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Task 1. Biodenitrification of low nitrate solar pond waters using sequencing batch reactors

Task 2. Solidification/stabilization of high strength and biodenitrified heavy metal sludges with a Portland cement/flyash system

Final Report

Biodenitrification of Low Nitrate Solar Pond Waters Using Sequencing Batch Reactors

Project No. 2555K0014-3Y, Task 1
Biodenitrification in Sequencing Batch Reactors

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EXECUTIVE SUMMARY

Due to the extensive use of nitric acid in the processing of actinide metals for nuclear fuel and weapons productions, waste streams generated by such operations often contain elevated nitrate concentrations. At the Department of Energy's Rocky Flats facility, nitrate containing process wastewaters were produced and accumulated on site in solar ponds. The pond waters and solids have since been transferred to storage tanks.

Biodenitrification has been identified as a viable process to remove nitrate from these chemically complex waters. Sequencing batch reactors have been shown to be capable of removing nitrate to the drinking water standard for other aqueous solutions containing high nitrate concentrations. Little information, however, is available for denitrification of industrial waters containing low concentrations (300-2100 mg/L nitrate) and the fate of Cr(VI) during denitrification. Objectives of this investigation were to optimize biodenitrification of low nitrate solar ponds waters using sequencing batch reactors and to evaluated the fate of Cr(VI) in the presence of denitrifying bacteria.

Two 34 L bench scale sequencing batch reactors (SBRs) were used to denitrify a surrogate pond water containing nitrate, calcium and magnesium carbonates above saturation, and significant concentrations of sodium, potassium, chloride, and sulfate. The rate of nitrate degradation and reactor stability were examined for an influent nitrate concentration of 250-2500 mg NO_3^-/L. The pH was controlled in two ranges, pH 7.4-8.4 and pH 8.4-9.4. Reduction of Cr(VI) was monitored in 500 mL respirometers inoculated with a denitrifying culture from an SBR.

At pH 7.4-8.4, denitrification was first order, with an average rate constant of 0.15/min. The rate of denitrification was not first order with respect to the concentration of total solids or organic solids. In this pH range, inorganic solids from the reactor feed were incorporated into activated sludge flocs and produced rapidly settling reactor solids with a sludge volume index of 70 mL/g.

At pH 8.4-9.4, the rate of denitrification changed from first order to zero order after the pH range was raised. The average zero order rate observed was 12 mg NO_3^-/L/min. The sludge also settled well at this pH range. Inorganic feed solids were not incorporated into the flocs and a steady decline in the organic fraction of total solids was observed. Because of their lower density, organic solids appeared to be preferentially washed out of the reactor over inorganic solids.

Cr(VI) was reduced from 100 mg/L to below 5 mg/L within 24 hours in the respirometer. The concurrent rate of denitrification was unaffected by the presence of Cr(VI) compared to SBR experiments without Cr(VI).

Denitrification in sequencing batch reactors was successfully accomplished for wastes with an influent nitrate concentration of 250-2500 mg/L in pH ranges of 7.4-8.4 and 8.4-9.4. The system was operationally robust, successfully denitrifying without pH control and without an additional carbon source for short periods. In the pH range 7.4-8.4, the rate of denitrification was first order with respect to nitrate concentration. In the pH range 8.4-9.4, the rate evolved to a zero order degradation. Inorganic solids in the feed were not well incorporated into the reactor solids at pH 8.4-9.4; long term operation at pH 8.4-9.4 is not recommended. Cr(VI) was completely reduced by the denitrifying culture but a longer reaction time was required than for denitrification alone.

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INTRODUCTION

Process wastewater and sludges were accumulated on site in solar evaporation ponds during operations at the Department of Energy's Rocky Flats Plant (DOE/RF). Because of the extensive use of nitric acid in the processing of actinide metals, the process wastewater has high concentrations of nitrate. Solar pond waters at DOE/RF contain 300-60,000 mg NO_3^-/L. Additionally, the pond waters contain varying concentrations of many other aqueous constituents, including heavy metals, alkali salts, carbonates, and low level radioactivity. Solids, both from chemical precipitation and soil material deposition, are also present.

Options for ultimate disposal of the pond waters are currently being evaluated and include stabilization and solidification (S/S) by cementation. Removal of nitrates can enhance a wastes' amenability to S/S, or can be a unit operation in another treatment scheme. Nitrate removal is also a concern for other sources of pollution at DOE/RF, including contaminated groundwater collected by interceptor trench systems. Finally, nitrate pollution is a problem at many other DOE facilities where actinide metals were processed.

The primary objective of this investigation was to optimize biological denitrification of solar pond waters with nitrate concentrations of 300-2100 mg NO_3^-/L to below the drinking water standard of 45 mg NO_3^-/L (10 mg N/L). The effect of pH upon process stability and denitrification rate was determined. In addition, the effect Cr(VI) on denitrification and fate of Cr(VI) in the presense of denitrifying bacteria was evaluated.

BACKGROUND

Waste Characteristics

This investigation focused on denitrification of solutions formerly contained in four solar evaporation ponds at DOE/RF (207 A, B North, B Center, and B South). Liquids and solids from these ponds were pumped into 10,000 gallon polyethylene containers to await development of an ultimate disposal plan. Nitrate concentrations in the A and B solar ponds ranged from 300-2100 mg NO_3^-/L. Other major constituents include calcium, magnesium, potassium, sodium, carbonate/bicarbonate, chloride, and sulfate. Solids from chemical precipitation and the deposition of soil material are present in the water.

Treatment Standard

The final disposition of this waste is still under consideration. A reasonable standard applied in many Resource Recovery and Conservation Act (RCRA) and Comprehensive Environmental Response Compensation Act (CERCLA) treatment schemes is the drinking water standard. For nitrate, this standard is 45 mg NO_3^-/L (10 mg N/L).

Biological Denitrification

The application of biodenitrification to industrial wastewaters is widely accepted (Dorr-Oliver, 1986). Biodenitrification has been accomplished in suspended culture, fluidized bed and fixed film reactors, using acetate, ethanol or methanol as carbon sources for a wide range of influent nitrate concentrations.

Industrial denitrification has been studied, and operating plants constructed, for a wide variety of wastes. In addition to the pond waters' saturation with calcium and magnesium carbonates, the pond water can be characterized as having low biological oxygen demand (BOD) and an absence of ammonia. Therefore, industrial systems that combine nitrification/denitrification, or BOD removal/denitrification are not directly applicable to the solar pond water. The most applicable are other studies focusing on waters produced in the processing of actinide metals. Also, wastewaters from conventional explosive manufacturing are similar except that they may contain higher concentration of ammonia (Bosman and Hendricks, 1980).

Extensive pilot scale work has been conducted at Oak Ridge National Laboratories (ORNL) for wastewaters from the DOE's Feed Materials Production Center (FMPC, Fernald, OH). A feed containing 7000-10000 mg NO_3^-/L was diluted to approximately 1000 mg NO_3^-/L prior to treatment in a fluidized bed reactor (FBR) (Walker et al., 1989). Chem-Nuclear Systems conducted a review of an operating fluidized bed reactor treatment system located at the DOE's Portsmouth, Ohio plant that was designed based on pilot plant data from ORNL. The FBRs were fed a solution containing approximately 400 mg/L nitrate after dilution of a waste containing 30,000-40,000 mg/L nitrate (Chem-Nuclear, 1988). Investigators have reported rates 10-15 time faster for fluidized bed reactors than for suspended growth systems (Eggers and Terlouw, 1979; Francis and Hancher, 1980). However, the operation of FBRs is subject to many problems. Walker et al. (1989) reported problems with bed fluidization, clogged lines, and failed denitrification related to high calcium carbonate concentration. Chem-Nuclear (1988) examined why the DOE Portsmouth, OH plant's denitrification system was operating at only 25% of design capacity. Problems noted included difficulties in fluidization, biomass clogging, and operational difficulties with providing media of the correct size and quantity (Chem-Nuclear, 1988).

Suspended growth systems for nitrate waste generated in the production of actinide metals also have been investigated. Early work on nitrate wastes at ORNL focused on Union Carbide Corporation's Y-12 Plant (Oak Ridge, TN), and used modified continuously stirred tank reactors (CSTRs) (Clark et al., 1975; Clark et al., 1977; Francis and Mankin, 1977). Lawson (1981) conducted developmental work for a proposed Union Carbide Plant with a CSTR. The surrogate waste used in this work contained influent nitrate of 4000-5000 mg NO_3^-/L and a significant BOD. Cook et al. (1993) and Veydovec (1994) studied SBRs for denitrification of a surrogate waste based on a DOE/RF waste stream. Influent nitrate concentrations invetigated were 6000 to 48000 mg/L. Although denitrification was effective the reactors were not always stable and in some cases the culture washed out (Cook et al., 1993; Hund, 1993; Veydovec, 1994). Clifford and Lui (1993) conducted SBR denitrification of spent ion exchange regenerate brine containing 3000-3700 mg NO_3^-/L. Although not an actinide processing waste, the waste contained significant concentrations of NaCl (.17-.5 N), sulfate and bicarbonate.

Operational considerations, both of the reactor itself and of the waste stream to be treated, are considerations in selecting reactor type. Clifford and Lui (1993) noted that SBRs are ideal for treatment systems where waste to be treated is produced in a batch process, that SBRs are very flexible operationally, and SBRs may require fewer unit operations and less equipment. The discretely containerized, varied composition, and finite volume of pond waters to be denitrified at DOE/RF lends itself to an operationally flexible batch type treatment system. Additionally, it is postulated that the operational complexity of fluidized bed reactors negate their advantage of faster kinetics of denitrification when time is not the paramount consideration. Therefore, SBRs were selected for this study. The use of an SBR for denitrification of a waste saturated with calcium and magnesium carbonates, and with an influent nitrate concentration of 1000 mg NO_3^-/L has not been documented. The primary difficulty in denitrifying relatively low levels of nitrate has been an inability to maintain a sufficient quantity of reactor solids to sustain the denitrification (Clark et al., 1975). Past investigations on SBR systems indicate that denitrification at levels of about 3000 mg/L is possible, but long term stability was problematic (Cook et al., 1993). Additionally, the effect of saturation of calcium and magnesium carbonates on flocculation and SBR stability has not been established.

Biodenitrification Theory

In biodenitrification, nitrate nitrogen is reduced to elemental nitrogen by serving as the terminal electron acceptor. The bacteria reducing nitrate are facultative (i.e., also able to use oxygen as the electron acceptor) and require an anoxic environment (absense of oxygen). The electron to be accepted is donated by a carbon source. Acetate is an inexpensive carbon source that has been used successfully in previous SBR studies (Cook, 1993), sodium acetate was selected as the carbon substrate for this investigation.

A pseudostoichiometry for denitrification with acetate was developed and is presented below. Equation 1 reflects an electron flow from the carbon source of 35% for cell synthesis, with the remaining portion used for energy production. Equation 1 is written for a pH of 8.3; at a higher or lower pH the major carbonate species would be carbonate or carbonic acid, respectively.

$$\begin{gathered} NO_3^- + .877CH_3COO^- \Leftrightarrow \\ 1.30HCO_3^- + .0877C_5H_7O_2N + .456N_2 + .0700H_2O + .578OH^- \end{gathered} \tag{1}$$

Effect of Influent Constituents on Biodenitrification

The pond waters' major constituents besides nitrate are calcium, magnesium, potassium, sodium, carbonate/bicarbonate, chloride, and sulfate. Additionally, trace levels of heavy metals (e.g., Cr(VI)) and low level radioactivity are present. Other investigators have determined that most of these factors have little impact on biodenitrification. Kristensen and Jepsen (1991) and Clifford and Lui (1993) examined the treatment of industrial wastewaters in SBRs and found no significant decline in the rate of denitrification with up to 0.5 N NaCl (15 g/L chloride and 11.5 g/L sodium) in solution. Kristensen and Jepsen (1991) also demonstrated that sulfate concentrations as high as 4000 mg SO_4^-/L had no effect on the rate of denitrification. Walker et al.(1989) observed that calcium concentrations of up to 150-200 mg/L did not affect the rate of denitrification, but caused operational difficulty because of precipitation. High carbonate concentrations do not inhibit denitrification but coupled with calcium and magnesium will for solids that may cause operational problems. Francis and Hancher (1980) investigated the effect of radiation on denitrification and found that dosages in excess of 10^5 rads were necessary to affect the rate of denitrification. They also examined the effect of heavy metals, particularly nickel on denitrification. Nickel initially did inhibit the rate of denitrification but microbial populations acclimated and later inhibition was no longer observed. The above review, led us to postulate that the composition of the pond water will not negatively impact denitrification.

METHODS AND MATERIALS

APPROACH

The goal of this investigation was to optimize biodenitrification of DOE/RF solar evaporation pond waters which contain nitrate ranging from 300-2100 mg NO_3^-/L, and significant concentrations of calcium, magnesium, potassium, sodium, chloride, and sulfate. Objectives included a determination of the long term stability and robustness of the system, as well as the ability to operate within different pH ranges, and at different nitrate concentrations. With accomplishment of these objectives in mind, the following approach was taken: preliminary studies, long term stability, effect of operation within a controlled pH, and determination of successful treatment at lower nitrate strengths. To facilitate this investigation, and represent the overall character of the pond waters, a non-hazardous surrogate pond water was developed for the experimentation.

