2:1 mixture was used to investigate the effects of a lower flyash content in the pozzolanic mixture on contaminant stabilization and product strength. S/S reagents were "off the shelf;" therefore the potential existed for leaching of contaminants from the S/S reagents themselves.

The required quantities of cement and flyash were weighed out and added, flyash first, to the evaporated surrogate waste. The quantity of flyash was manually mixed

completely before addition of the cement, which was then completely mixed manually. Water to Pozzolan (W/P) ratios tested were 0.4, 0.5, and 0.6.

Replicate molds of 210 ml volume (2 × 4 in. plastic cylinders) of the waste/reagent slurry were prepared in accordance with ASTM C192, "Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory," with the exception that molds were not removed until the entire 14 day cure time had elapsed.

4.1.4. Cure: Test specimens were cured in the 210 ml plastic molds in a sealed plastic container, under a wet towel. Curing occurred at ambient laboratory temperature which varied over a range of approximately 17 to 23°C. A curing time of 14 days was used throughout this study.

The 14 day curing time was selected based on a study by Cullinane et al. (1987). That study reported UCS as a function of curing time and NaOH interference concentration with several different binding mixtures, including a Portland cement and flyash mixture. The data from that study indicated that the majority of strength development in samples with NaOH interference occurs prior to 14-16 days of curing time.

4.1.5. Specific Gravity Determination and Strength Assessment: Sample batches generally filled at least two 210 ml cylindrical molds completely and one mold only partially. Final waste form volume was determined by weighing the water required to fill

the void in the partially filled cylinder, converting the water weight to a volume (1g = 1ml), subtracting the water volume from 210 ml, and adding that figure to the volume of completely filled cylinders. Total product weight was determined by summing waste and reagent weights, which were measured directly. Specific gravity is the bulk density of the final waste form (waste form weight/volume) divided by the density of water (1 g/ml).

Test cylinders were prepared in accordance with ASTM C617, "Standard Practice for Capping Cylindrical Concrete Specimens," prior to unconfined compressive strength testing. Plaster of Paris was used to cap the first several 210 ml final waste form cylinders. This method resulted in inconsistent UCS measurements. Subsequent capping was accomplished with sulfur mortar, which yielded more consistent results. UCS was tested in accordance with ASTM C39, "Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens."

4.2. PHASE II: PROCESS ASSESSMENT

The protocol followed in Phase II, Process Assessment, was the same as that used for Phase I, Process Development and Solidification Assessment, with the following additions and modifications:

4.2.1. Surrogate Waste Preparation and Lime Addition: The surrogate waste was prepared the same as in Phase I up to the point of contaminant addition. Contaminants were added as the waste was stirred in the water bath. Contaminants were added in

solutions (by burette) into the continuously stirred waste over a period of about 5 minutes per solution to ensure uniform distribution of contaminants throughout the waste.

Two contaminant spike stock solutions with completely dissolved complexes of the metals of interest (cadmium, chromium, and nickel in one, and silver in a second) were mixed to the concentrations presented in Table 2.1. The contaminant spike stock solutions were designed to be added at a dosage of 2 ml spike per 100 g brine.

Table 4.2: Contaminant Spike Stock Solutions

Component	Concentration (g/L)
Solution No. 1	
$CdCl_2$	19.52
CrO_3	32.90
$NiCl_2 \cdot 6H_2O$	10.38
Solution No. 2	
Ag_2SO_4	4.96

4.2.2. Surrogate Waste Dewatering: Based on the results of Phase I testing, spiked surrogate wastes were dewatered by evaporation to four target solids contents, 43%, 63%, 73%, and 78% solids.

4.2.3. S/S Reagent Addition: Again based on the results of Phase I testing, the pozzolanic mixture was added at a single water to pozzolan ratio, 0.5. Both cement to flyash ratios, 2:1 and 1:2, were tested.

4.2.4. TCLP and CCWE Analysis: The TCLP was performed in accordance with 40 CFR Pt. 261, App. II. Analysis of contaminant constituents in the waste extract (CCWE) for cadmium, chromium, nickel, and silver was performed by Pace, Inc., Environmental Laboratories. Pace Laboratories originally attempted analysis of the extracts by inductively coupled plasma atomic emissions spectroscopy (ICP--EPA Method 6010). Detection limits below LDR standards for cadmium, nickel, and silver were not attained due to sodium interference. Pace Laboratories then analyzed the extracts for cadmium, nickel, and silver concentrations by flame atomic adsorption spectroscopy (Flame AAS--EPA Methods: 7130 for cadmium, 7520 for nickel, and 7760 for silver). Detection limits below LDRs were obtained with Flame AAS. Analytical detection limits for ICP (chromium only) and Flame AAS (cadmium, nickel, and silver) are presented in Table 4.3. LDRs are also presented for comparison to detection limits.

Table 4.3:
Land Disposal Restrictions and Analytical Detection Limits

Analyte	LDR, CCWE (mg/L)	MDL (mg/L)
Cd	0.066	0.02
Cr	5.0	0.2
Ni	0.32	0.2
Ag	0.072	0.05

MDL = Method Detection Limit

4.2.5. Control Sample Preparation: To measure the amount of stabilization of each added metal which occurred in the Pond 207C surrogate waste in the absence of S/S reagents, two control samples were prepared and analyzed. The control samples were prepared identically to other samples in Phase II, but no S/S reagents (lime, cement, or flyash) were added. One control sample was unevaporated and a second was evaporated to the highest solids content attainable in the water bath.

The unevaporated control sample was stirred for over 24 hours to allow any kinetically limited reactions to take place. The unevaporated waste was then filtered through a 0.7 μm filter (the size required for TCLP extract filtration). The filtrate was analyzed for the metals of concern, cadmium, chromium, nickel, and silver. The concentrations of contaminants not present in the filtrate were assumed to be immobilized by the other constituents of the surrogate waste.

The evaporated control sample was dewatered to the highest solids content attainable in the water bath. The dewatered sample had no free liquids, so a filtrate could not be collected as with the unevaporated sample. The degree of stabilization was determined by TCLP extraction. The TCLP extract was analyzed for the four contaminant constituents, cadmium, chromium, nickel and, silver. As with the unevaporated control sample, the concentrations of contaminants not present in the TCLP extract were assumed to be immobilized in the evaporated surrogate waste.

4.3. PHASE III: INVESTIGATION OF THE EFFECTS OF BIODENITRIFICATION PRETREATMENT

As addressed in Chapter 1, actual bioreactor residuals were not available for use in this portion of the S/S treatability study. The theoretical output derived in Appendix I was used as the waste to be treated by S/S processing. The fundamental changes in the surrogate waste resulting from biodenitrification pretreatment are the following:

- addition of biomass
- increase in chloride content due to HCl pH adjustment in the bioreactor
- increase in sodium content due to sodium acetate feed addition (sodium acetate serves as source of electron acceptors in the bioreactor)
- removal of NO_3 as N_2 off-gas.

Procedures used for S/S of the simulated bioreactor residuals were the same as those used in previous phases of this study except as noted below.

4.3.1. Simulated Bioreactor Residuals Preparation: The biomass constituent of the simulated residuals was taken from settled return activated sludge (RAS). The RAS was obtained from the City of Broomfield Wastewater Treatment Plan, Broomfield, Colorado. It was settled and clear liquor was decanted. Average volatile suspended solids of the concentrated RAS was 1.58 g/L with nonvolatile solids of 0.54 g/L, determined by drying to constant weight at 105°C and oxidizing volatiles at 550°C, respectively.

The constituents of the simulated bioreactor residuals are listed in Table 4.4. The constituents were added to the concentrated RAS in the amounts indicated. Thus, the water content of the concentrated RAS (still >97% water) served as the solvent for mixing of the simulated effluent. The mixture was continuously stirred (with the 300 rpm motors used during evaporation) as the inorganic constituents were added. The constituents of the bioreactor residuals did not completely dissolve when mixed. However, because the objective of this phase of the study was to investigate the effects of all bioreactor products on the S/S treatment process, all constituents were added to the waste regardless of whether they dissolved or remained as particulate matter.

Table 4.4: Simulated Bioreactor Residuals

Constituent	Mass Added (g)
K_2SO_4	22.6
$KHCO_3$	138.2
NaCl	315.6
$NaHCO_3$	59.6
NaOH	3.0
$C_5H_7O_2N$ (Biomass)	12
H_2O	845

Notes: 1. Residuals from biodenitrification of approximately 1 L of surrogate waste (approximately 42% dissolved and suspended solids).
2. H_20 and $C_5H_7O_2N$ from approximately 860 ml settled return activated sludge

HCl is the acid used to regulate the bioreactor pH during the biodenitrification process. The higher chloride content of the above theoretical residuals reflects this HCl addition.

The constituents outlined in Table 4.3 were designed to simulate bioreactor residuals from treatment of 1000 g of brine influent (i.e., 1000 g of brine--water and dissolved solids-- plus the silt and contaminant constituents which make up the Pond 207C surrogate waste). Therefore, the silt fraction added was 42 g, or 0.14 x bioreactor influent TDS, as used in the Pond 207C surrogate waste preparation. The contaminant spike was also added based on the theoretical influent to the bioreactor and in the same proportions as outlined in Section 5.2. Reagent lime was added based on the solids content of the simulated effluent at the ratio of 5% of bioreactor effluent TDS.

4.3.2. Control Sample Preparation: As with the S/S process, control samples were prepared with an unevaporated waste, and a sample dewatered to the extent possible in the water bath. The unevaporated waste required pre-filtering before it could be filtered at 0.7 μm. Like the evaporated control sample for the S/S process, the evaporated control sample for the bio-S/S process was subjected to the TCLP and the extract was analyzed for the metals of concern.

4.3.3. CCWE Analysis: Analysis of all Phase III CCWEs was performed by Pace Laboratories by Flame AAS. The detection limit for chromium (EPA Method 7190) was 0.5 mg/L. Method numbers and detection limits for cadmium, nickel, and silver were the same as those reported in Section 4.2.4.

Chapter 5

RESULTS

The results of the three phases of this research are presented in the following chapter. In several instances, where significant trends were observed, data is presented in both tabular and graphical form. The last section of this chapter presents an interpretation of the TCLP results, which are expressed as percent fixation of contaminants, for both the S/S and the bio-S/S processes. The results are discussed in Chapter 6.

5.1. PHASE I RESULTS

Phase I, Process Development and Solidification Assessment, entailed development of viable process formulations and determining the extent to which the waste could be dewatered while maintaining sufficient mixability. The ability of those formulations to solidify the Pond 207C surrogate waste, and final product specific gravity were also evaluated.

The Pond 207C surrogate waste was evaporated to solids contents greater than 80% without becoming to viscous to mix with the S/S reagents cement and flyash. The sludge became too viscous to mix at approximately 82% solids. To allow a margin of safety, S/S process assessment was limited to maximum TS levels of 78%.

The 0.5 water to pozzolan (W/P) ratio produced waste-S/S reagent slurries of acceptable consistency over the entire range of solids contents tested. The 0.4 W/P ratio produced dry slurries that were not mixable (i.e., a homogeneous mixture of waste and reagents was not attainable) at 73% and 78% solids. The 0.6 W/P ratio produced watery slurries and resulted in final products with bleed water present at 43% solids. Because it yielded the best results across the largest range of percent solids, the 0.5 W/P ratio was the only W/P ratio used for Phase II and Phase III testing.

All tested S/S products had a UCS above 50 psi. During early testing, UCS measurements for different specimens from the same sample varied by up to 30%. This effect was reduced to approximately 10%, or less, after the specimen capping material was changed from plaster of Paris to sulfur mortar (this change was first noted in Section 4.1.5).

The results of Phase I testing for the two different Portland cement to flyash ratios (PC/FA) at the 0.5 W/P ratio are presented in Table 5.1.