MATERIALS

Surrogate Waste

Based on a technique of weighted averages Mosher (1995), a surrogate pond water was developed for the solar pond data (Siegrist, 1994). This solution contained 1000 mg/L nitrate, and was super-saturated with calcium and magnesium carbonates. The composition of the standard surrogate pond water is presented in Table 1.

Table 1: Standard Surrogate Pond Water

Calcium	mg/L	74
Magnesium	mg/L	143
Potassium	mg/L	476
Sodium	mg/L	94
Chloride	mg/L	305
Bicarbonate	mg HCO_3^-/L	225
Sulfate	mg SO_4^{--}/L	320
Nitrate	mg NO_3^-/L	1000

Unless otherwise noted, the standard surrogate waste recipe in Table 1 was used for all experiments. When nitrate concentrations other than 1000 mg/L were used, the basic recipe remained the same and only potassium and nitrate were varied.

Equation 1 shows that the C:N ratio for the feed is 100:67. Grady and Lim (1980) recommend that phosphorous be supplied at the rate of 1/5 of the nitrogen requirement, on a mass basis. Thus, a C:N:P ratio of 100:67:13 was the basis for reactor feed. Ten percent excess carbon was fed so that the rate limiting substrate would be nitrate.

Trace nutrients are also necessary for microbial growth. Such trace quantities are likely already present in the pond water. To ensure that such nutrients are included in the reactor feed, the recipe in Table 1 was prepared using tap water. To minimize microbial growth in the feed storage tank, the carbon substrate was fed from a separate feed tank, and was prepared with deionized water.

Feeds solutions were prepared from technical grade potassium nitrate, magnesium chloride, sodium acetate, and magnesium carbonate. Sodium chloride was of food grade, and magnesium sulfate, and calcium carbonate were industrial grade. Technical grade potassium phosphate monobasic provided the phosphorus source.

Experimental Apparatus

The preliminary and long term reactor stability study were conducted using a single 34 L acrylic SBR. All other nitrate experiments were conducted using two parallel 34 L acrylic SBRs. Each SBR was nominally airtight, a single half inch overflow line providing the only inflow and outflow of gas. Influent was provided and effluent decanted with Masterflex peristaltic pumps. Nitrate surrogate waste and sodium acetate feeds were contained in 100 gallon and 20L Nalgene tanks, respectively. pH was monitored using VWR pH probes connected to Cole Parmer pH controllers. The pH controllers were connected to Masterflex drives and pumps providing 1 N HCl and 1 N NaOH to maintain the pH between the specified set points. pH was recorded every five minutes by a Fluke Databucket™. Reactor mixing was provided by 1/30 horsepower variable speed motors operated at a speed of 60 rpm. Each mixer motor was coupled to a shaft with a 7 inch impeller, a 4.5 inch impeller, and a 4 inch impeller. Impellers were arranged with the largest impeller at the bottom of the reactor, and the smallest nearest to the top. Feed tank mixing was necessary due to the undissolved/precipitated solids in tank, and was provided by a fixed speed Lightin mixer.

The above equipment (with the exception of the Fluke Databucket) was controlled on four circuits by a Chron-Trol programmable controller. The controller initiated and terminated the fill, react, settle decant, and idle periods. The eight hour cycle consisted of: fill = 0.5 hr, react = 4 hr, settle = 2.5 hr, decant = 0.5 hr and idle = 0.5 hr. When other cycle lengths were used, only the duration of the react cycle was varied.

The pH controllers were only functional during the react period and the feed tank mixer only operated during the fill cycle. A schematic of a single reactor system is displayed in Figure 1.

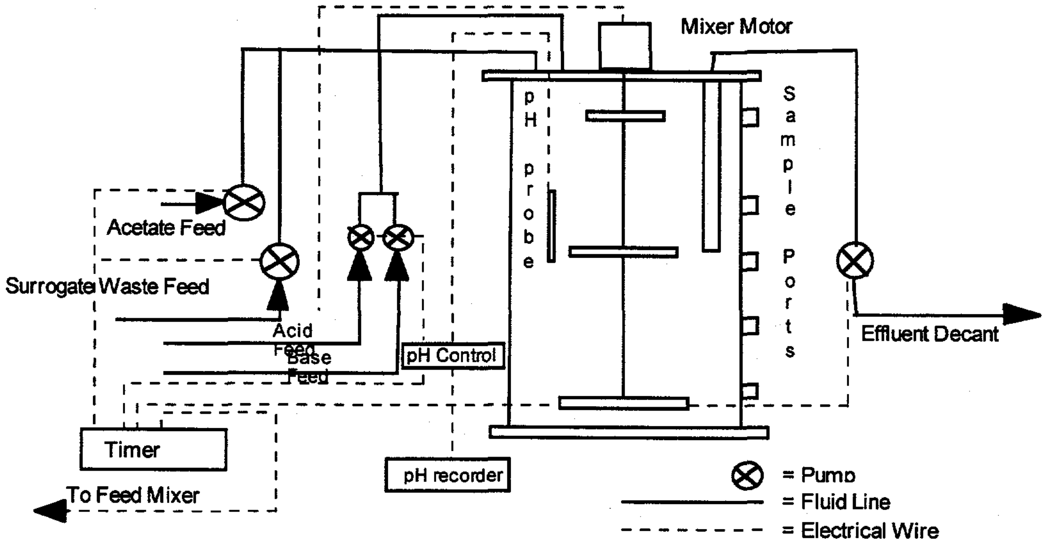

Figure 1: Schematic of a 34 L Sequencing Batch Reactor System

A Challenge Environmental Systems (Lafayette, AR) respirometer was used to evaluate concurrent nitrate and Cr(VI) reduction. The respirometer was interfaced to an IBM 286 SX computer that recorded the gas production data.

EXPERIMENTAL METHODS

Preliminary Studies

The goal of the preliminary studies was to develop operating characteristics for the SBR system receiving the surrogate solar pond water. Objectives included determination of a suitable mixing system, appropriate cycle lengths and decant ratios while meeting the drinking water standard (45 mg NO_3^-/L).

The SBR was inoculated with activated sludge obtained from the Broomfield, Colorado Waste Water Treatment Plant. The influent nitrate concentration started at 2500 mg/L, and was stepped down to 1000 mg/L in 500 mg/L increments. The recycle:decant ratio was set at a 1:1 ratio (Cutter, 1992; Hund ,1993). Cycle lengths (a complete series of fill, mix, settle, decant and idle periods) of eight and twelve hours were evaluated.

Long Term Reactor Stability Studies

The acclimated culture from the preliminary study was carried forward. The reactor was operated continuously for 71 days to evaluate long term trends in denitrification, solids production, solids accumulation, effluent quality, and general process robustness. Data was collected during two time periods of approximately 14 days each, separated by 46 days.

Effect of pH Studies

The purpose of this study was to evaluate system of operation in two pH ranges. Other investigators have noted that rates of denitrification are depressed below a pH of 6.0 and above 8.0. (U.S. EPA, 1993). Since the equilibrium pH of a denitrification system has been reported in the range of 9.0-9.6, pH control was necessary to keep the pH within the optimal range (Hund, 1993; Walker et al., 1989). However, Hund (1993), noted no difference in the rate of denitrification between reactors operating with and without pH control.

To evaluate the effect of pH two parallel reactors were operated: one reactor was controlled at pH 7.4 - 8.4, and the second between 8.4 - 9.4. The standard surrogate waste solution (Table

1) was used. The reactors were identical, fed from the same feed tanks, and operated under the same conditions.

The acclimated culture from the long term stability study was split equally between the two reactors. The reactors were allowed to acclimate to the new pH control ranges for three cycles before the first samples were taken. Samples were then taken daily for the next six days to evaluate solids·production, solids accumulation, effluent quality, and reagent consumption. At the end of this sample series, samples for denitrification kinetic evaluation were taken. No samples were taken for eight days, then another series of three daily samples were taken to evaluate possible changes in steady state conditions. Samples for kinetic evaluation were taken during this sample series as well. In total, the reactors were operated for 19 days to evaluate pH effects.

Stability at Lower Nitrate Concentrations Studies

The goal was to evaluate the reactor stability and performance at lower nitrate concentrations. The reactors were control at pH 7.4 - 8.4. The culture from the pH 7.4-8.4 reactor in the pH study was split between two reactors. Both reactors initially received an influent nitrate concentration of 500 mg NO_3^-/L. After three cycles, one reactor was changed to an influent of 250 mg NO_3^-/L. After three more cycles, sampling for treatment performance and solids production and accumulation was initiated.

The standard surrogate waste, presented in Table 1, was used. Carbon and phosphorous feeds were modified to maintain the 100:67:13 C:N:P ratio. After two days of acclimatization (six cycles), samples were taken over 14 days.

Cr(VI) Reduction

Cr(VI) reduction experiments used the standard surrogate pond water spiked to 100 mg/L Cr(VI). The respirometer was inoculated with solids from an SBR with pH 7.4-8.4 control. Biosorption of Cr(VI) to the reactor solids was evaluated in batch experiments where the carbon source and nutrients were omitted.

SAMPLING AND ANALYTICAL METHODS

While conducting experiments, grab samples of influent, effluent, and mixed liquor were taken daily. Generally 100 mL samples of effluent and influent and 10 mL samples of mixed liquor were taken. Duplicate samples of effluent and mixed liquor were taken. Effluent samples were captured from the discharge during the decant cycle, influent samples taken directly from the nitrate surrogate waste feed tank, and mixed liquor samples were taken during the mix cycle from the middle sample port on the reactor.

Periodically, mixed liquor samples were drawn vs. time over one react cycle to determine the kinetics of denitrification. Approximately 60 ml samples were drawn via the middle sample port on the reactor, and acidified with 1 ml of concentrated HCl. The sample was allowed the clarify, then decanted, filtered, and analyzed as described below.

All samples were filtered through Gelman A/E series glass fiber filters. Filtrants were dried and muffled according to <u>Standard Methods</u> (1992), Sections 2540D and E to determine total suspended solids (TSS) and fixed/volatile solids (FSS/VSS), respectively.

The influent, effluent, and mixed liquor filtrates were analyzed for nitrate using method set forth in Section 4500-NO_3^- Ultraviolet Spectophotometric Screening Method, <u>Standard Methods</u> (1992). Acidification with 1 N HCl, as recommended by <u>Standard Methods</u> (1992) to eliminate interference from hydroxide and carbonate concentrations, required a significant volume of acid. Therefore, one mL of concentrated HCl was used to acidify samples. The correction for organic interference was neglected because of the small effect the correction had on the nitrate data above 45 mg NO_3^- /L (drinking water standard). Nitrate analysis for the mass balance was done by an outside laboratory using Ion Chromatorgraphy.

Cr(VI) was anaylzed using the HACH (Loveland, CO) colorimetric method with a detection limit was 5 mg/L. The nitrate analysis for the Cr(VI) reduction experiment was done on a Dionex Ion Chromatograph (Standard Methods, 1992).

RESULTS

PRELIMINARY STUDIES

The goal of the preliminary studies was to establish the operating conditions for biological denitrification of the surrogate pond water in sequencing batch reactors. These parameters included: appropriate inoculum, cycle length, decant ratio, feed ratios, and mixing system.

Initial experiments showed that poor mixing was a prime cause of failure. Under mixing resulted in incomplete denitrification during the reaction cycle. When this occurred, the denitrification continued after the mixing stopped and nitrogen gas was trapped in the reactor solids. The result was a floating aggregated sludge blanket. Over mixing, on the other hand, sheared the flocculating culture so severely that it did not settle and the culture was washed out of the reactor with the effluent. The other potential problem with under mixing is mass transfer limited kinetics.

Low pH shocks below 5.5-6.0, resulting from acid over correction during pH adjustment, killed the denitrifying culture. The system showed greater tolerance to high pHs drifts. When acid was not fed, the system equilibrated at a pH of 9.5.

Unintentional pH swings were caused by using high strength acids and bases; by the time the pH probe reached equilibrium, too much reagent had been dispensed. The situation was averted by using lower strength acids and bases, and by operating the pH control system only during the react cycle.

Several different inoculums, cycle lengths, and mixing setups were investigated. Ultimately, an inoculum of return activated sludge from the Broomfield, Colorado Wastewater Treatment Plant, a cycle length of 8 hours, and a 60 rpm mixer with three propellers (described in the experimental apparatus section) were selected. At the completion of the preliminary studies, one half of the reactor was filled with reactor solids and reactor solids in excess of 17 L were wasted during the decant cycle.

LONG TERM REACTOR STABILITY

The long term stability of the system was evaluated by analyzing influent and effluent nitrate and solids concentrations, and solids accumulation.

Nitrate and Solids Data

Data sets were collected during two time periods (the first of 13 days, the second of 12 days), separated by 46 days. During the 46 days, periodic samples were taken to monitor reactor performance. Influent and effluent samples were analyzed for nitrate. Influent, effluent, and mixed liquor samples were analyzed for TSS, FSS, and VSS. The averages nitrate and solids from the twotime periods, along with 90% confidence intervals and statistical difference are present in Table 2.

Table 2: Average nitrate and solids concentration data over two time periods, influent nitrate 1000 mg/L, pH 7.4-8.4.

	Nitrate (as NO_3^-)			Influent			Effluent			Mixed Liquor		
	Influent	Effluent	η	TSS	FSS	VSS	TSS	FSS	VSS	TSS	FSS	VSS
Days 1-13	1000	7	99%	200	170	31	59	36	23	5700	1700	4100
+/-	40	1		10	10	3	5	4	3	260	90	190
Days 59-71	1100	9	99%	220	190	30	61	36	25	7000	1500	5400
+/-	30	1		30	30	3	3	3	2	400	70	300
Δ?	Yes	No	No	No	No	No	No	No	No	Yes	Yes	Yes

All quantities reported in mg/L, to two significant figures, +/- indicates a 90% confidence interval
η = Treatment efficiency, Δ? = statistical difference between data set means

As illustrated in Table 2, there was no statistical difference in any of the parameters except for influent nitrate concentration and mixed liquor solids. The influent nitrate concentration increased slightly and was related to mixing inaccuracies in the nominal 100 gallon containers. For the mixed liquor samples, the second time period showed an increase in total and volatile solids, and a slight decrease in fixed solids.

Kinetic Analysis

At the end of the second time period, two sets of data for kinetic analysis were taken. Samples of mixed liquor were drawn at specified time intervals and analyzed for nitrate to determine the rate of biodenitrification. The data sets were taken on the same day, one during the morning cycle and one during the afternoon cycle, and are shown in Figure 2. Observed data best fit a first order rate equation with nitrate concentration ($dN/dt = k_1N$ where N is nitrate concentration and t is time).

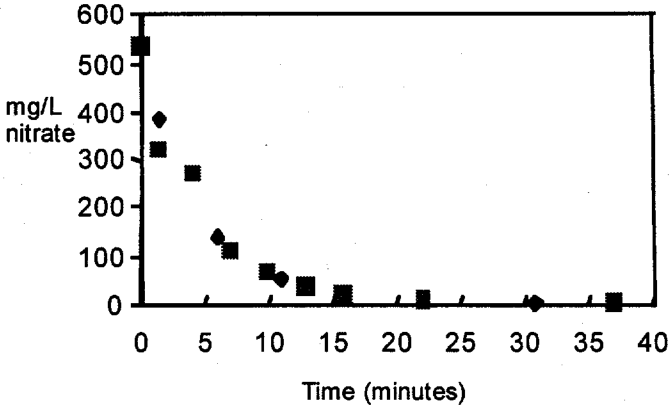

Figure 2: Typical nitrate concentration vs. time over 71 days, influent nitrate 1000 mg/L, pH 7.4-8.4.

The first order kinetic and correlation coefficients are presented in Table 3. MLVSS averaged 5400 mg/L during kinetic data collection.

Table 3: First order denitrification rate and correlation coefficients, influent nitrate 1000 mg/L, pH 7.4-8.4.

	k(1/min)	r^2
2/1/95, AM	.14	.99
2/1/95, PM	.20	.99
Average	.16	--

Denitrification was complete after 30 minutes and the drinking water standard (45 mg NO_3^- /L) was achieved in 20 minutes.

Other Observations

The reactor solids formed large flocs (estimated at 0.5-2 mm), and settled well. Visually, there was no accumulation of fixed solids within the reactor. At the beginning of the study, the sludge volume index was 100 mL/g. Seventy days later, the SVI had decreased to 70 mL/g. Throughout the study, 100 % of settling occurred during the first 30 minutes of the settling period. A slight odor of sulfate reduction was regularly noted. A bottom agar tube was inoculated from the reactor and incubated. The presence of sulfate reducers was confirmed in this test.

In order to quantify the significance of sulfate reduction, validate sample storage and preservation, and confirm an understanding of the system, an analysis for other chemical constituents in addition to nitrate was conducted by an outside laboratory. Table 4 tabulates the predicted and measured influent concentrations, the predicted change in the reactor, and the measured effluent concentrations. Predicted changes were based on the pseudostoichiometry previously developed (Equation 1), feed additions, and acid/base additions for pH control.

Table 4: Predicted and Actual Mass Balance of Selected Constituents, Influent nitrate of 1000 mg/L, pH 7.4-8.4.

	Influent		Change		Effluent		
	Predicted	Observed	Predicted	Observed	Predicted	Observed	Source of Change
Calcium (mg/L)	74	30	0	+16	30	45	
Magnesium (mg/L)	143	137	0	-3	137	134	
Potassium (mg/L)	532	670	0	-53	670	617	
Sodium (mg/L)	94	116	+340	+268	456	384	Sodium acetate feed
Chloride (mg/L)	305	228	+420	+346	648	574	HCl for pH adjustment
Nitrate (mg/L)	1000	1040	-1035	-1032	5	8	Denitrification
Sulfate (mg/L)	320	580	↓	170	<580	410	Sulfate reduction
HCO3- mg/L	218	240	+1340	+1270	1580	1510	Product of denitrification
Tot Alk (as CaCo3), mg/L	179	193	+1100	+1047	1293	1240	Function of bicarbonate

The predicted concentrations above do not account for any constituents contained in the Golden, Colorado tap water used for feed make up water. The use of Golden tap was did not significantly affect the results because alkalinity, total hardness and TDS in Golden tap water is low.

pH variation of during each cycle was constant throughout the study. The pH plot shown in Figure 3 shows the pH during the morning of February 1, 1995. Although there is no mixing during the fill period, denitrification still occurs to some extent, and pushes the pH up. Denitrification accelerates once mixing is initiated, and the pH climbs to the high set point of 8.4, when the pH control system begins dispensing acid. This pushes the pH down, and the acid feed stops. The pH climbs again, and is again controlled by acid feed. At this point, denitrification is essentially complete, and the pH begins a steady decline until the next fill period.

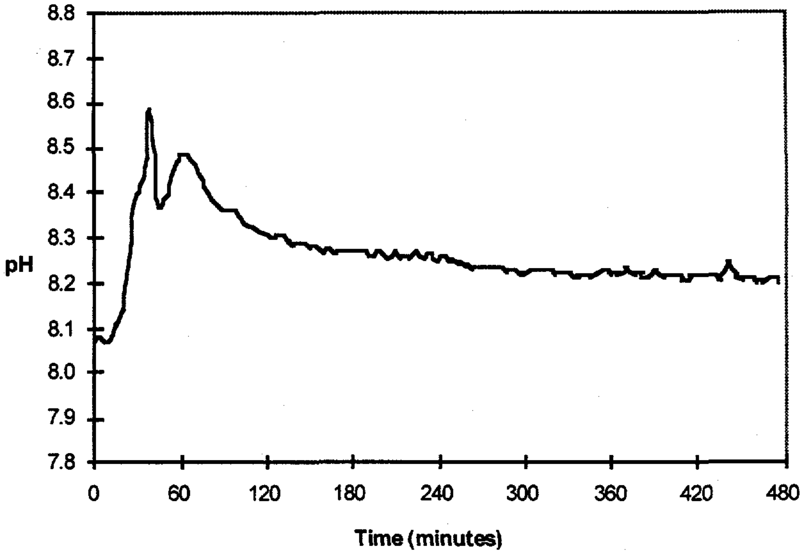

Figure 3: Typical pH profile for 71 days, pH 7.4-8.4, influent nitrate 1000 mg/L

EFFECT OF pH

The goal of the pH study was to determine the effect of operating the system at a higher pH which could minimize the cost of a pH adjustment system and improve performance.

Nitrate and Solids Data

Statistical analysis showed no difference between the first data set of six days and the second data set of three days; the data sets are consolidated in Tables 5 and 6. Both reactors used the same influent, the solids analysis for which is presented in Table 5. The effluent solids and nitrate data from the two reactors are presented in Table 6

Table 5: Average Influent Solids Concentrations for pH 7.4-8.4 and 8.4-9.4 Reactors.

	Influent		
	TSS	FSS	VSS
Average	200	160	37
+/-	8	8	3

All quantities reported in mg/L, to two significant figures, with +/- indicating a 90% confidence interval

Table 6: Average Nitrate and Effluent Solids Data for pH 7.4-8.4 and 8.4-9.4 Reactors

	Nitrate (as NO_3^-)			Effluent		
	Influent	Effluent	η	TSS	FSS	VSS
pH 7.4-8.4	1100	6	99%	55	35	20
+/-	130	1		3	2	1
pH 8.4-9.4	1100	6	99%	110	75	38
+/-	130	1		6	4	3
Δ?	n/a	No	No	Yes↑	Yes↑	Yes↑

All quantities reported in mg/L, to two significant figures, with +/- indicating a 90% confidence interval
η = Treatment efficiency, Δ? = statistical difference between data sets

Because the reactors did not operate at steady state with respect to solids, but rather were allowed to accumulate or lose solids, averages for mixed liquor solids do not reflect reactor stability. A better measure of reactor stability was the rate of change of solids concentrations. A positive rate of change (slope) indicates a reactor that was stable, while a negative slope represents a reactor that would be ultimately unstable. Additionally, the relative slope of TSS, FSS, VSS versus time is an indicator of how the composition of the solids are changing. Parallel plots of TSS, FSS, and VSS versus time indicate no change in solids composition. Mixed liquor solids data are presented in Figure 4 for the pH 7.4-8.4 reactor and Figure 5 for the pH 8.4-9.4 reactor. Trend lines depict best fit linear regressions.

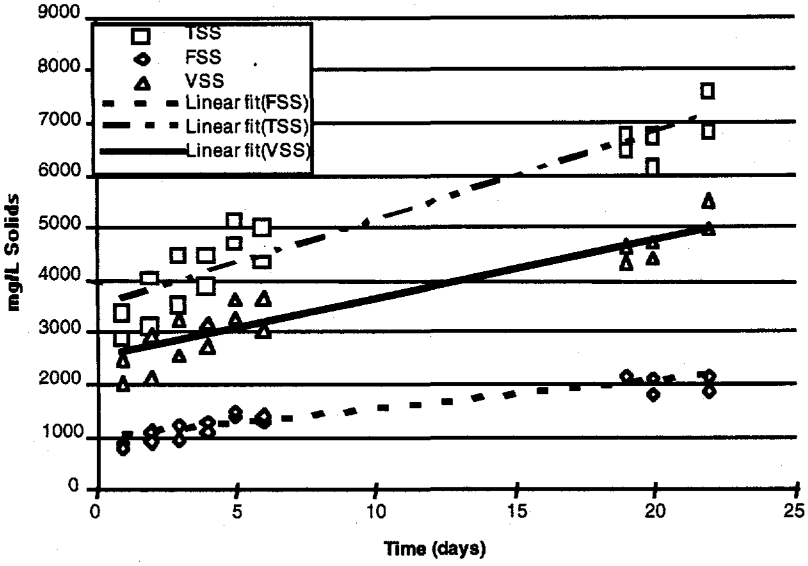

Figure 4: Suspended solids trends, pH 7.4-8.4, influent nitrate 1000 mg/L

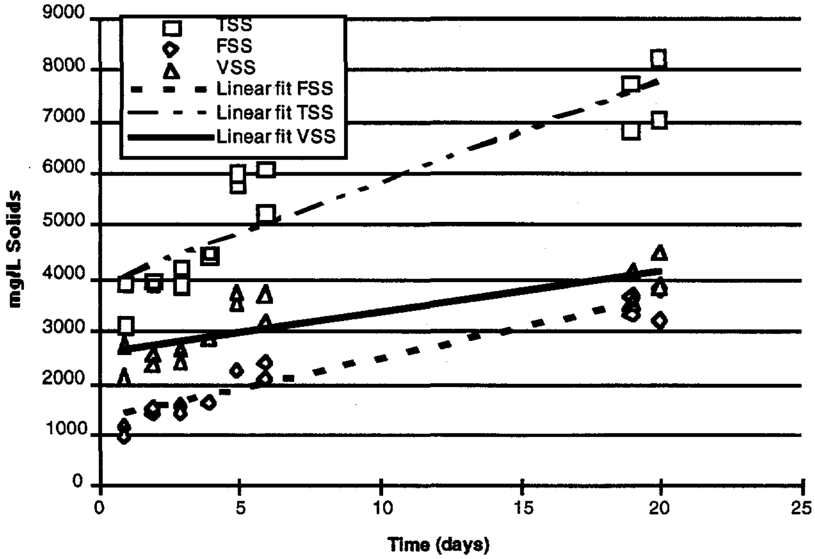

Figure 5: Suspended solids trends, pH 8.4-9.4, influent nitrate 1000 mg/L

In addition to overall growth of solids, it is of interest to note the composition of the solids. As indicated in Figure 6, the solids in at pH 7.4-8.4 were of relatively constant composition. At pH 8.4-9.4 the reactor shows a steady increase in the percentage of fixed suspended solids. Both reactors began with the same solids concentrations.

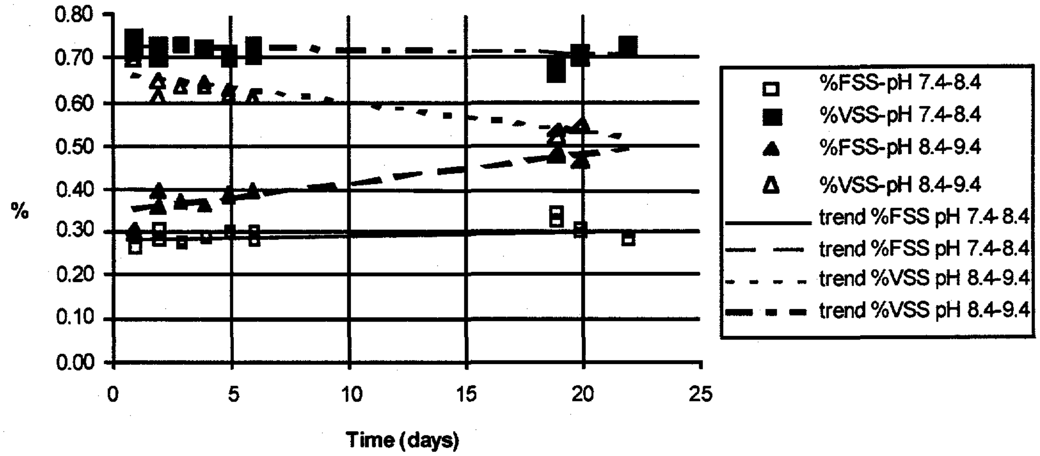

Figure 6: Distribution of solids vs. operation time at pH 7.4-8.4 and 8.4-9.4.