Table 5.1:
Final Waste Form Physical Characteristics
(Unspiked Samples)

% Solids	Waste Loading (%)	Specific Gravity	Ave UCS (psi)
PC/FA = 2/1			
53	28	1.90	503
65	40	1.87	137
75	52	2.09	134
79	60	1.96	212
PC/FA = 1/2			
53	28	1.87	570
64	38	1.85	164
77	56	1.86	99
79	59	1.94	128

5.2. PHASE II RESULTS

During Phase II, Process Assessment, the process formulations developed in Phase I were evaluated in terms of the three study objectives: final product volume reduction, contaminant stabilization, and waste solidification. Based on the results of Phase I the S/S process was tested on sludges dewatered to solids contents of approximately 43%, 63%, 73%, and 78%. The data describing the physical characteristics and contaminant leaching of the final waste forms are presented in separate sections below.

5.2.1. Physical Characteristics: Evaporation of the Pond 207C surrogate waste to 78% solids yielded residuals that were substantially more viscous than at the original 43% solids

content. However, because S/S reagents were added in proportion to the remaining water, a workable waste-S/S reagent slurry was obtained.

As the process formulation and testing methods were refined, results for different specimens of the same surrogate sample became more consistent. All samples had an average UCS greater than 100 psi. Viable process formulations were demonstrated at waste loadings significantly higher than the approximately 20% waste loading of the baseline process. At 78% solids, over 53% waste loading, the volume of the final waste form was less than half of that produced with the baseline formulation.

The physical characteristics of the final products for both PC/FA ratios are presented in Table 5.2.

Table 5.2:
Final Waste Form Physical Characteristics
(Spiked Samples)

% Solids	Waste Loading (%)	Specific Gravity	Ave UCS (psi)
PC/FA = 2/1			
45	21	1.89	670
64	37	1.91	230
73	47	1.94	151
80	55	1.93	186
PC/FA = 1/2			
45	21	1.86	650
64	36	1.88	252
73	47	1.91	101
78	53	1.89	102

Specific gravity and UCS versus waste loading for the two process formulations are shown graphically in Figures 5.1 and 5.2. The UCSs of individual replicates, rather than average UCSs, are shown in Figure 5.2.

Figure 5.1:
Specific Gravity vs. Waste Loading
(S/S Process)

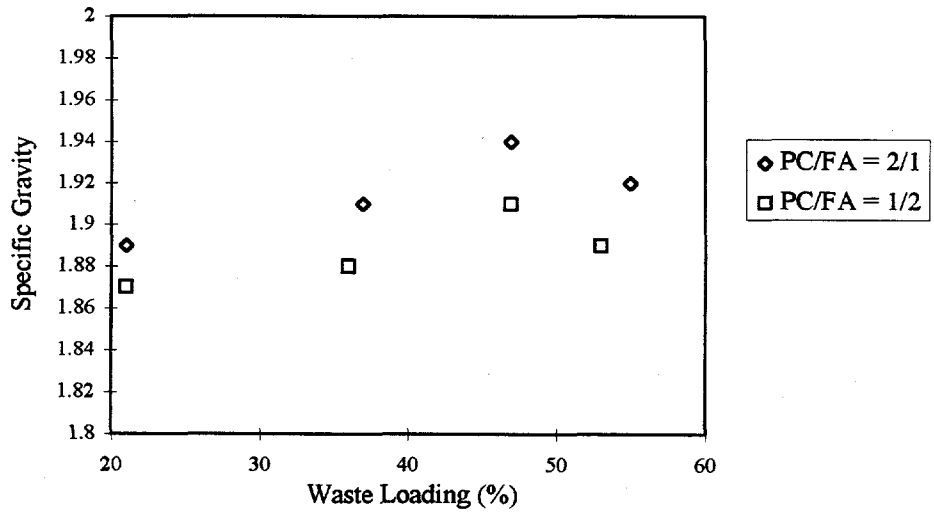
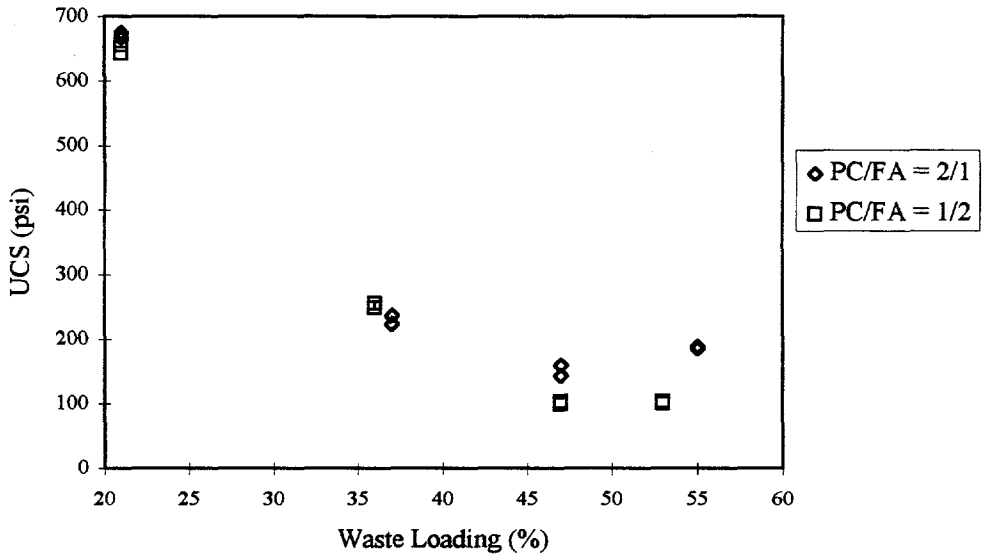


Figure 5.2:
UCS vs.Waste Loading
(S/S Process)



5.2.2. Contaminant Leaching: After the physical characteristics of final waste forms were measured, the leachability of the contaminant constituents cadmium, chromium, nickel, and silver was assessed. Method blanks (Pond 207C surrogate waste without the contaminant spike, treated with the S/S reagents), control samples (as explained in Section 4.2.5), and treated Pond 207C surrogate waste were evaluated. The results are presented in three separate sections below.

All TCLP extracts had a pH greater than 12. The filtrate analyzed for the unevaporated control sample had a pH greater than 13.5.

5.2.2.1. Method Blanks: Method blanks were tested by TCLP extraction to determine contaminant leachability from surrogate waste constituents and S/S reagents, as well as from possible sample contamination during waste preparation and S/S processing. Chromium and silver concentrations were below detection limits for all samples tested. The CCWEs for cadmium and nickel for unspiked matrices are tabulated below:

Table 5.3: Method Blanks CCWE (mg/L)

PC/FA = 2/1			PC/FA = 1/2		
% Solids	Cd	Ni	% Solids	Cd	Ni
55	0.03	0.2	55	ND	0.2
65	0.03	0.2	64	0.02	0.2
75	0.03	0.3	77	0.03	0.3
75	0.03	0.2	78	0.03	0.3

ND = Non-detect

5.2.2.2. Control Samples: As noted in Chapter 4, the surrogate waste used for control samples was prepared identically to that used for S/S process testing, but no S/S reagents were added. The fractions of contaminants recovered from control samples are presented in Table 5.4. A fraction recovered of 0.0 would imply that all of the contaminant had been immobilized in the untreated waste. Conversely, a fraction recovered of 1.0 would imply that none of the contaminant had been immobilized.

Table 5.4:
Fraction of Contaminant Recovered in Untreated Wastes
(S/S Process)

		Fraction of Contaminant Recovered			
Sample	**% Solids**	**Cr**	**Cd**	**Ni**	**Ag**
Unevaporated Waste	33.5	0.9	0.1	0.3	0.1
Evaporated Waste	89.5	0.6	0.0	0.3	0.1

5.2.2.3. Pond 207C Surrogate Waste: Cadmium, chromium, and nickel leached in detectable quantities at every solids content tested, except for one nickel non-detect. The nickel non-detect occurred at 45% solids with the 1/2, PC/FA formulation. Only one spiked sample had a detectable quantity of silver in the waste extract, 64% solids with a 2/1, PC/FA ratio. The results of TCLP extractions for cadmium, chrome, nickel, and silver are presented in Table 5.6 and graphically, with the exception of silver, in Figures 5.3 through 5.5. The non-detect point for nickel was plotted at the method detection limit (Figure 5.5). To facilitate comparison with bio-S/S process results, CCWE data are presented as a function of percent solids in the waste after evaporation.

Table 5.5: CCWE (mg/L)
(S/S Process)

% Solids	Cd	Cr	Ni	Ag
PC/FA = 2/1				
44	0.03	4.9	0.2	ND
64	0.03	10	0.5	0.28
73	0.04	8.0	1	ND
80	0.04	5.2	1.3	ND
PC/FA = 1/2				
45	0.02	5	ND	ND
64	0.03	9.8	0.6	ND
73	0.04	11	0.9	ND
78	0.04	7.8	1.1	ND

Figure 5.3:
Cadmium CCWE vs. % Solids
(S/S Process)

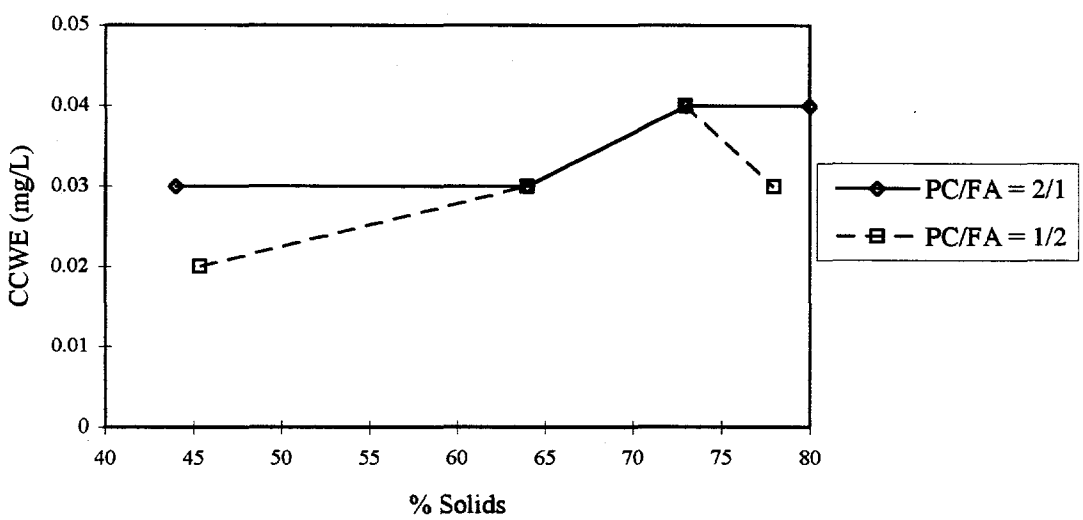


Figure 5.4:
Chromium CCWE vs % Solids
(S/S Process)

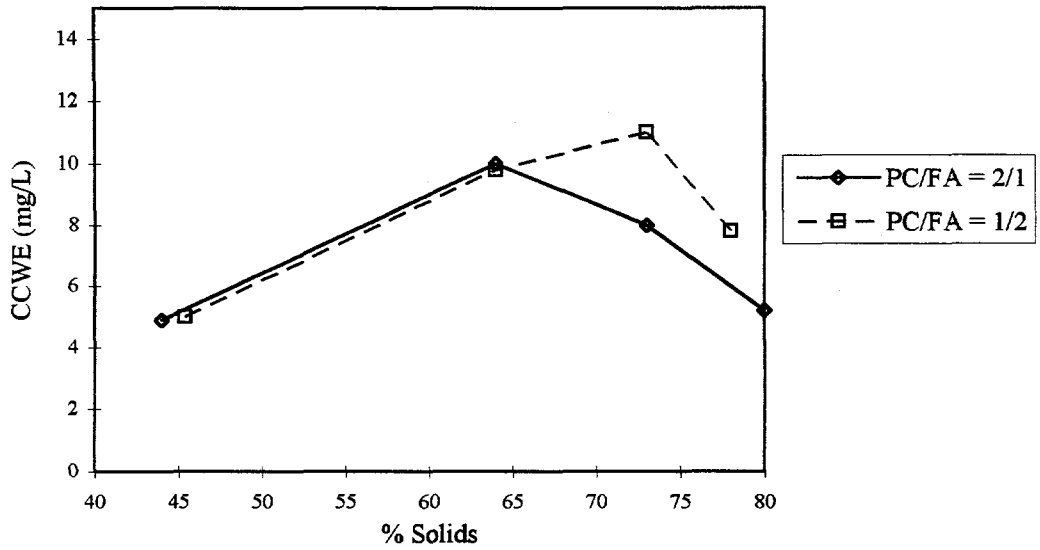
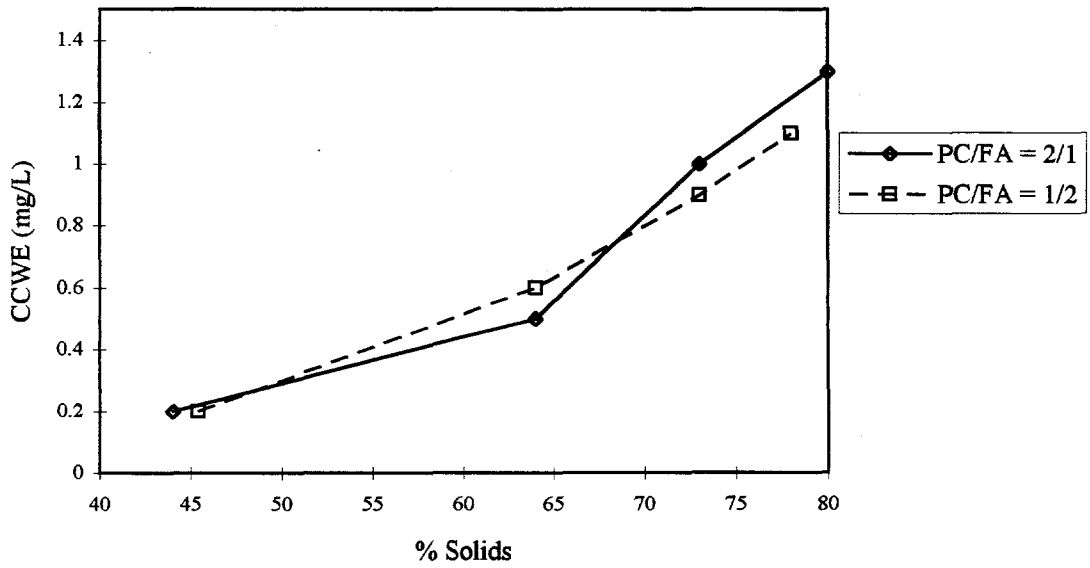


Figure 5.5:
Nickel CCWE vs. % Solids
(S/S Process)



5.3. PHASE III RESULTS

The theoretical bioreactor residuals were dewatered by evaporation to solids contents up to 56%. Like the stand-alone S/S process, increased viscosity of the sludge was the limiting factor as the sludge was dewatered to progressively higher percent solids. Three distinct solids contents were tested, approximately 38%, 48%, and 56% total solids. The results are presented below.

5.3.1. Physical Characteristics: Waste loading for S/S of the theoretical biodenitrification surrogate can be interpreted as if the bioreactor residuals were the target waste (absolute waste loading), or as if the influent to that reactor (the Pond 207C surrogate waste) was the waste of concern (relative waste loading). Equations 5.1 and 5.2 were used to calculate the two different measures of waste loading.

$$Absolute\ Waste\ Loading = \frac{Bioreactor\ Effluent\ Solid\ Weight}{Final\ Product\ Weight} \tag{5.1}$$

$$Relative\ Waste\ Loading = \frac{Bioreactor\ Influent\ Solids\ Weight}{Final\ Product\ Weight} \tag{5.2}$$

The relative waste loading describes the results of implementing an integrated biodenitrification and S/S process with Pond 207C residuals.

The increased concentration of suspended solids in the bioreactor residuals when compared to the untreated Pond 207C residuals resulted in much less workable sludge/reagent slurries. The consequent difficulty in mixing made getting uniform distribution of reagents problematic. The heterogeneities in several integrated process samples caused large variation in unconfined compressive strengths, in some cases greater than 50%. Therefore, both replicate and average compressive strengths are presented. The data describing the physical characteristics of the bio-S/S process waste form are presented in Table 5.6.

Table 5.6:
Final Waste Form Physical Characteristics
(Bio-S/S Process)

% Solids	Waste Loading (%) Absolute	Waste Loading (%) Relative	Specific Gravity	UCS (psi) 1	UCS (psi) 2	UCS (psi) 3	UCS (psi) 4	Ave. UCS
PC/FA = 2/1								
39	17	11	1.83	1369	1152	923	493	984
48	23	15	1.78	840	668	630		713
56	30	19	1.78	1003	700	1012	662	844
PC/FA = 1/2								
39	17	11	1.83	1464	1194	334	293	821
49	24	16	1.79	891	653	503		682
54	28	18	1.86	1146	1019	478	668	828

Table 5.6 data, specific gravity and average UCS, are presented versus absolute waste loading in Figures 5.6 and 5.7. below.

Figure 5.6:
Specific Gravity vs. Relative Waste Loading
(Bio-S/S Process)

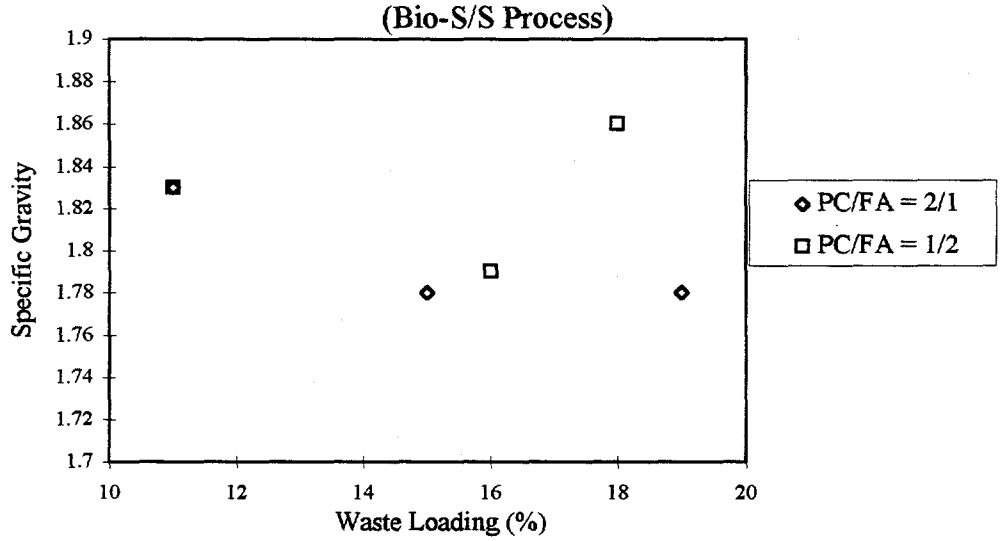
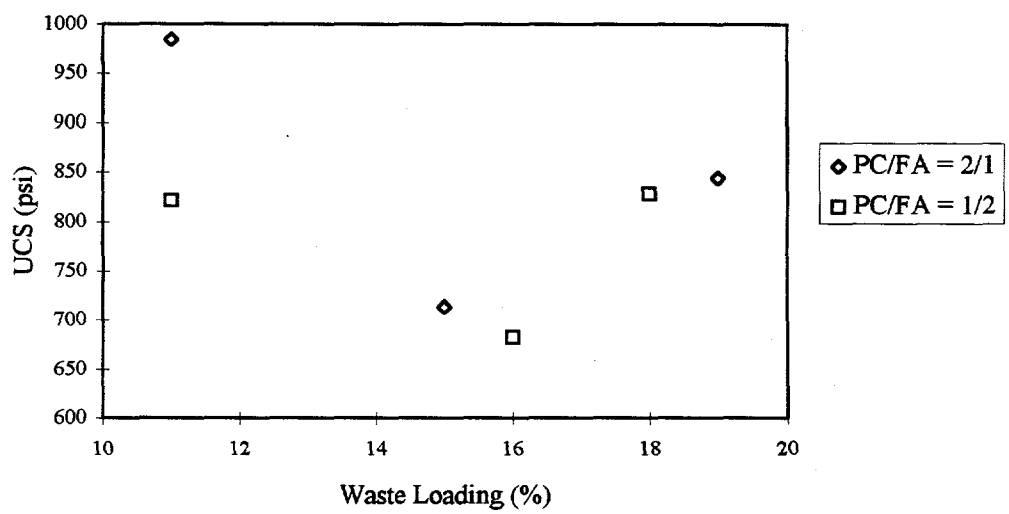


Figure 5.7:
UCS vs. Relative Waste Loading
(Bio-S/S Process)



5.3.2. Contaminant Leaching: Control (untreated) and spiked surrogate samples were prepared and tested for the integrated biodenitrification-S/S process. The results are presented separately, below.

5.3.2.1. Control Samples: The fraction of contaminant spikes recovered for untreated bio-S/S process samples (here untreated means after simulated biodenitrification treatment but before reagent addition) were calculated identically to those for the S/S process (see Section 5.2.2.2). The fraction of the contaminant spike recovered for unevaporated and evaporated integrated process samples are presented in Table 5.7.

Table 5.7:
Fraction of Contaminant Recovered in Untreated Wastes
(Bio-S/S Process)

		Fraction of Contaminant Recovered			
Sample	**% Solids**	**Cr**	**Cd**	**Ni**	**Ag**
Unevaporated Waste	32.1	1.0	0.7	0.2	0.0
Evaporated Waste	59.8	0.1	0.7	0.5	0.1

5.3.2.2. Surrogate Bioreactor Residuals: Extract pH's ranged from 4.6 to 5.6, with one exception at pH = 11.1. The exception occurred at 48% solids with the 2/1 PC/FA formulation (all other parameters measured for that sample were consistent with measurements from other samples).

The results of TCLP extractions for cadmium, chrome, nickel, and silver for the bio-S/S process are presented in Table 5.8. The reader will note that silver was not

detected in any extracts. The results are also presented graphically, with the exception of silver, in Figures 5.8 through 5.10.