Kinetic Analysis

A total of four data sets were collected during the 19 days for kinetic analysis. Two sets of data were collected on the six and seventh days (February 18 and 19) of operation. For these data, the mean VSS concentration was 3400 mg/L for the pH 7.4-8.4 reactor, and 3500 mg/L for the pH 8.4-9.4 reactor. The nitrate removal over time is shown in Figure 7.

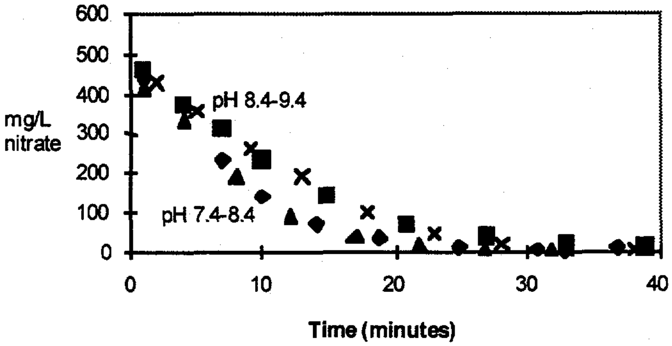

Figure 7: Nitrate concentration vs. time, pH 7.4-8.4 and 8.4-9.4, influent nitrate 1000 mg/L, 2/18/95 and 2/19/95.

First order nitrate rate and correlation coefficients are tabulated in Table 7.

Table 7: First Order Rate Constants and Regression Coefficients influent nitrate 1000 mg/L, reactor pH 7.4-8.4 and 8.4-9.4.

	pH = 7.4-8.4		pH = 8.4-9.4	
Date	k (1/min)	r^2	k(1/min)	r^2
2/18/95	.16	.99	.11	.99
2/19/95	.17	.99	.13	.99
Average	.17	--	.12	--

The second data set for kinetic analysis were collected on the sixteenth and seventeenth days (February 28 and March 1) of operation. Nitrate concentration versus time for these data are plotted in Figure 8; the mean VSS for the pH 7.4-8.4 reactor was 4500 mg/L and 4000 mg/L for the pH 8.4-9.4 reactor. The pH 8.4-9.4 reactor no longer exhibited first order kinetics, the data were best fit by a zero order nitrate kinetic model ($dN/dt = k_oN$). The pH 7.4-8.4 reactor remained first order.

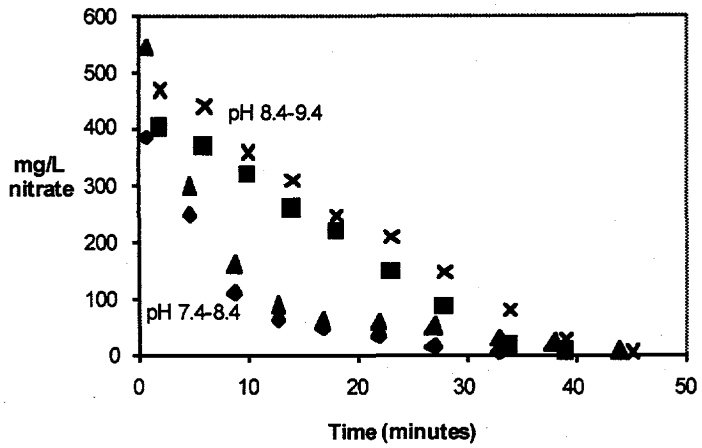

Figure 8: Nitrate concentration vs. time at pH 7.4-8.4 and 8.4-9.4, 2/28/95 and 3/1/95.

The above data have been fit to first and zero order kinetic models; the rate constants and correlation coefficients are tabulated in Table 8.

Table 8: Kinetic Rate Constants and Regression Coefficients, pH 7.4-8.4 and 8.4-9.4, influent nitrate 1000 mg/L, 2/28/95 & 3/1/95.

	pH = 7.4-8.4		pH = 8.4-9.4	
Date	k_1 (1/min)	r^2	k_0(mg/L/min)	r^2
2/28/95	.12	.97	12	.99
3/1/95	.08	.94	11	.98
Average	.10	--	12	--

Other Observations

The solids in both reactors displayed excellent settling characteristics. Settling was complete within 30 minutes, with the pH 8.4-9.4 reactor settling slightly faster. The SVI at pH 7.4-8.4 was 60 mL/g and 50 mL/g in the pH 8.4-9.4 reactor. Qualitatively the mean floc size in the pH 8.4-9.4 reactor evolved, over 19 days, to a smaller average size than in the pH 7.4-8.4 reactor, although both reactors had particles in the range 0.5-2 mm.

The pH profiles during the react cycle were constant. Typical plots of pH vs. time from 3/1/95 are shown in Figure 9. The pH initially climbs due to denitrification, and is adjusted downward after hitting the high pH set point. This cycle continues until denitrification is complete, and the pH then gradually declines until the start of the next cycle.

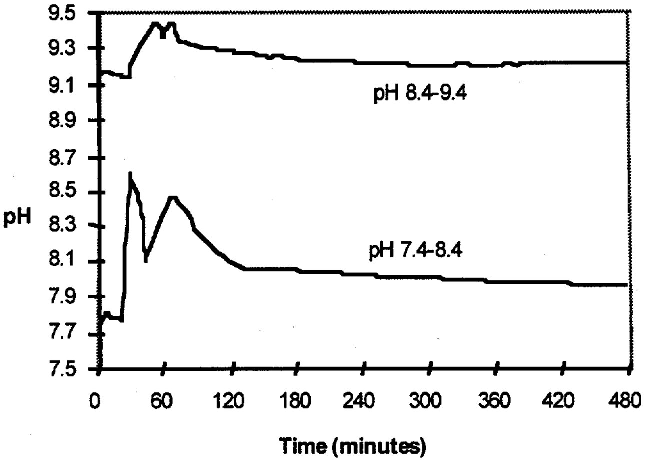

Figure 9: pH profile for one cycle, influent nitrate 1000 mg/L, pH 7.4-8.4 and 8.4-9.4

STABILITY AT LOWER CONCENTRATIONS

Operation at 500 mg/L Nitrate

Reactor performance was stable and the reactor solids increased slightly during operation. This is reflected in the solids data presented in Table 9 and Figure 10.

Table 9: Solids data vs. time, influent nitrate 500 mg/L and pH 7.4-8.4.

	Nitrate (as NO_3^-)			Influent			Effluent			Mixed Liquor		
	Influent	Effluent	η	TSS	FSS	VSS	TSS	FSS	VSS	TSS	FSS	VSS
Ave	515	5	99%	200	150	49	38	22	16	4600	1800	2800
+/-	10	1		30	20	10	3	3	2	180	90	130

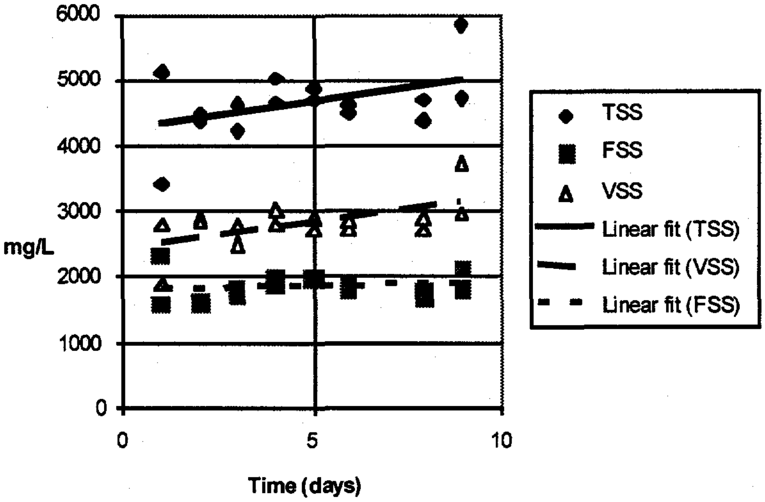

Figure 10: Solids production vs. time, influent nitrate 500 mg/L and pH 7.4-8.4

Nitrate removal over time best fit a first order model. Nitrate concentration vs. time is plotted in Figure 11, and model coefficients are tabulated in Table 10. Average MLVSS for these data was 2800 mg/L.

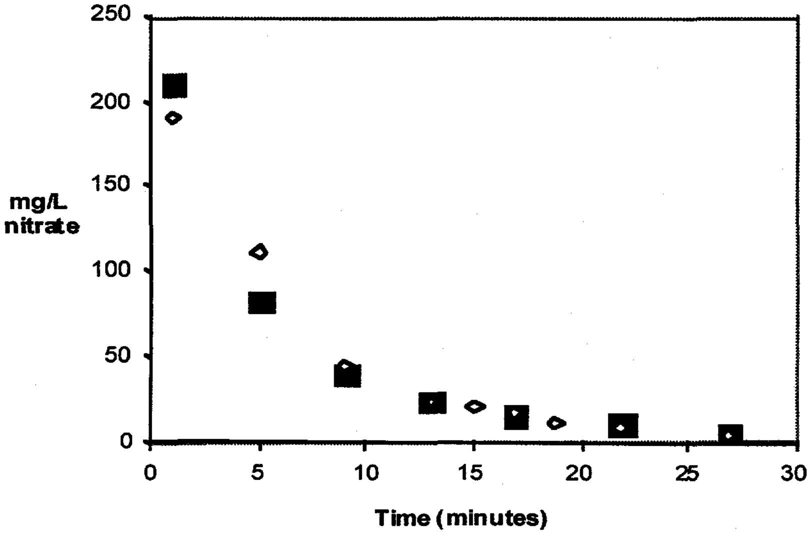

Figure 11: Nitrate concentration vs. time, influent nitrate 500 mg/L and pH 7.4-8.4.

Table 10: First Order Rate Constants and Regression Coefficients, 500 mg/L influent nitrate concentration, pH 7.4-8.4.

	500 mg/L influent nitrate	
	k (1/min)	r^2
3/14/95, AM	.13	.97
3/14/95, PM	.16	.99
Average	.14	--

The qualitative characteristic of the floc were unchanged from the low pH range (7.4-8.4) experiment in the previous study. The reactor solids continued to settle completely in less than 30 minutes, with an SVI of 70 mL/g. Again, pH behavior during the cycle was very constant. A typical plot, morning of March 14, is depicted in Figure 12. After the pH decline at the cessation of denitrification, a gradual rise in pH was typical of this set of operating conditions.

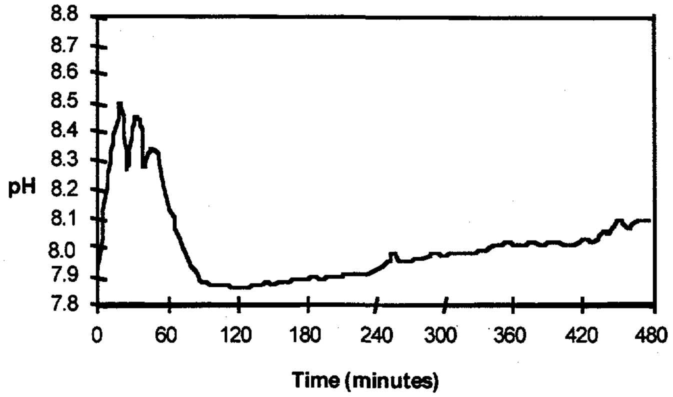

Figure 12: pH Profile vs. time, 500 mg/L influent nitrate concentration and pH 7.4-8.4.

Operation at 250 mg/L Nitrate

The reactor did not receive carbon during the third through ninth days of the experiment. In spite of this, nitrate removal and solids were stable. Additionally, the feed was inadvertently switched to 450 mg NO_3^-/L on day four for three days. On the fourth day with no carbon, and the first day after increasing the nitrate influent, the reactor solids began to show signs of instability. On the sixth day of the experiment, the influent nitrate was lowered to 290 mg NO_3^-/L. Up to this point, the reactor was still denitrifying down to 10 mg NO_3^-/L. After the sixth day, denitrification declined dramatically, although it did not completely cease for another three days (Day 9). After nine days of operation, carbon was finally restored. Denitrification resumed immediately and denitrification to less than 10 mg/L nitrate was observed within one day. During this period of operational dysfunction, the reactor solids did not wash out. The total solids were relatively constant, although the FSS increased in relation to VSS.

After normal operating conditions were resumed on the ninth day of operation, denitrification performance was monitored for four days (Days 10-13), and data for kinetic analysis were taken on the 14 and 15 day of operations. The denitrification best fit a first order model with nitrate concentration, the data are shown in Figure 13. First order rate constants and correlation coefficients are presented in Table 11. The rate constants and correlation for all the nitrate data and the nitrate data above 24 mg nitrate/L also were calculated, because the organic interference was high for low nitrate concentrations.

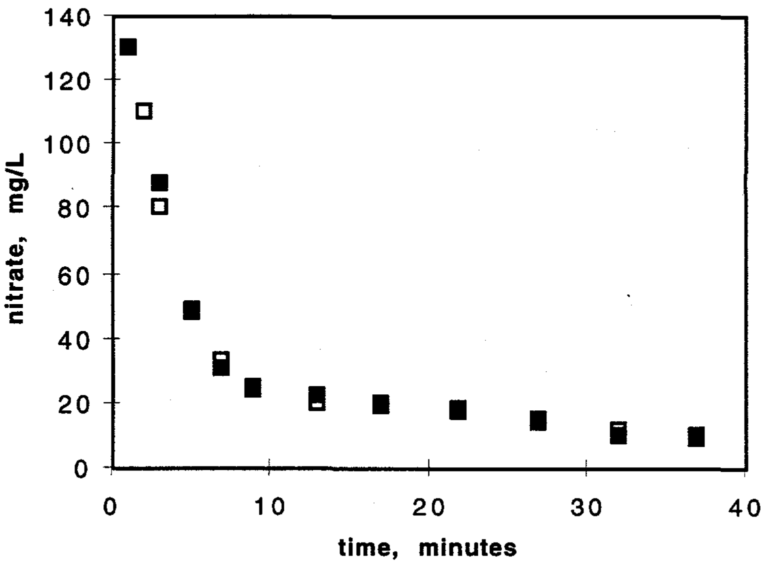

Figure 13: Nitrate concentration vs. time, influent nitrate 250 mg/L and pH 7.4-8.4.

Table 11: First Order Rate Constants and Regression Coefficients, influent nitrate 250 mg/L and pH 7.4-8.4.

	250 mg NO_3^-/L Feed ($N \geq 24$ mg/L)		250 mg/L Feed NO_3^- (total)	
	k (1/min)	r^2	k (1/min)	r^2
3/18/95	.26	.95	.07	.77
3/19/95	.25	.96	.07	.76
Average	.26	--	.07	--

The qualitative characteristic of the flocs were unchanged from the low pH range (7.4-8.4) experiment in the previous study. The reactor solids continued to settle completely in less than 30 minutes, with an SVI of 70 mL/g. Again, pH behavior during the cycle was constant. A typical pH plot, taken when the kinetic data was collected, is shown in Figure 14. A smaller acid feed pump was used in this study to avoid overshooting (to compensation for lower bicarbonate production) when adjusting the pH downward; selection of this pump was not optimized, and as a result, the pH climbed above the high set point until the feed pump could deliver enough acid to lower the pH.

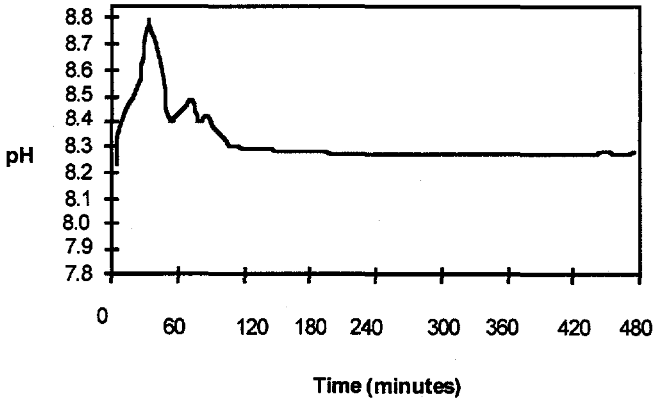

Figure 14: pH profile for one cycle, influent nitrate 250 mg/L and pH 7.4-8.4

CR(VI) REDUCTION

Cr(VI) was reduced from 100 mg/L to below 5 mg/L in the respirometer with concurrent nitrate reduction; the data is presented in Figure 15. Cr(VI) did not sorb to the reactor solids when incubated with the surrogate pond water.

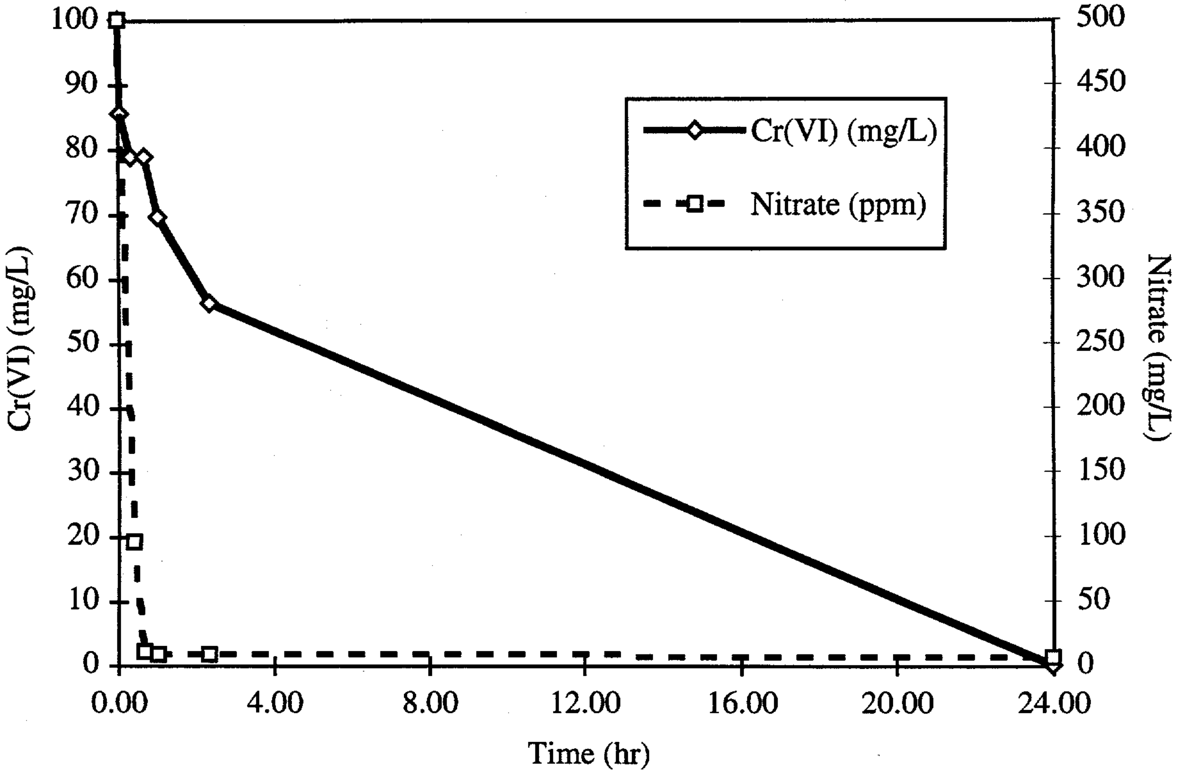

Figure 15: Concurrent Cr(VI) and nitrate reduction, influent nitrate 1000 mg/L, no pH control

DISCUSSION

EFFECT OF INFLUENT SOLIDS:

It was anticipated that inorganic solids (magnesium and calcium carbonates) in the feed would act as flocculation nuclei and increase the floc density so that a more efficient solids:liquid separation could be effected when mixing ceased. If incorporation did not occur, wash out of organic solids was expected; because inorganic solids have a higher density than organic solids and the less dense organic fraction were expected to settle on top of the inorganic fraction

Inorganic feed solids were incorporated into flocs very well, in reactors operating at pH 7.4-8.4, with a resulting floc size of 0.5-2 mm. However, flocs in the pH 8.4-9.4 reactor did not incorporate inorganic feed solids as well. This was noted visually by smaller average floc particles and by an accumulation inorganic solids in the reactor. Walker et al. (1989) reported problems with bed fluidization, clogged lines, and failed denitrification related to high calcium carbonate concentration. The effect of influent carbonate precipitates varied in this investigation from positive for SBRs operated at pH 7.4-8.4 to negative for SBRs operated at pH 8.4-9.4.

KINETICS

Denitrification in SBR systems with excess carbon supplied typically has been modeled by zero order kinetics with nitrate and first order with MLVSS, unless substrate inhibited at high nitrate concentrations or substrate limited at very low concentrations (Cook et al., 1993; Clifford and Lui, 1993). Kinetics of biofilm systems, however, can be limited by diffusional transfer through the biofilm (Grady and Lim, 1980) and thus, half-order reactions are often observed (Chem-Nuclear, 1988; Dorr-Oliver, 1986). Alternately, Francis (1975) observed that denitrification could often be modeled by first order nitrate removal for both suspended and attached growth systems.

The incorporation of inorganic solids into the reactor floc and particle size appeared to affect the observed nitrate removal rate. When the organic fraction of the flocs was 70% with an larger average particle size, first order nitrate kinetics were observed and for an organic fraction of 50% with smaller average particle, zero order kinetics were observed. When all the data for reactors operated at pH 7.4-8.4 were evaluated there was no correlation between MLVSS concentration and rate of denitrification. A linear regression of the MLVSS and k_1 values yielded an $r^2 \leq 0.01$, Table 12. Lawson (1981) also found that denitrification was not first order with respect to MLVSS in a CSTR. Conversely, Cook (1993) found that denitrification was zero-order with nitrate and first order MLVSS in an SBR. The major difference between the surrogate solar pond water used in this investigation and the nitrate waste used by Cook (1993) was the presence of carbonate precipitates.

Table 12: Summary of all first order denitrification kinetic coefficients

Test Date	Conditions influent nitrate,pH range (mg NO_3^-/L, pH units)	k_1 (1/min)	r^2	MLVSS (mg/L)
2/1/95, AM	1000, 7.4-8.4	.14	.99	5400
2/1/95, PM	1000, 7.4-8.4	.20	.99	5400
2/18/95	1000, 7.4-8.4	.16	.99	3400
2/19/95	1000, 7.4-8.4	.17	.99	3400
2/18/95	1000, 8.4-9.4	.11	.99	3500
2/19/95	1000, 8.4-9.4	.13	.99	3500
2/28/95	1000, 7.4-8.4	.12	.97	4500
3/1/95	1000, 7.4-8.4	.08	.94	4500
3/14/95, AM	500, 7.4-8.4	.13	.97	2800
3/1/95, PM	500, 7.4-8.4	.16	.99	2800
3/18/95[1]	250, 7.4-8.4	.26	.95	2100
3/19/95[1]	250, 7.4-8.4	.25	.96	2100
Average	--	.15	--	--

[1] rate constant when N ≥ 24 mg nitrate/L

Cook et al.(1993) observed a zero order denitrification of 14-18 mg NO_3^-/L/min in a SBR system with an initial concentration of 3000 mg NO_3^-/L . A denitrification rate of approximately

4.5 mg NO_3^-/L/min was observed by Clifford and Lui (1993) in a SBR with an initial nitrate of 2200 mg NO_3^- /L. The zero order rate observed in this study at pH 8.4-9.4 was 12 mg NO_3^-/L/min. The average first order rate constant over all nitrate concentrations was $k_1 = 0.15$ 1/min in this study. This rate and the rate observed by Cook et al.(1993) both predict 30 minutes to reduce an initial nitrate concentration of 500 mg NO_3^- /L to 10 mg NO_3^-/L. The zero order rate observed in this study predicts 45 minutes for the same nitrate removal.

The method routinely used for nitrate analysis was less accurate when nitrate concentration were less than 25 mg NO_3^-/L due to higher organic interference. The kinetic analysis at 250 mg/L nitrate reflected this with a lower correlation coefficient for the first order model fit when half of the data were below 25 mg NO_3^-/L.

PROCESS STABILITY

In 160 reactor days of operation (not counting operation during preliminary studies), nitrate levels exceeding 15 mg/L nitrate were recorded on only five days; every high reading was directly attributable to a failure to provide a carbon source. Floating reactor solids were noted on only one occasion, an incident where no carbon was fed. On several occasions, the pH was not controlled due to a failure to replenish acid feed stock. The pH in the affected reactor equilibrated at about 9.5, and no adverse effect to denitrification or solids stability was observed.

CONCLUSIONS

Denitrification of the surrogate waste was successful at all influent nitrate concentrations examined, 250 to 2500 mg NO_3^-/L. Denitrification with pH control of 8.4-9.4 was slightly slower than at 7.4-8.4. However, it is anticipated that long term operation at pH 8.4-9.4 will not be successful because of the decrease in organic solids in the reactor with time

Inorganic solids in the feed were probably responsible for the extremely good solids:liquid separation observed in this study. Flocs formed in the pH range of 7.4-8.4 were larger and showed a better qualitative incorporation of influent feed solids than those formed in the pH range 8.4-9.4.

Denitrification rates were observed to be first order at pH 7-4-8.4 and zero-order at pH 8.4 -9.4. Rates were not proportional to concentration of reactor solids. The observed average rate of 340 g NO_3^- N/day/m^3 is comparable to the low range of rates reported for fluidized bed reactors. Improved daily rate per unit volume can be achieved by increasing number of feed cycles per day.

Cr(VI) (100 mg/L) was completely reduced by the denitrifying culture but a longer reaction time was required than for denitrification alone.

Biodenitrification in sequencing batch reactors is a feasible process to denitrify solar pond waters at DOE/RF. Because a surrogate waste was used in this study, it is recommended that a pilot scale study with the actual waste be conducted prior to constructing a full scale plant.

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Final Report

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

Project No. 2555K0014-3Y, Task 2
Biodenitrification in Sequencing Batch Reactors

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September 22, 1995

EXECUTIVE SUMMARY

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 investigation 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 investigation. 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 investigation. 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 investigation

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INTRODUCTION

This investigation 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 investigation 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.