Table 5.8: CCWE (mg/L)
(Bio-S/S Process)

% Solids	Cd	Cr	Ni	Ag
PC/FA = 2/1				
39	0.02	2.3	0.4	ND
48	0.03	4.1	0.5	ND
56	0.06	3.9	0.6	ND
PC/FA = 2/1				
39	0.03	2.2	0.3	ND
49	0.04	4.0	0.3	ND
54	0.03	2.3	0.4	ND

Figure 5.8:
Cadmium CCWE vs. % Solids
(Bio-S/S Process)

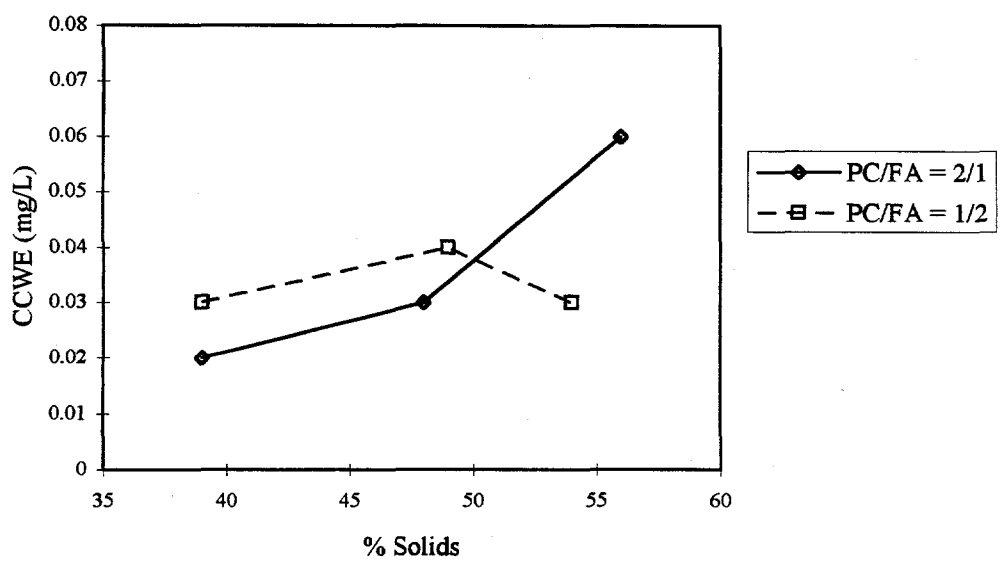


Figure 5.9:
Chromium CCWE vs. % Solids
(Bio-S/S Process)

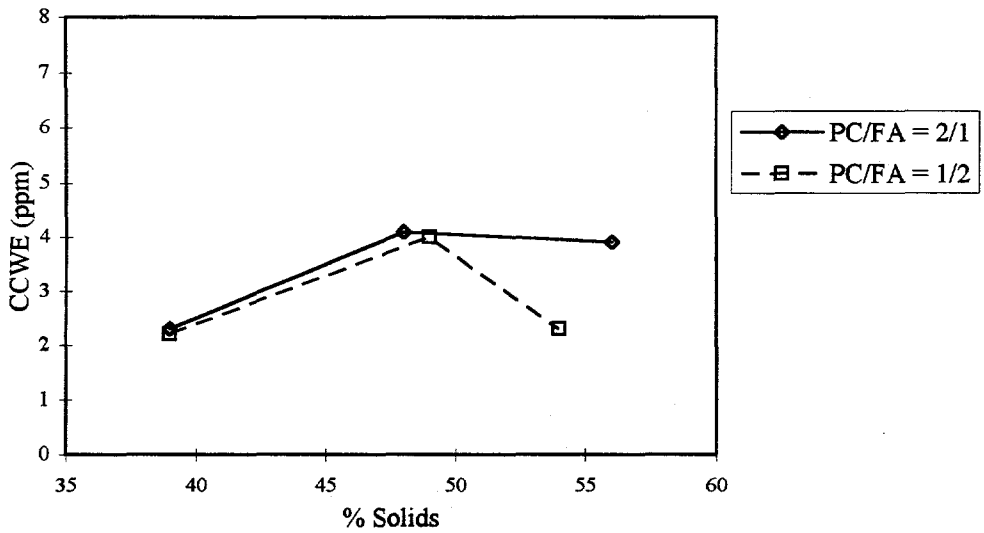
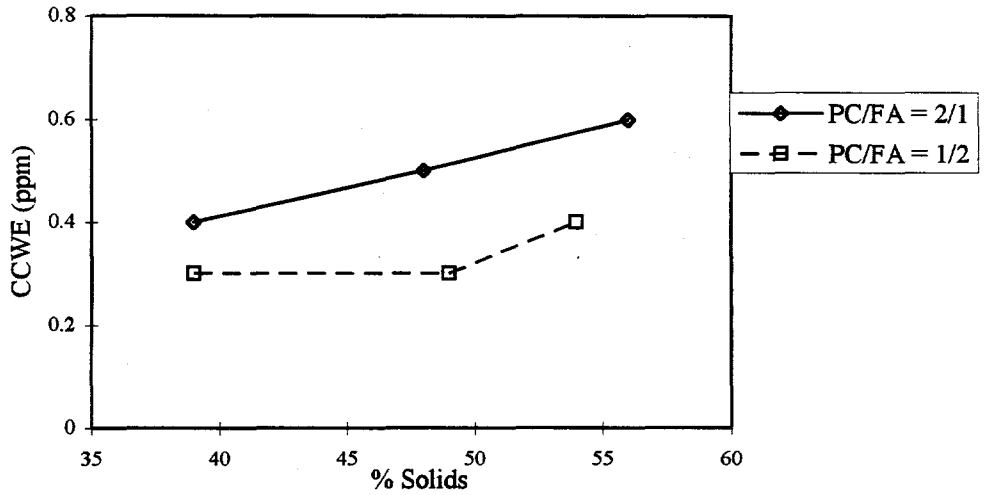


Figure 5.10:
Nickel CCWE vs. % Solids
(Bio-S/S Process)



5.4. PERCENT FIXATION

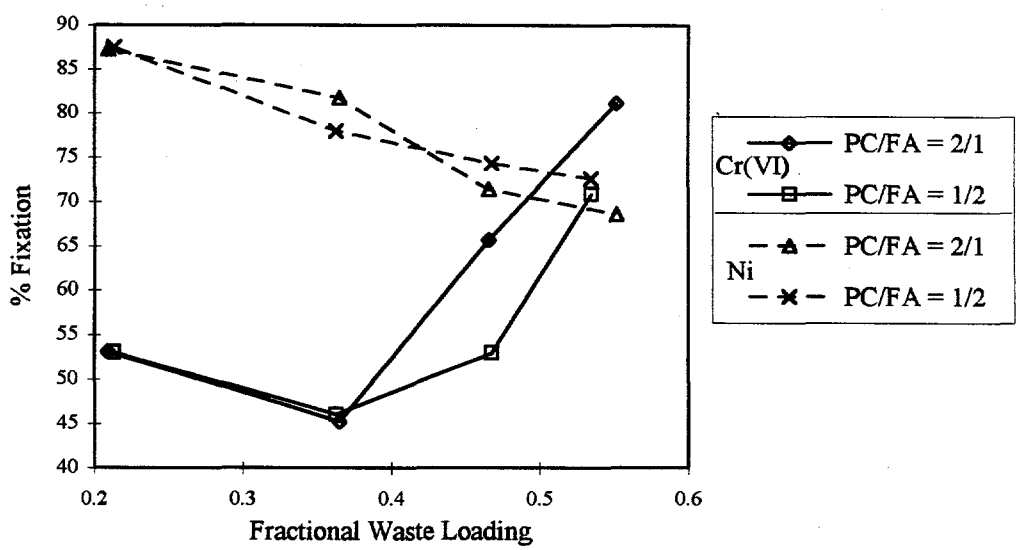
Up to this point in this thesis, the term stabilization has been used to define the treatment effects which limit the solubility of contaminant constituents in the treated waste. Stabilization has been expressed in terms of contaminant concentrations in waste extracts (CCWEs). In this section, the solubility limiting effects of S/S treatment will be addressed in terms of the amount of a given contaminant constituent that is rendered immobile in the final waste form. The degree of immobilization will be expressed as percent fixation. A derivation of the equation used to calculate percent fixation for this study is presented in Appendix III.

5.4.1. S/S Process: Percent fixation data for the two S/S process formulations are presented in Table 5.9. Percent fixation data presented as greater than values (">") were calculated based on method detection limits. The percent fixation data for chromium and nickel are present graphically in Figure 5.11.

Table 5.9:
Percent Fixation of Contaminants
(S/S Process)

Waste Loading	Cadmium CCWE	Cadmium % Fix.	Chromium CCWE	Chromium % Fix.	Nickel CCWE	Nickel %Fix.	Silver CCWE	Silver %Fix.
PC/FA = 2/1								
21%	0.03	99.6	4.9	53.1	0.2	87.2	<0.05	>97.6
37%	0.03	99.8	10.0	45.2	0.5	81.7	0.28	92.3
47%	0.04	99.8	8.0	66.7	1.0	71.3	<0.05	>98.9
55%	0.04	99.8	5.2	81.1	1.3	68.6	<0.05	>99.1
PC/FA = 1/2								
21%	0.02	99.7	5.0	53.1	<0.2	>87.5	<0.05	>97.7
36%	0.03	99.8	9.8	46.0	0.6	78.0	<0.05	>98.6
47%	0.04	99.8	11.0	53.0	0.9	74.4	<0.05	>98.9
53%	0.03	99.8	7.8	70.8	1.1	72.6	<0.05	>99.1

Figure 5.11:
Percent Fixation of Cr(VI) and Ni
vs. Waste Loading
(S/S Process)



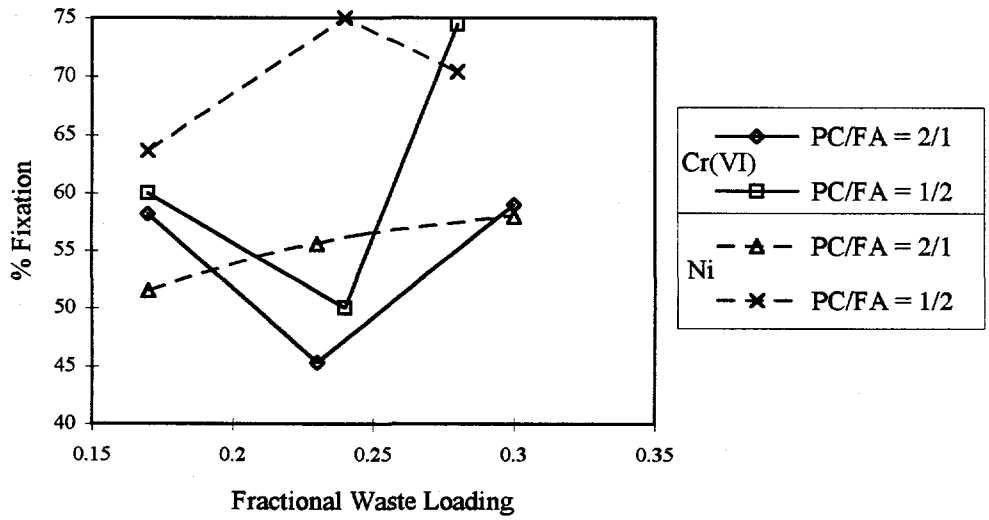
5.4.2. Bio-S/S Process: Percent fixation data for the bio-S/S process are presented in Table 5.10. To facilitate direct comparison with the percent fixation results for the S/S process, percent fixation data are presented versus absolute waste loadings.

Table 5.10:
Percent Fixation of Contaminants
(Bio-S/S Process)

Waste Loading	Cadmium		Chromium		Nickel		Silver	
	CCWE	% Fix.	CCWE	% Fix.	CCWE	%Fix.	CCWE	%Fix.
PC/FA = 2/1								
17	0.02	99.5	2.3	58.2	0.4	51.5	<0.05	>95.5
23	0.03	99.4	4.1	45.3	0.5	55.6	<0.05	>96.7
30	0.06	99.1	3.9	58.9	0.6	57.9	<0.05	>97.4
PC/FA = 1/2								
17	0.02	99.2	2.2	60.0	0.3	63.6	<0.05	>95.5
24	0.04	99.3	4.0	50.0	0.3	75.5	<0.05	>96.9
28	0.03	99.5	2.3	74.4	0.4	70.4	<0.05	>97.2

The percent fixation data for chromium and nickel are presented graphically in Figure 5.12.

Figure 5.12:
Percent Fixation of Cr(VI) and Ni
vs. Waste Loading
(Bio-S/S Process)



Chapter 6

DISCUSSION

The results which were presented in Chapter 5 will be discussed in three separate sections, Waste Loading, Solidification, and Stabilization, below.

6.1 WASTE LOADING

By reducing the sludge water content and holding the water to pozzolan ratio constant, waste loadings substantially higher than that of the baseline S/S process were achieved. Due to increased concentrations of suspended solids and changes in the character of the waste, the bioreactor residuals could not be dewatered to the same solids contents as the un-biotreated surrogate. The waste loadings possible with the bio-S/S process were consequently much lower.

6.1.1. S/S Process: Following dewatering to 78% solids, which resulted in over 53% waste loading, the volume of the final waste form was less than half of that produced with the baseline formulation.

The total volume of Pond 207C sludge has been estimated to be 487,200 gal (Halliburton, 1992). Previous characterization studies reported composite samples had an

average total solids of approximately 43% and a specific gravity of 1.244 (Halliburton, 1992 and Dames and Moore, 1991). This implies 5.05 x 10^6 lbs of residuals with 2.17 x 10^6 lbs of waste solids. Assuming waste solids and S/S product specific gravity of 2.0 (based on current study results), product weight and volume were estimated. Waste loadings achieved in this study and estimates of the results of implementation at RFETS are tabulated below.

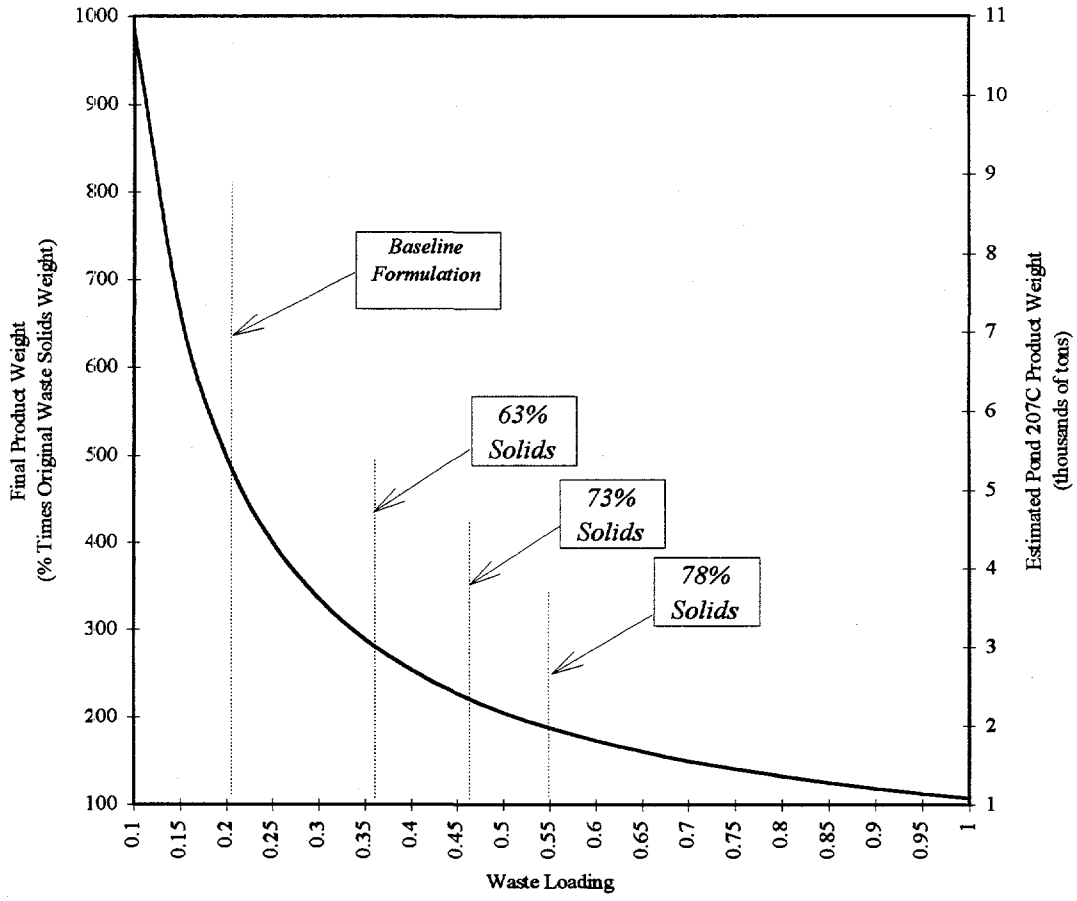
Table 6.1: S/S Process Waste Loading with Estimated Product Weight and Volume

Feed Total Solids	Waste Loading	Est. Product Weight (tons)	Est. Product Volume (yd^3)
43%	21%	5400	3200
63%	36%	3000	1800
73%	47%	2300	1400
78%	54%	2000	1200

Note: A sample calculation is presented at Appendix IV

The data in Table 6.1 are presented graphically in Figure 6.1. This figure was first presented in Chapter 2 with only the waste loading achieved with the baseline formulation indicated. The waste minimization achieved through increased waste loading is readily evident.

Figure 6.1:
Product Weight vs. Waste Loading



6.1.2. Bio-S/S Process: As noted in the preceding chapter, waste loading for S/S of the biodenitrification surrogate can be described as an absolute or relative term depending on whether the bioreactor influent or residuals are viewed as the S/S process input. The highest absolute waste loading achieved was 30%, this equates to a 19% relative waste

loading. Stated differently, the best overall result of biodenitrification-S/S processing of the Pond 207C surrogate waste was a waste loading of approximately 19%. Solidification of the bioreactor residuals with no dewatering resulted in an absolute waste loading of 17%, equivalent to a relative waste loading of only 11%.

The lower waste loadings can be attributed to the difficulty in dewatering the biodenitrification residuals. The highest percent solids achieved after evaporation was 56%. The difficulty in dewatering the effluent may be attributed to increased concentrations of suspended solids, when compared to the stand-alone S/S process. Another possible cause of the difficulty in dewatering is the "binding" of water in the biomass. Katsiris and Kouzeli-Katsiris (1985) concluded that "water in activated . . . sludge exists in two states, as 'free' or bulk water and as 'bound' [water] which is not free to exhibit the characteristic properties of free water." A decrease in the amount of "free" water may have resulted in increased viscosity of the waste.

Using the same technique for estimating product weight and volume as presented in Section 6.2.1, final waste form weight and volume estimates resulting from the implementation of the integrated process at RFETS were computed. These estimates are presented in Table 6.2.

Table 6.2: Bio-S/S Process Waste Loading with Estimated Product Weight and Volume

Sludge Total Solids	Absolute Waste Loading	Relative Waste Loading	Est. Product Weight (tons)	Est. Product Volume (yd^3)
39%	17%	11%	9900	5900
48%	23%	15%	7200	4300
56%	29%	19%	5700	3400

Comparison of the results presented in Tables 6.1 and 6.2 reveals that the highest relative waste loading achieved with the bio-S/S process is roughly the same as the baseline waste loading for the S/S process without biodenitrification pretreatment. Thus, biodenitrification had a significant detrimental effect on the waste weight and volume reduction achievable through evaporation.

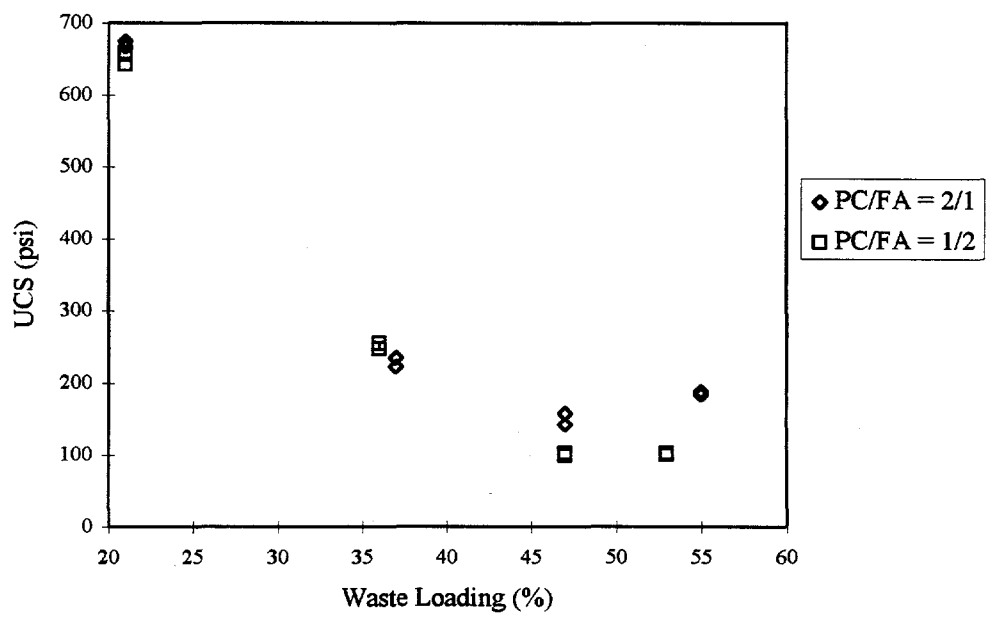
6.2 SOLIDIFICATION

EPA's definition of solidification, "the production of a monolithic block of treated waste with a high structural integrity (U.S. EPA, 1982)," and the guideline of a UCS of ≥50 psi were first presented in Chapter 2. Based on these criteria, satisfactory stabilization was achieved at every waste loading tested in Phases II and III of this study. The physical characteristics of the final waste forms are discussed below.

6.2.1. Product Strength: S/S Process: For the convenience of the reader, Figure 5.2, is presented again as Figure 6.2, below. The rapid decline in compressive strength as waste loading increased was expected. The ratio of the pozzolanic material, which provides

compressive strength, to overall product weight is roughly twice as high at the lower waste loadings than at the higher waste loadings presented in Figure 6.2. Increased interference due to higher salt concentrations was probably another significant cause of reduced product strength at higher waste loadings. The fact that strengths did not significantly decrease for samples containing contaminant spikes (when compared to unspiked samples) indicates that the contaminants are a relatively small source of interference in the cement matrix when compared to the other salts in the waste.

Figure 6.2:
UCS vs.Waste Loading
(S/S Process)



A noteworthy phenomenon is the lack of a significant decrease, or possibly even a slight rise, in UCS observed at the highest waste loadings. This effect was also observed during process development (See Table 5.1). In Chapter 3, it was noted that excess pore water is exponentially related to loss of strength. If one accepts that the waste solids and reagents in the mixture have a fixed water demand, it is conceivable that the increased strengths at higher waste loadings are attributable to a decrease in excess pore water. A reduction in excess water may be due to the increased relative water demand of the waste solids in the waste matrix at higher waste loadings, as illustrated in Figure 6.3 (following page), and explained below.