A surrogate waste of known composition was developed and used throughout this investigation. 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. Surrogate biodenitrification residuals were used.

The study 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 the investigation, 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.

Halliburton's (1992) process formulation and results, for Pond 207C waste, were used as the baseline S/S treatment process in this investigation. A summary of Halliburton's (1992) recommended operating range for S/S of the Pond 207C waste is presented in Table 1:

Table 1: Pond 207C S/S Process
Recommended Operating Range (Halliburton, 1992)

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

PROJECT OBJECTIVES

Project objectives were formulated based on Pond 207C waste characteristics and the results reported in the previous studies.

Final Product Volume Reduction

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

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; Jones and Sams, 1994; 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. 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:

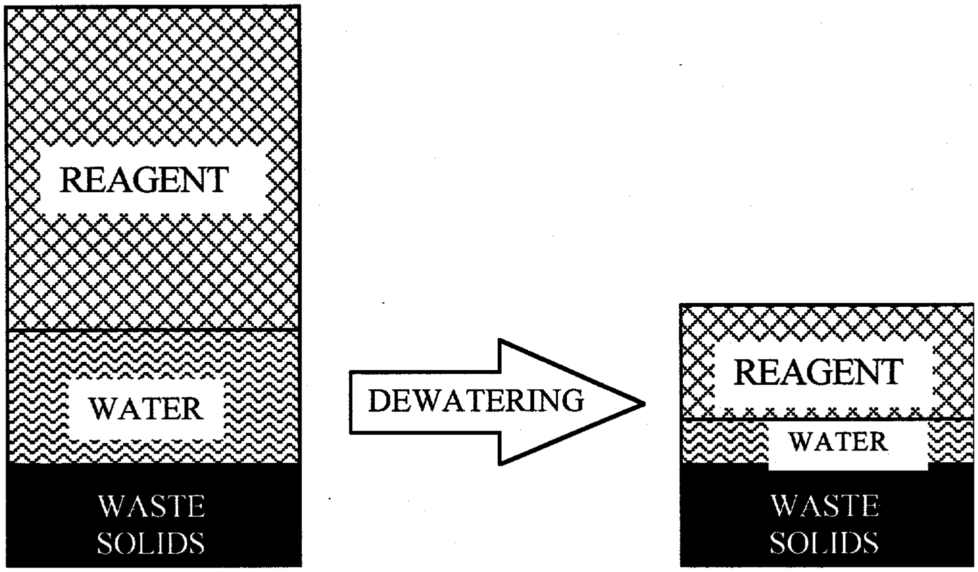
$$Waste\ Loading = \frac{Weight\ of\ Waste\ Solids}{Final\ Product\ Weight} \tag{1}$$

where: *Final Product Weight = Weight of Waste Solids +*
Weight of Water + Weight of Reagents (2)

Waste solids refers to the dry weight of all dissolved and suspended solids in a given waste.

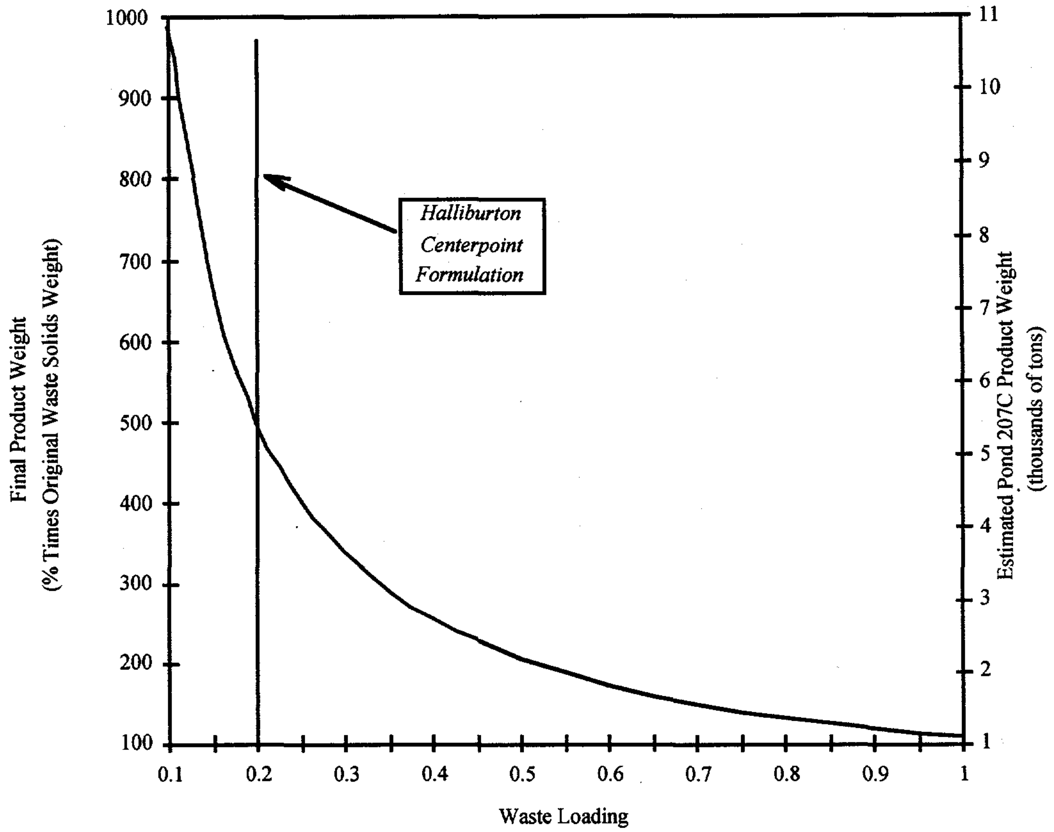
Dried Pond 207C solids would probably not meet land disposal restrictions (Halliburton, 1992). Therefore, S/S reagents must be added. Sufficient water must be present to hydrate the pozzolans for them to be effective. The final waste form will therefore consist of waste solids, water, and pozzolanic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

Figure 1: Effects of Dewatering on Final Product Volume



The relationship between waste loading, and the product weight is illustrated in Figure 1. The figure was constructed using Equation 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: 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. Relatively small increases in waste loading can result in significant S/S product weight reductions, Figure 2.

Given the demonstrated importance of waste loading in terms of final wasteform and volume reduction, the primary goal of this objective 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.

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 limit the solubility or detoxify waste contaminants even though the physical characteristics of the waste may not be changed (U.S. EPA, 1982). TCLP is the laboratory method recommended by the EPA to determine the mobility of organic and inorganic analytes present in wastes (40 CFR 261, 1994). The land disposal restrictions (LDRs) for contaminant concentrations in TCLP waste extracts were promulgated by the EPA in 40 CFR 268 (1994).

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 for inorganics and volatile organics.

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 Canonico (1995). LDRs are taken from 40 CFR 268.41 (1994), Table CCWE (Constituent Concentrations in Waste Extract).

Table 2: 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 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) 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.

No metals of regulatory concern showed potential for leaching above the LDR standards after S/S processing with the possible exception of cadmium. The data suggest that if the TCLP extract pH falls below 6, 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; Kindness et al., 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 (Appendix I or Canonico, 1995) indicated that all Pond 207C 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 for cadmium, chromium, nickel, and silver. In order to evaluate stabilization of a "worst case" waste, contaminant constituents were added as soluble salts at the given concentrations. The degree of stabilization achieved was determined by TCLP tests.

Volatile Organics:

No volatile organics are present in concentrations exceeding regulatory concern (Halliburton, 1992). Therefore, volatile organic contaminants were not investigated.

Solidification

The third objective of this project 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 investigation 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 et al., 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 solidification. 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.

THEORY OF CEMENT-BASED WASTE FORMS

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.

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

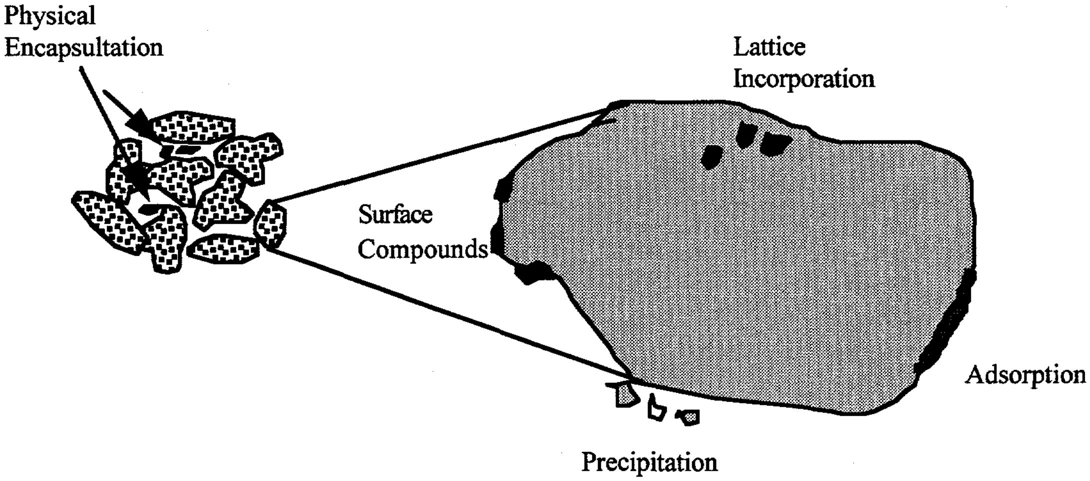
Table 3: Cement Stabilization Mechanisms[a]

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 are graphically depicted in Figure 3.

Figure 3: Graphical Representation of Stabilization Mechanisms Active in the Cement Matrix



(Adapted from Cocke and Mollah, 1993)

The primary objective of cement-based S/S process formulation is the maximization of stabilization mechanisms such as those listed in Table 3 and depicted in Figure 3, while minimizing associated losses of desirable physical characteristics. By maximizing 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.

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.

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). Minimization of mixing water is exponentially related to a decrease in porosity and an increase in strength (Roy and Scheetz, 1993). However, the cement paste requires a substantial excess of mixing water, 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 for making a good quality structural concrete (Czernin, 1980).

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.

Cement Replacement with Flyash

Flyash is a pozzolan, and was a constituent of both Halliburton’s recommended pozzolanic mixture (Halliburton, 1992) and the pozzolanic mixtures used in this investigation. Partial replacement of cement with flyash may result in a product of reduced strength and delayed strength development (Inst Mat’l and Env Res, 1992). However, it has several advantages for S/S systems. It reduces the heat of the hydration reaction. The fly ash particles are believed to: improve particle packing, and reduce permeability, improve workability due to the spherical shape of flyash particles, and improve interface between waste solids and the cementitious matrix. In addition it lowers water demand, improves the pozzolanic reaction, and possibly reduces the tendency to form bleed water (Inst Mat'l Env Res, 1992) and increases reduction of Cr^{6+} to Cr^{3+} (Kindness et al. 1994).

Several of the characteristics of flyash and pozzolan mixtures incorporating flyash are of particular importance to the current investigation. 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.

METHODS AND MATERIALS

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

PHASE I: PROCESS DEVELOPMENT AND SOLIDIFICATION ASSESSMENT

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.

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.

Table 4: Surrogate 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

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. The added insoluble solids will hereafter be called “silt.”

Hydrated lime [$Ca(OH)_2$], a S/S reagent, was also added during surrogate waste preparation. 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.

Surrogate Waste Dewatering:

Dewatering of prepared wastes was accomplished by evaporation in a water bath at 60 to 80 °C. It was necessary to stir the mixture continuously during evaporation.

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%. 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.

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.

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 (1990), with the exception that molds were not removed until the entire 14 day cure time had elapsed.

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 investigation.

Specific Gravity Determination and Strength Assessment:

Sample batches generally filled at least two 210 ml cylindrical molds completely and one mold only partially. Weight and volume of the solidified waste in the partially filled cylinder was determined by water addition to compute specific gravity.

Test cylinders were prepared in accordance with ASTM C617 (1994), 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 (1993).

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:

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. Contaminant solutions were slowly added to 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 (Table 5) 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. The contaminant spike stock solutions were designed to be added at a dosage of 2 ml spike per 100 g brine.

Table 5: 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

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.

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.

TCLP and CCWE Analysis:

TCLP was performed in accordance with 40 CFR Pt. 261 (1994), 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 6. LDRs are also presented for comparison to detection limits.

Table 6:
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

Control Sample Preparation:

To measure the baseline stabilization of each metal in the 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 untreated and a second was evaporated to the highest solids content attainable in the water bath.

The untreated control sample was stirred for over 24 hours to allow any kinetically limited reactions to take place. The sample was then filtered through a 0.7 µm. The filtrate was analyzed for cadmium, chromium, nickel, and silver.

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 was not collected. The sample was sugjected to a TCLP extraction. The TCLP extract was analyzed for cadmium, chromium, nickel and, silver.

PHASE III: INVESTIGATION OF THE EFFECTS OF BIODENITRIFICATION PRETREATMENT

Actual bioreactor residuals were not available for use in this portion of the S/S treatability study. The predicted changes in the surrogate waste resulting from biodenitrification pretreatment were: addition of biomass, increase in chloride content due to anticipated HCl pH adjustment in the bioreactor, increase in sodium content due to sodium acetate feed addition, and 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.

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 7. The waste constituents were added to the concentrated RAS in the amounts indicated. The mixture was continuously stirred 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 form or precipitated.

Table 7: 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

The constituents outlined in Table 7 were designed to simulate bioreactor residuals from treatment of 1000 g of brine influent. The contaminant spike was added based on the theoretical waste volume influent to the bioreactor. Reagent lime was added based on the solids content of the simulated effluent at the ratio of 5% of bioreactor effluent TDS.

Control Sample Preparation:

As with the S/S process, control samples were prepared with an untreated bioreactor effluent sample, and a bioreactor effluent sample dewatered to the maximum extent possible in the water bath. The untreated waste required pre-filtering before it could be filtered at 0.7 μm. The evaporated control sample for the bio-S/S process was subjected to the TCLP. Both the filtrate and extract were analyzed for cadmium, chromium, nickel and, silver.

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 Table 6.

RESULTS

PHASE I

The Pond 207C surrogate waste was evaporated to total solids (TS) contents greater than 80% without becoming too 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 ≤ 10%, after the specimen capping material was changed from plaster of Paris to sulfur mortar.

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 8.

Table 8:
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

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.

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.

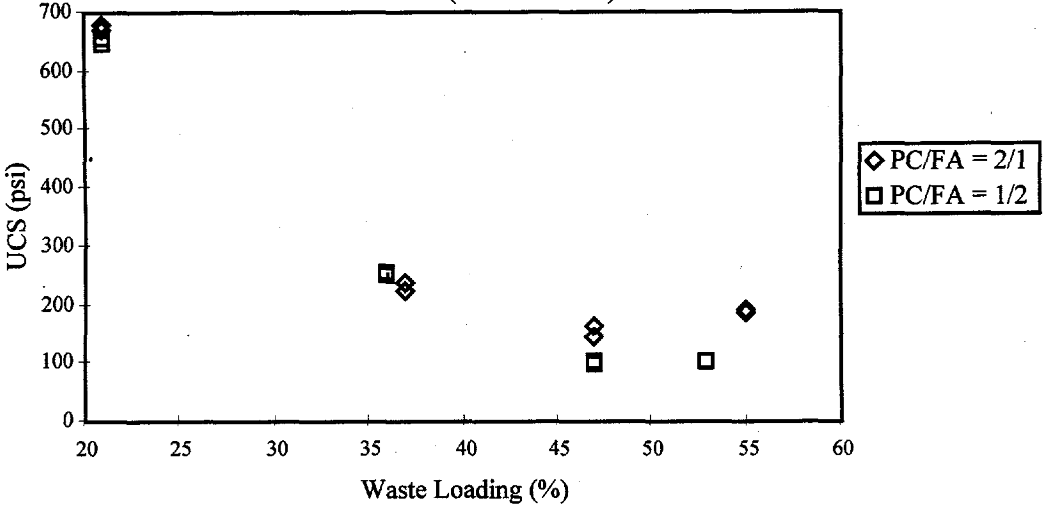
All samples had an average UCS greater than 100 psi. Viable process formulations were demonstrated at waste loadings significantly higher than the approximately 20% waste loading of the baseline process. At 78% solids, over 53% waste loading, the volume of the final waste form was less than half of that produced with the baseline formulation.

The physical characteristics of the final products for both PC/FA ratios are presented in Table 9 and the average UCS vs. waste loading is plotted in Figure 4.

Table 9:
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

Figure 4:
UCS vs.Waste Loading
(S/S Process)



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 (surrogate waste without metal spike, treated with the S/S reagents), control samples and treated 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.

Method Blanks:

Method blanks were evaluated by TCLP extraction to determine potential contaminant leachability from surrogate waste constituents, S/S reagents, and laboratory protocols. Chromium and silver concentrations were below detection limits for all samples tested. The CCWEs for cadmium and nickel for blanks are tabulated below:

Table 10: 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

Control Samples:

The fractions of contaminants recovered from control samples are presented in Table 11. A fraction recovered of 0.0 reflects no metal in extract and 1.0 reflects complete recovery of metal in extract.

Table 11: Fraction of Contaminant Recovered
in Untreated Wastes (S/S Process)

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

Treated 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 12 and graphically, with the exception of silver, in Figures 5 through 7. The non-detect point for nickel was plotted at the method detection limit (Figure 7). 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 12: 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:
Cadmium CCWE vs. % Solids
(S/S Process)

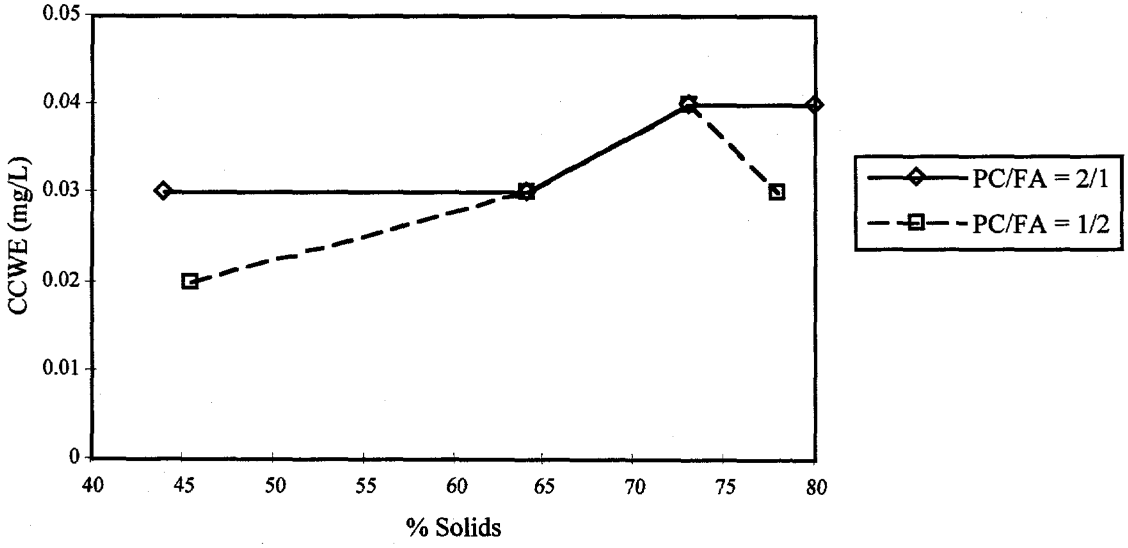


Figure 6:
Chromium CCWE vs % Solids
(S/S Process)

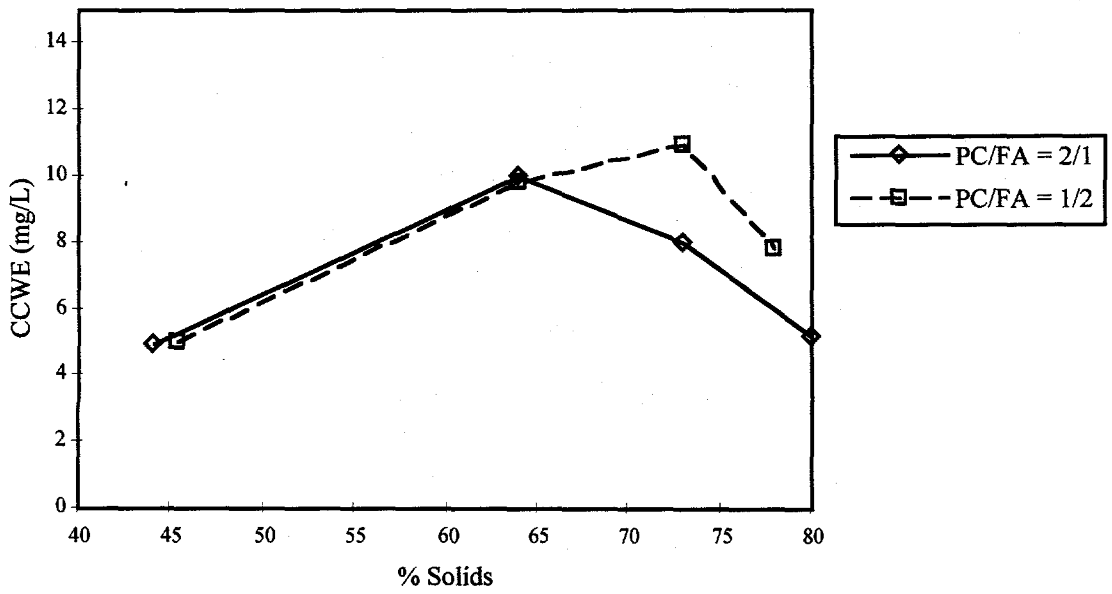
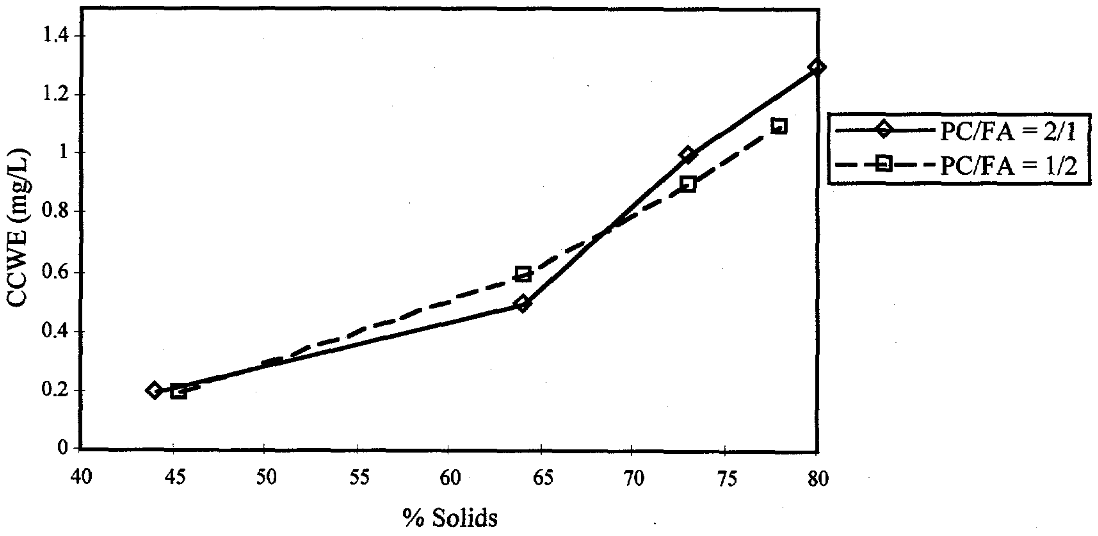


Figure 7:
Nickel CCWE vs. % Solids
(S/S Process)



PHASE III

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 solids levels were tested, 38%, 48%, and 56% total solids. The results are presented below.

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 3 and 4 were used to calculate the two different measures of waste loading.

$$Absolute\ Waste\ Loading = \frac{Bioreactor\ Effluent\ Solid\ Weight}{Final\ Product\ Weight} \qquad (3)$$

$$Relative\ Waste\ Loading = \frac{Bioreactor\ Influent\ Solids\ Weight}{Final\ Product\ Weight} \qquad (4)$$

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 obtaining uniform distribution of reagents difficult. 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 13.

Table 13:
Final Waste Form Physical Characteristics
(Bio-S/S Process)

% Solids	Waste Loading (%) Absolute	Relative	Specific Gravity	UCS (psi) 1	2	3	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 13 data, specific gravity and average UCS, are presented versus absolute waste loading in Figures 8 and 9. below.

Figure 8:
Specific Gravity vs. Relative Waste Loading
(Bio-S/S Process)

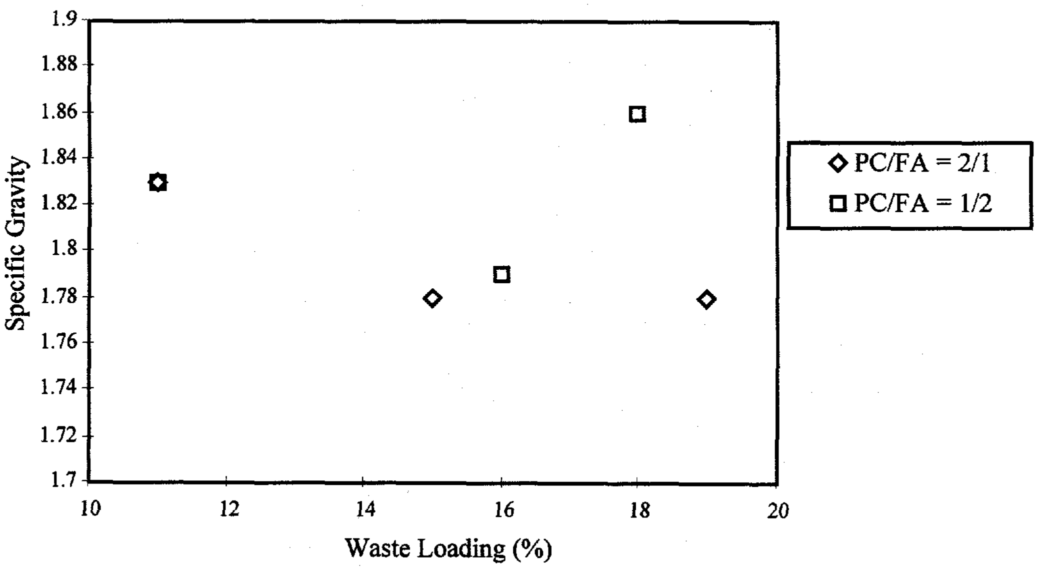
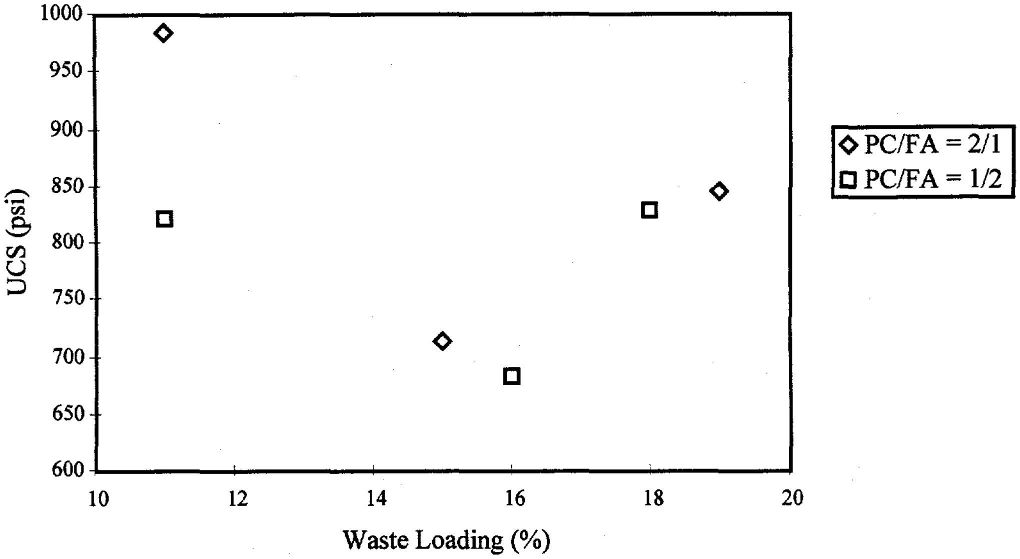


Figure 9:
UCS vs. Relative Waste Loading
(Bio-S/S Process)



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.