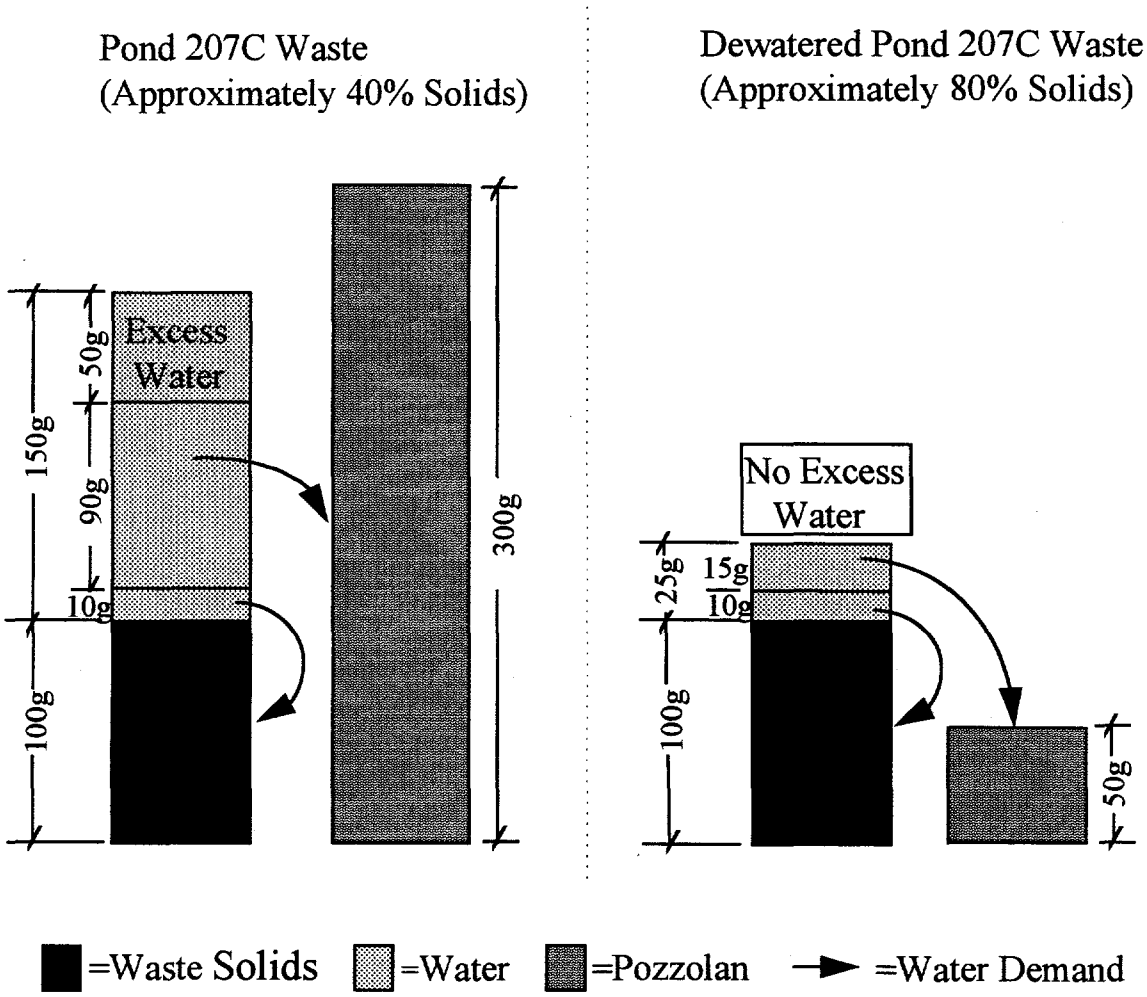
Figure 6.3 was constructed under the assumption that waste solids and pozzolans have constant water demands. For the purposes of this illustration, the water demand, by weight, was assumed to be 10% for waste solids, and 30% for pozzolans.

The left side of Figure 6.3 represents Pond 207C waste prior to dewatering, approximately 40% solids. This implies a 100 g mass of waste solids will be mixed with 150 g of water. The 0.5 water to pozzolan ratio used throughout this research requires addition of 300 g of pozzolan to the waste. With the assumed water demands, 100 g of water will be required for reaction with the waste solids and the pozzolan, and 50 g will be in chemical excess.

The right side of Figure 6.3 represents the same waste after dewatering to 80% solids. The same 100g mass of waste solids is now mixed with only 25 g of water. The

S/S formulation calls for addition of 50 g of pozzolan. The water demand of the waste solids remains unchanged, 10 g, but is now a much greater fraction of the total water content. The water demand of the pozzolan is equal to the remaining unreacted water content. Thus no excess water exists in the final waste form matrix.

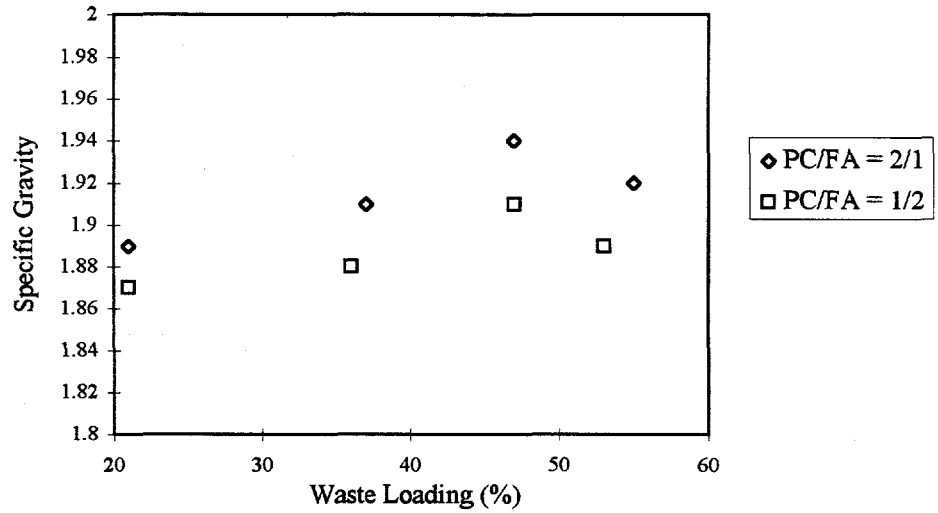
Figure 6.3:
Theoretical S/S System Water Budget



6.2.2. Product Strength: Bio-S/S Process: Direct comparison of product strengths between the S/S and the bio-S/S processes is not possible because the two processes had only one waste loading in common. At that waste loading, approximately 20%, the products of the two processes had similar strengths.

6.2.3. Product Specific Gravity: S/S Process: Waste product specific gravity varied over a range of 1.89 to 1.94 for the 2:1 cement to flyash mixture and 1.87 to 1.91 for the 1:2 mixture. The value reported by in a previous treatability study with actual Pond 207C residuals for the same water to pozzolan ratio of 0.5, with a feed solids content of approximately 40%, was 1.905 (the previous study only tested a 1:2 cement to flyash mixture) (Halliburton, 1992). The general trend was an increase in specific gravity as waste loading increased. This is consistent with expectations since the specific gravity of water is 1.0, and the specific gravities of waste solid particles and pozzolans are approximately 2.0 and 3.0, respectively (Halliburton, 1992) (i.e., a higher percentage of constituents with higher specific gravities produces a more dense product). The upward trend is very evident in Figure 6.4, Specific Gravity vs. Waste Loading (S/S Process) which was first presented as Figure 5.1 and is presented again here for the convenience of the reader.

Figure 6.4:
Specific Gravity vs. Waste Loading
(S/S Process)



The pozzolan formulation with the lower flyash content had consistently higher specific gravity. This result was expected because flyash is a "bulking agent" and yields greater weight and volume increase than Portland cement (Conner, 1990 and Inst for Mat'l and Env Research, 1980).

6.2.4. Product Specific Gravity: Bio-S/S Process: Measurements of specific gravity for the bio-S/S process were less accurate than for the S/S process because a drier mix made handling and transferring the waste between containers difficult. This resulted in losses of product volume during processing. The losses of volume may have resulted in artificially high specific gravity values. The bio-S/S process specific gravity data were presented in Table 5.7 and Figure 5.6. The data do not present a decided trend, but it is readily evident

through comparison to specific gravities for the S/S process that the bio-S/S process final products have lower specific gravities (the average specific gravity for all bio-S/S process formulations is about 1.8 while that of the S/S process is about 1.9).

6.3. STABILIZATION

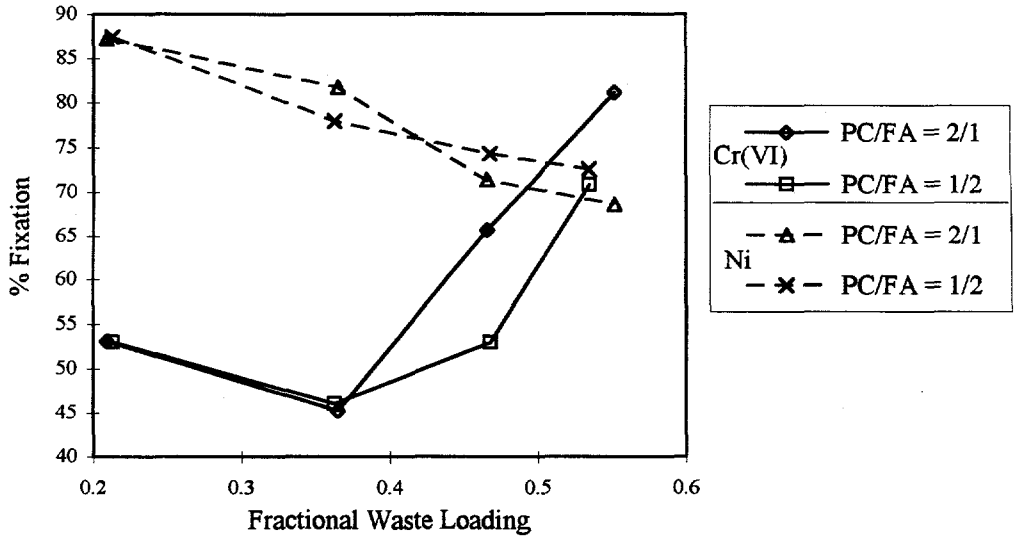
In the following section, contaminant constituent stabilization will be discussed in terms of contaminant fixation, as first presented in Section 5.4. The results of this study will also be compared to the results reported in a previous treatability study, which was conducted with actual Pond 207C waste. Comparison to previously reported results allows prediction for performance of the current process if implemented for treatment of Pond 207C waste.

6.3.1. Percent Fixation: S/S Process: Silver was fixed to levels below the detection limit of 0.05 mg/L at every waste loading tested with the exception of the anomalous 0.28 mg/L measurement at a waste loading of 37% and PC/FA ratio of 2/1. As stated in Chapter 2, fixation of silver is generally not problematic in cement-based S/S systems (Conner, 1990). Silver forms thermodynamically favorable insoluble complexes with at least two of the constituents of the surrogate waste. These complexes are AgCl (pK_{sp} = 9.75, ΔGf^{o} = -26.24), and Ag_2CO_3 (pK_{sp} = 11.09, ΔGf^{o} = -104.4) (properties from Dean, 1985).

Cocke and Mollah (1993) characterized the surface species in a cadmium doped Portland cement matrix by Fourier Transform Infrared Spectroscopy. They observed the presence of two primary cadmium species, $Cd(OH)_2$ precipitate, and $Cd(OH)_4^{2-}$. They believe that the latter species, which is formed at the high pHs (pH = 11 to 13) within the cement matrix is strongly sorbed to surface calcium. Regardless of which mechanism is at work, or if both are functioning in combination, cadmium fixation is at least 99.7% at every waste loading.

The results of leach testing for chromium and nickel vary significantly over the range of waste loadings. The percent fixation versus waste loading for these two constituents is presented graphically in Figure 6.5 (first presented as Figure 5.11).

Figure 6.5:
Percent Fixation of Cr(VI) and Ni
vs. Waste Loading
(S/S Process)



Inspection of Figure 6.5 reveals that nickel fixation declines with increased waste loading. The fixation of chromium, however, exhibits a substantial increase at higher waste loadings.

Roy and others (1993) studied S/S of a synthetic electroplating sludge containing Cr, Ni, Cd, and Hg and varying concentrations of NaOH. Based on the fact that "sludge and binders formed a mechanical mixture irrespective of the NaOH concentration," they suggested that "physical encapsulation was the primary mechanism of solidification/stabilization."

Other researchers have concluded that different mechanisms may be active in the fixation of chromium in cementitious matrices. Kindness, Macias, and Glasser (1994) offer two possible chemical fixation mechanisms for chromium. "One is the substitution of Cr in place of Al in the calcium aluminates present in hydrated cements. The other is the chemical reduction of Cr(VI) to Cr(III) . . . ."

The decreasing fixation of nickel with increased waste loading observed in the present study is consistent with expectations based on a physical encapsulation mechanism. As the amount of pozzolan in the waste matrix decreases relative to the amount of contaminant constituents, nickel fixation decreases. The behavior of chromium, however, is not explained by physical encapsulation.

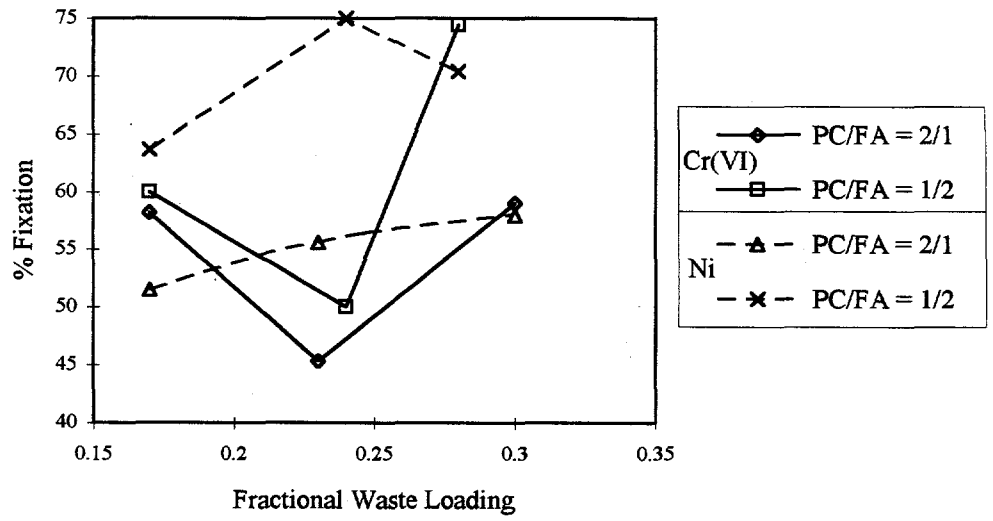
A possible explanation for the increased fixation of chromium, despite a decrease in the relative amount of reagents at higher waste loadings, is the optimization of the effective water to pozzolan ratio and corresponding reduction of excess pore water (the effects of waste loading on pore water were discussed in Section 6.2.1). As waste loading increases, the amount of pore water in the matrix most likely decreases. The decrease in pore water would result in a corresponding increase in the concentration of soluble reductant chemical complexes, such as NaOH and $Ca(OH)_2$. The pozzolan matrix may then become a more reducing environment. Cr(VI) would thus be more readily reduced to the less soluble Cr(III).

A greater increase in fixation of chromium was observed with the 2/1 PC/FA formulation when compared to the 1/2 PC/FA formulation. Flyash has a lower water demand than Portland cement (Inst for Mat'l and Env Research, 1992) and therefore more pore water probably exists in the matrix of the higher flyash formulation at equal waste loadings. Therefore, the greater increase in fixation observed for the 2/1 PC/FA formulation supports the explanation that reduction of excess pore water is the cause of improved chromium fixation.

6.3.2. Percent Fixation: Bio-S/S Process: Similar to the results for the S/S process without pretreatment, cadmium and silver fixation was virtually complete at all waste loadings investigated. Percent fixation of chromium differed by less than 10 percentage points between the two processes at waste loadings of 21% (S/S process) and 24% (bio-S/S process), for both pozzolan formulations. However, nickel fixation is much higher (e.g., 87.2% vs. 55.6% at similar waste loadings) with the S/S process. This may indicate that while the biomass present in the bio-S/S process does not interfere with chemical fixation mechanisms (postulated as active in the fixation of chromium) it has significant detrimental effects on physical encapsulation (the mechanism postulated as active in the fixation of nickel). A possible cause of the loss of physical encapsulation is the large increase in suspended solids with the bio-S/S process, which may increase the matrix porosity.

Percent fixation versus absolute waste loading for chromium and nickel is presented in Figure 6.6 (first presented as Figure 5.12).

Figure 6.6:
Percent Fixation of Cr(VI) and Ni
vs. Waste Loading
(Bio-S/S Process)



It should be noted that the percent fixation data presented in Figure 6.6 represent small changes in extract concentrations (especially for nickel). For example, the change in percent fixation of nickel observed with the 1/2, PC/FA ratio represents a change in extract concentrations from 0.3 to 0.4 mg/L.

A phenomenon similar to that observed with the S/S process, increased fixation of chromium at higher waste loadings, is evident with the bio-S/S process, as well. This may have the same causes in both processes despite the fact that the waste loadings are almost

twice as high when this effect was observed in the stand alone process. If the biomass incorporated into the waste matrix has a significant water content, and that water is unavailable for reaction (this was called "bound water" in Section 6.2.1), the amount of excess pore water will decrease at much lower waste loadings with the bio-S/S process when compared to the S/S process.

6.3.3. Predicted Process Performance with Pond 207C Waste: The present study was conducted with a surrogate waste, designed to be representative of Pond 207C residuals. A conservative approach was applied throughout this investigation. A prime example of the conservative approach is the use of soluble contaminant complexes at the highest concentrations reported in any available Pond 207C characterization data to spike the surrogate sludge. Results with actual Pond 207C residuals may therefore be better than those achieved with the Pond 207C surrogate waste used in this research.

In this section, the author will attempt to predict the performance of the processes investigated if the processes were applied to actual Pond 207C waste rather than the waste surrogate. Treatability data from the Halliburton study will serve as the reference for these predictions. The effects of increased waste loadings on S/S processing of Pond 207C residuals are estimated based on the relative performance of the baseline process, waste loading equal to approximately 20%, and Halliburton's reported results at similar waste loading.

Halliburton tested two process formulations similar to that used as the experimental control in this study. These are referred to as Batch 18 and 24 in the Halliburton Treatability Study Report (1992). Both batches were prepared with a water to pozzolan ratio of 0.5 and a Portland cement to fly ash ratio of 2/1. The results of TCLP extractions on these specimens are reported in Table 6.3.

Table 6.3:
Halliburton Batch 18 and 24 Results

	Batch 18	**Batch 24**
% Solids	44	49.1
Waste Loading	21%	24%
Cure Time (days)	7	7
CCWE (μg/L)		
Cadmium	<5	<5
Chromium	211	310
Nickel	<20	<20
Silver	<5	<5

(Source: Halliburton, 1992)
Note: Less than data ("<") represent method non-detects.

Predictions are presented in Table 6.4 (following page), in terms of TCLP CCWE for the target contaminants. Predictions were made with Equation 6.1, also presented on the following page.

$$\left(\frac{\textit{CCWE w / Pond 207C @ ~ 20\% Waste Loading}}{\textit{Present Study CCWE @ ~ 20\% Waste Loading}}\right)\left(\begin{array}{c}\textit{Present Study CCWE}\\ \textit{@ Higher Waste Loading}\end{array}\right)=\left(\begin{array}{c}\textit{Predicted CCWE w / Pond207C}\\ \textit{@ Higher Waste Loadings}\end{array}\right) \tag{6.1}$$

Table 6.4:
S/S Process Predicted Performance on Pond 207C Waste

PC/FA = 2/1									
% Solids		44		64		73		80	
Waste Loading (%)		21		37		47		57	
CCWE (μg/L)	**LDR**	**Act.**	*Pred.*	**Act.**	*Pred.*	**Act.**	*Pred.*	**Act.**	*Pred.*
Cadmium	66	30	*5*	30	*5*	40	*7*	40	*7*
Chromium	5000	4900	*310*	10,000	*633*	8000	*507*	5200	*329*
Nickel	320	200	*20*	500	*50*	1000	*100*	1300	*130*
PC/FA = 1/2									
% Solids		45		64		73		78	
Waste Loading (%)		21		37		47		57	
CCWE (μg/L)	**LDR**	**Act.**	*Pred.*	**Act.**	*Pred.*	**Act.**	*Pred.*	**Act.**	*Pred.*
Cadmium	66	20	*5*	30	*8*	40	*10*	30	*8*
Chromium	5000	5000	*310*	9800	*608*	11,000	*682*	7800	*484*
Nickel	320	200	*20*	600	*60*	900	*90*	1100	*110*

Act. = Actual results with surrogate sludge
Pred. = Predicted results with Pond 207C sludge

The contaminant silver was not included in Table 6.4 because silver was below detectable concentrations for all samples tested in this and the Halliburton Study (except for a single anomalous detection in this study). Comparative analysis with two non-detect values would not yield meaningful predictions. Based on the high levels of fixation of silver observed in both studies, it is reasonable to predict sufficient stabilization of silver to meet regulatory limits.

The predictions made in Table 6.6 are based on several unverifiable assumptions. The relationship between process performance on the actual and surrogate sludges may not be linear as assumed for construction of the table. Also, because Halliburton used only one Portland cement to fly ash ratio (1/2), the data generated with that formulation were used for prediction of the 2/1 cement to fly ash formulation's performance under the assumption that contaminant fixation would be similar with both process formulations. (Both formulations, however, did perform similarly at the baseline waste loading, ~20%.)

It is also important to note that all of Halliburton's CCWE values, except for chromium, are reported as less than values (method non-detects). Thus the CCWE Pond 207C @ ~20% Waste Loading values for cadmium and nickel used in Equation 6.1 to predict contaminant leachability at higher waste loadings are greater than actual results achieved through S/S processing. If true CCWE values were known, predictions for contaminant leachability could be much lower.

A comparison of predicted process performance to regulatory limits reveals a significant margin of safety for cadmium and chromium. Highest predicted leachate concentrations are close to an order of magnitude below LDRs. Predictions for nickel leachate concentrations are closer to regulatory limits. At the highest waste loadings, where process performance for the fixation of nickel is the poorest, a safety factor of slightly under 3 is observed with both pozzolan formulations.

The bio-S/S process formulation is substantially different from any system previously tested for S/S of Pond 207C sludge. Direct comparison with prior studies is not feasible.

However, with the same contaminant concentrations as used with the S/S process, most contaminants leached at levels below regulatory limits at every waste loading tested with the bio-S/S process. The exception was nickel which leached at concentrations near or above the LDR standard with all formulations tested. Given that the observed leachate concentrations for nickel were lower with the bio-S/S process when compared to S/S alone, and that predicted leachate concentrations for the S/S process are below LDRs, it is likely that the bio-S/S process would also meet LDR standards if implemented on Pond 207C residuals.

Chapter 7

CONCLUSIONS AND RECOMMENDATIONS

This study was undertaken to investigate the effects of increased waste loadings, achieved by waste dewatering, on S/S process performance. The target waste was Pond 207C residuals at RFETS. A representative surrogate waste was developed to facilitate conduct of this research. A process previously tested on Pond 207C residuals was used as the baseline process for this research.

Process performance was evaluated in terms of product volume reduction (or increased waste loading), the extent of contaminant stabilization as determined by TCLP extraction, the degree of solidification as measured by unconfined compressive strength testing, and the specific gravity of the final waste form. Process performance after simulated biodenitrification pretreatment was also investigated.

Conclusions based on the results of this study and recommendations for process implementation and future research are presented in this chapter.

7.1. CONCLUSIONS

The following conclusions are based on the results of this research:

- Significant volume reduction of S/S processing final products can be achieved by evaporating a portion of the waste water content and using a proportionately smaller amount of reagents.
- The volume reduction is possible without critical losses of contaminant stabilization or desirable physical characteristics. All process formulations tested yielded unconfined compressive strengths of at least 100 psi, well above the 50 psi standard adopted for this study. The general trend was decreasing UCS with increasing waste loading.
- Based on comparison of the results of the baseline process of the present study and a previous study conducted with Pond 207C residuals, Pond 207C waste would be sufficiently stabilized to meet LDR standards at every waste loading tested (21, 37, 47, and 53% with the S/S process).
- Final product volume reduction is not possible with the surrogate waste pretreated by biodenitrification because the bioreactor effluent could not be dewatered to the same extent as the un-biotreated surrogate waste.
- Bio-pretreatment resulted in reduction of the specific gravity of the final waste form.
- Benefits of reduced nitrate concentration, achieved by simulated biodenitrification, were not evident in this study, with the possible exception of slightly increased final product UCS.

The following conclusions are based on trends observed during the conduct of this research:

- A change in the trend of decreasing UCS as waste loading increased at the highest waste loading tested (approximately 53%) was possibly due to a reduction in the amount of excess pore water within the final waste form matrix.
- The improved chromium fixation observed at higher waste loadings was possibly due to a reduction in excess water in the final waste form matrix. A postulated decrease in the amount of pore water may have facilitated chemical reduction of Cr(VI) to less soluble Cr(III).
- The decrease in fixation of nickel observed as waste loading increased was possibly due to a reduction in physical encapsulation in the waste matrix at higher waste loadings. Other researchers have postulated that physical encapsulation is the primary fixation mechanism for nickel in S/S systems (Roy et al., 1991). The present results support those findings; as the ratio of contaminant constituents to encapsulating material (the pozzolans) increased, nickel leaching increased as well.
- A decrease in the fixation of nickel with the bio-S/S process was possibly due to an increase in final waste form porosity caused by increased suspended solids.
- The S/S process studied herein should be applicable to other waste streams. For S/S of non-radioactive wastes, which are less expensive to transport and dispose of, the costs of dewatering may not be offset by savings in transportation and disposal costs

realized due to reduced product volume. However, for wastes with a low water content, such as a contaminated soil, where water sufficient for S/S reagent hydration must be added, the high waste loadings applied in this study may yield sufficient stabilization to meet LDRs with considerably reduced final product volume without the need for dewatering.

7.2. RECOMMENDATIONS

Based on the results of this study, the author recommends the following:

- Conduct of a pilot-scale study with actual Pond 207C waste prior to full scale S/S process implementation.
- A detailed cost analysis, including the costs of dewatering Pond 207C residuals and transportation and disposal costs for the final waste form, should be conducted to determine the optimum waste loading from a cost/benefit perspective.
- Although the performance of the two pozzolan formulations (PC/FA = 2/1 and 1/2) was similar, the author recommends use of the high Portland cement formulation (PC/FA = 2/1) due to the higher specific gravity of the waste produced with that pozzolan.
- A target solids content of 75%, as opposed to the 78% used in this study, which will provide a greater operating range for dewatering of Pond 207C residuals without a substantial decrease in waste loading.

- Further research into the effects of optimizing the water to pozzolan ratio on fixation of heavy metals in cementitious matrices.
- Research into the crystallization of soluble constituents within a waste during dewatering and its effects on contaminant leachability.
- Investigation of the effects of water reducing concrete admixtures (also called superplasticizers) which have potential as a means to increase waste loading without significant losses in contaminant stabilization in S/S processes.

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40 CFR 268. 1994.

Appendix I

DEVELOPMENT OF THEORETICAL BIOREACTOR RESIDUALS

The following three reactions govern the behavior of the bioreactor:

$$\frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^- \rightarrow \frac{1}{10}N_2(g) + \frac{3}{5}H_20 \qquad (1)$$

$$\frac{5}{28}CO_2 + \frac{1}{28}NO_3^- + \frac{29}{28}H^+ + e^- \rightarrow \frac{1}{28}C_5H_7O_2N + \frac{11}{28}H_2O \qquad (2)$$

$$\frac{1}{8}NaCH_3COO + \frac{1}{4}H_2O \rightarrow \frac{1}{4}CO_2 + \frac{7}{8}H^+ + \frac{1}{8}Na^+ + e^- \qquad (3)$$

It is reasonable to assume 40% of the electrons produced by Reaction 3 are utilized in cell synthesis (Reaction 2) and 60% are utilized as energy (Reaction 1). Summing Reactions 1, 2, and 3 in that proportion and normalizing on NO_3^- results in Reaction 4:

$$NO_3^- + \frac{175}{188}NaCH_3COO + \frac{363}{188}H^+ \rightarrow$$
$$\frac{21}{47}N_2(g) + \frac{125}{94}CO_2 + \frac{175}{188}Na^+ + \frac{5}{47}C_5H_2O_2N + \frac{187}{94}H_2O \qquad (4)$$

Assuming all CO_2 is in the form of HCO_3^- (this assumption is based on an estimated output pH of 8.3) results in the final equation governing bioreactor behavior:

$$NO_3^- + \frac{175}{188} NaCH_3COO + \frac{113}{188} H^+ \rightarrow$$
$$\frac{21}{47} N_2(g) + \frac{125}{94} HCO_3^- + \frac{175}{188} Na^+ + \frac{5}{47} C_5H_2O_2N + \frac{31}{47} H_2O \qquad (5)$$

The influent (the Pond 207C surrogate--analysis presented in Section 5.1) contains 0.97 moles/L of KNO_3 as the sole source of nitrogen. Using this fact, the products of Equation 5 can be computed. Combining these products with the residual constituents not utilized in the reaction yields an estimate of the bioreactor residuals. The results of these calculations are presented in Table A1.1.

Table A1.1: Estimated Bioreactor Output

Constituent	Conc.[a] from Reaction 5	Residual Conc.[a] from Feed	Total Concentration[a]
$N_2(g)$	0.42		**0.43**
HCO_3^-	1.15	0.94	**2.17**
Na^+	0.88	5.30	**6.20**
$C_5H_7O_2N$	0.12		**0.10**
K^+		1.70	**1.70**
Cl^-		0.61	**0.61**
SO_4^-		0.16	**0.16**

[a]Concentrations in moles/L

Appendix II

SAMPLE CALCULATIONS: SAMPLE PREPARATION AND TESTING

Sludge Preparation and Lime Addition:

1000g Surrogate Brine (deionized water and soluble constituents)

30% Total Dissolved Solids (TDS)

$$(1000g)(0.30) = 300g\ TDS$$

$$(300g)(0.14) = 42g\ Silt$$

$$\Rightarrow 342g\ Total\ Solids\ (TS)$$

$$(300g)(0.05) = 15g\ Lime\ (reagent)$$

Sludge Dewatering:

810 g Total Weight After Dewatering

$$810g - 15g\ Lime = 795g\ Sludge$$

$$\frac{342g\ TS}{795g\ Sludge} = 0.43 \Rightarrow 43\%\ Solids$$

Reagent Addition:

$W/P = 0.5$

$PC/FA = 2/1$

$795g\ Sludge - 342g\ TS = 453g\ Water$

$$\frac{453g\ Water}{0.5} = 906g\ Pozzolan$$

$\Rightarrow Portland\ Cement = 604g$

$Flyash = 302g$

Specific Gravity Determination:

4 Full 210 ml Cylinders

1 Partially Full Cylinder (144g Water to Fill Void = 144ml)

$4(210ml) + (210ml - 144ml) = 903ml\ Total\ Product\ Volume$

810g Total Weight After Dewatering (Sludge + Lime)

906g Pozzolan

$810g + 906g = 1716g\ Product$

$$\frac{1716g}{903ml} = 1.9\frac{g}{ml} \Rightarrow Specific\ Gravity = 1.9$$

Contaminant Spike Addition (Chromium Spike):

Mole Fraction Cr in CrO_3 = 0.52

2 ml Spike Solution / 100g Surrogate Brine

1000g Brine ⇒ 20 ml Spike

TS = 342g

$$\left(32.9\frac{g\ CrO_3}{L}\right)(20ml) = 658mg\ CrO_3$$

$$(658mg\ CrO_3)(0.52) = 342mg\ Cr$$

$$\frac{342mg\ Cr}{342g\ TS} = 1000\frac{mg \cdot Cr}{kg \cdot Solids}$$

APPENDIX III

CALCULATION OF PERCENT FIXATION

Percent fixation, or the percent of a contaminant immobilized in a given waste form, is calculated with the following equation:

$$\%\ Fixation = \left[1 - \left(\frac{Contaminant Concentration\ Leached}{\begin{array}{c} Total\ Contaminant\ Concentration \\ in\ the\ Final\ Waste\ Form \end{array}} \right) \right] \times 100\% \qquad (1)$$

In this study, the leached concentration was measured by TCLP extraction, with the results expressed as contaminant concentration in the waste extract (CCWE). The CCWE represents the concentration of contaminant leached from 100 g of waste into 2000 g of extraction fluid. Therefore, to account for the 20:1 dilution, the CCWE concentration must be multiplied by a factor of 20. Thus,

$$Contaminant\ Concentration\ Leached = (CCWE)(20) \qquad (2)$$

The contaminant concentration in the waste prior to S/S reagent addition is known. However, the contaminant concentration in the final waste form is different from

the concentration in the waste because of the effective dilution caused by reagent addition. Recall that waste loading was defined as:

$$Waste\ Loading = \frac{Weight\ of\ Waste\ Solids}{Final\ Product\ Weight} \tag{3}$$

The contaminant concentration in the waste prior to S/S reagent addition is the weight of the contaminant constituent divided by the weight of the waste. Therefore, multiplying the contaminant concentration by waste loading yields the following result:

$$(Waste\ Loading)\begin{pmatrix} Contaminant\ Concentration \\ in\ the\ Waste \end{pmatrix} = \begin{pmatrix} Contaminant\ Concentration \\ in\ the\ Final\ Waste\ Form \end{pmatrix} \tag{4}$$

Substituting Equations 2 and 4 into Equation 1 yields the equation for percent fixation utilized in this study.

$$\%\ Fixation = \left[1 - \frac{(CCWE)(20)}{(Waste\ Loading)\begin{pmatrix} Contaminant\ Concentration \\ in\ the\ Waste \end{pmatrix}} \right] \times 100\% \tag{5}$$

A percent fixation of 0% implies that the entire concentration of a contaminant leaches out of the final waste form during TCLP extraction. Conversely, a percent fixation of 100% implies that none of a contaminant leaches; the entire concentration of the contaminant has been immobilized in the final waste form.

Appendix IV

SAMPLE CALCULATION: ESTIMATED PRODUCT VOLUME

Density of Water:

Density (ρ_W): 8.34 lbs/gal = 62.37 lbs/ft^3

Sludge Properties:

Volume: 487,200 gal

Specific Gravity (SG_S): 1.24

Percent Total Solids (%TS): 43%

⇒ Percent Water (%H_2O): 57%

Assumptions:

Product Specific Gravity (SG_{PROD}): 2.0

Water to Pozzolan (Reagent) Ratio (W/P):

W/P = 0.5 (this implies that reagent weight is twice water weight)

Sludge Weight:

$$V \times \rho_W \times SG_S$$

$$(487{,}200 gal)\left(8.34 \frac{lbs}{gal}\right)(1.244) = 5.05 \times 10^6 lbs$$

Solids Weight:

$$SludgeWeight \times \%TS$$
$$(5.05 \times 10^6 lbs)(0.43) = 2.17 \times 10^6 lbs$$

Water Weight:

$$SludgeWeight \times \%H_2O$$
$$(5.05 \times 10^6 lbs)(0.57) = 2.88 \times 10^6 lbs$$

Waste Loading (WL) :

$$\frac{SolidsWeight}{SolidsWeight + WaterWeight + ReagentWeight}$$

$$Where:\ ReagentWeight = 2 \times WaterWeight$$

$$\frac{2.17 \times 10^6\ lbs}{2.17 \times 10^6\ lbs + 3(2.88 \times 10^6)} = 0.20$$

Note: The weight of reagent lime (0.5 x Solids Weight) is ignored in this calculation. It's affects within the accuracy of this estimate are not significant.

Product Weight:

$$SolidsWeight \times \frac{1}{WL}$$
$$(2.17 \times 10^6 lbs)\left(\frac{1}{0.20}\right) = 10.85 \times 10^6 lbs = 5430 tons$$

$$ProductWeight \times \left(\frac{1}{SG_{PROD} \times \rho_W} \right)$$

<u>Waste</u> <u>Volume</u> :

$$(10.85 \times 10^6 lbs) \left(\frac{1}{(2)\left(62.37 \frac{lbs}{ft^3}\right)} \right) = 87{,}000 ft^3 = 3220 yd^3$$