Control Samples:

The fraction of the contaminant spike recovered for unevaporated and evaporated integrated process samples are presented in Table 14.

Table 14:
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

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 15. 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 10 through 12.

Table 15: 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 10:
Cadmium CCWE vs. % Solids
(Bio-S/S Process)

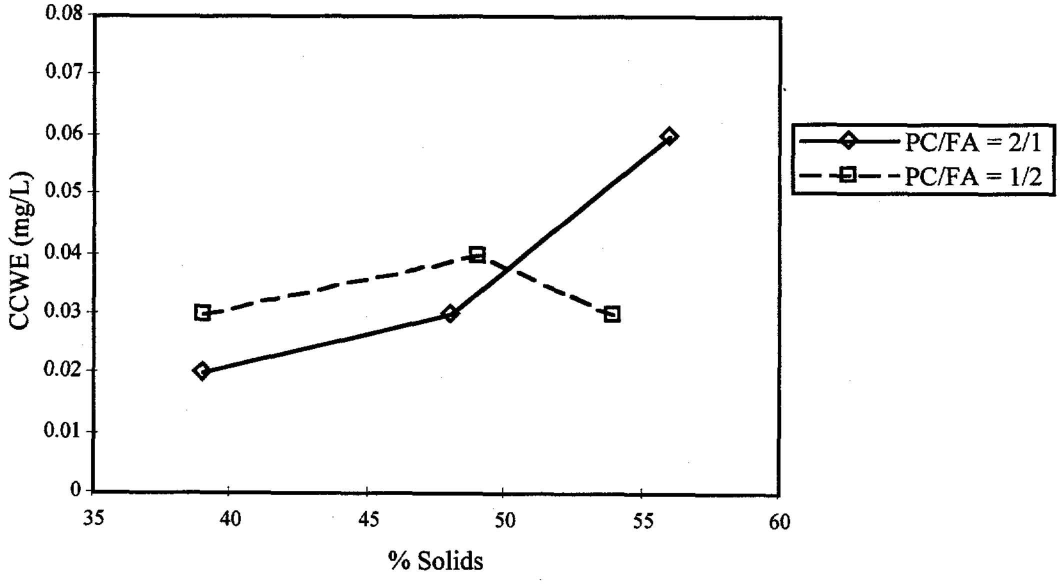


Figure 11:
Chromium CCWE vs. % Solids
(Bio-S/S Process)

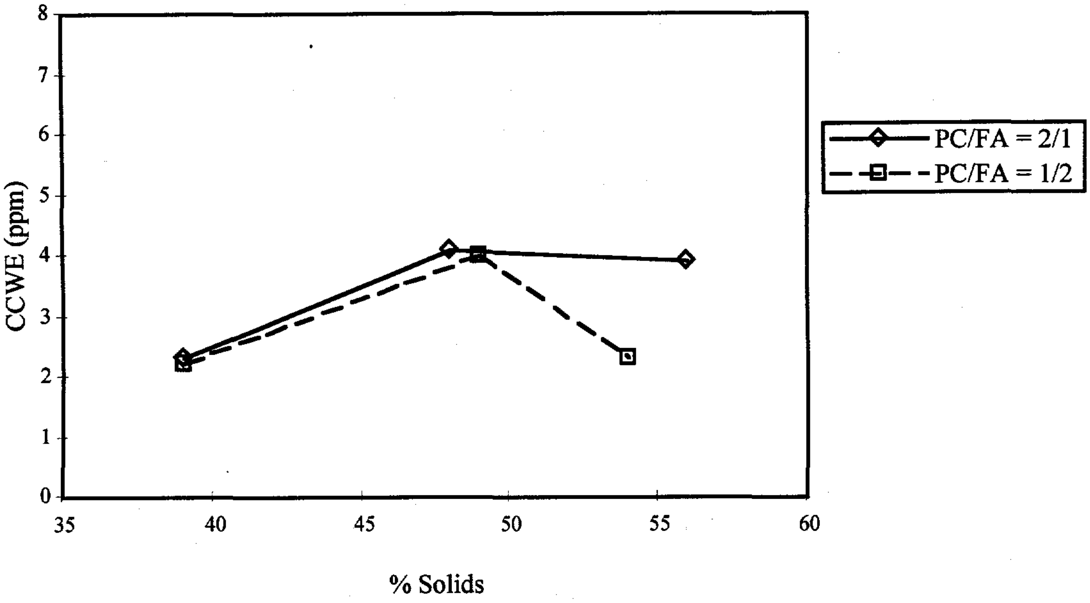
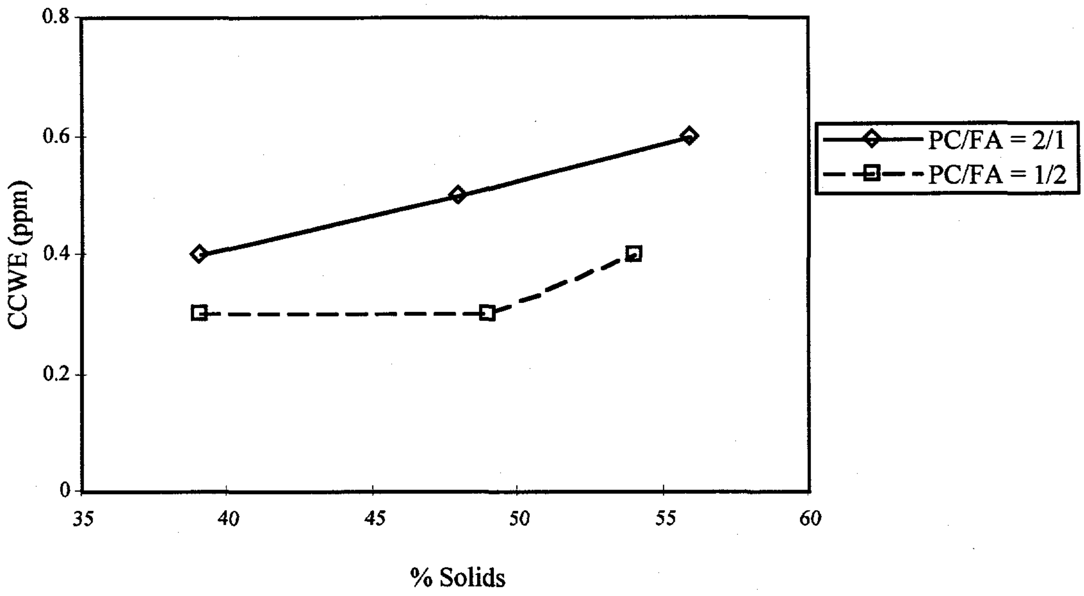


Figure 12:
Nickel CCWE vs. % Solids
(Bio-S/S Process)



PERCENT FIXATION

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 is presented by Canonico (1995).

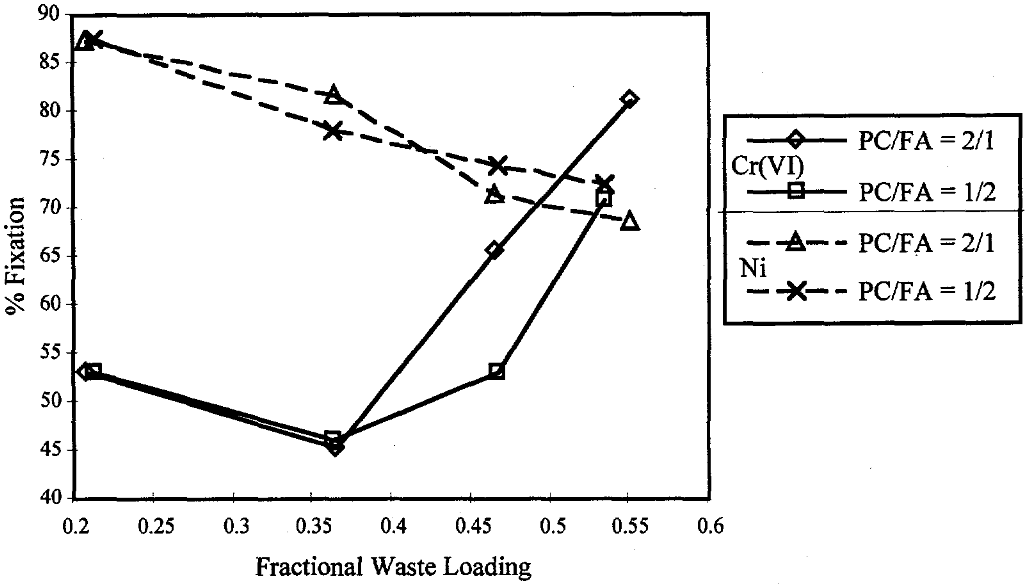
S/S Process:

Percent fixation data for the two S/S process formulations are presented in Table 16. 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 13.

Table 16:
Percent Fixation of Contaminants
(S/S Process)

Waste Loading	Cadmium		Chromium		Nickel		Silver	
	CCWE	% Fix.	CCWE	% Fix.	CCWE	% Fix.	CCWE	% 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 13:
Percent Fixation of Cr(VI) and Ni
vs. Waste Loading
(S/S Process)



Bio-S/S Process:

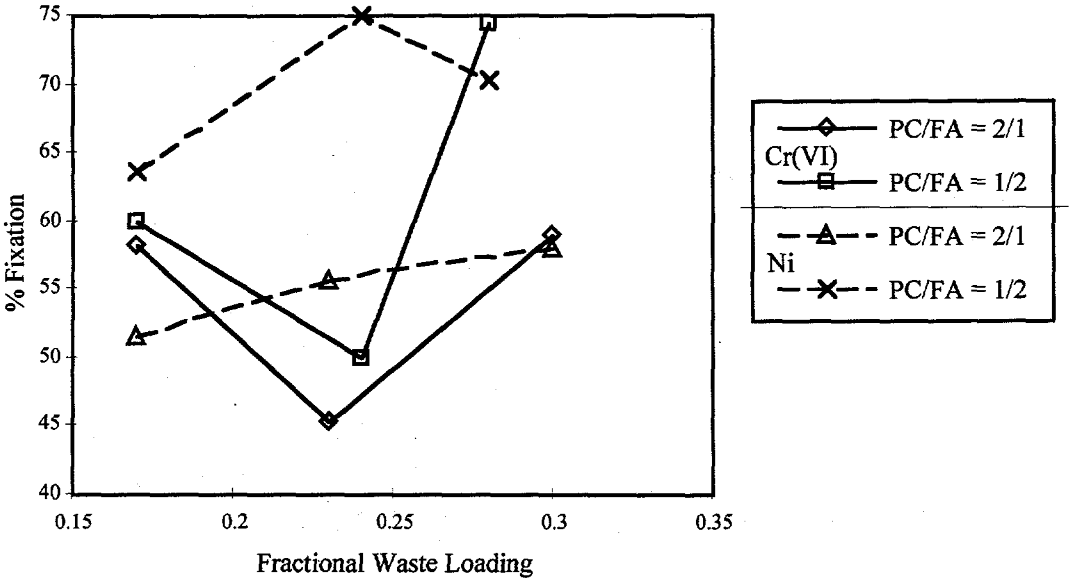
Percent fixation data for the bio-S/S process are presented in Table 17. To facilitate direct comparison with the percent fixation results for the S/S process, percent fixation data are presented versus absolute waste loadings.

Table 17:
Percent Fixation of Contaminants
(Bio-S/S Process)

Waste Loading	Cadmium CCWE	% Fix.	Chromium CCWE	% Fix.	Nickel CCWE	% Fix.	Silver 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 14.

Figure 14:
Percent Fixation of Cr(VI) and Ni
vs. Waste Loading
(Bio-S/S Process)



DISCUSSION

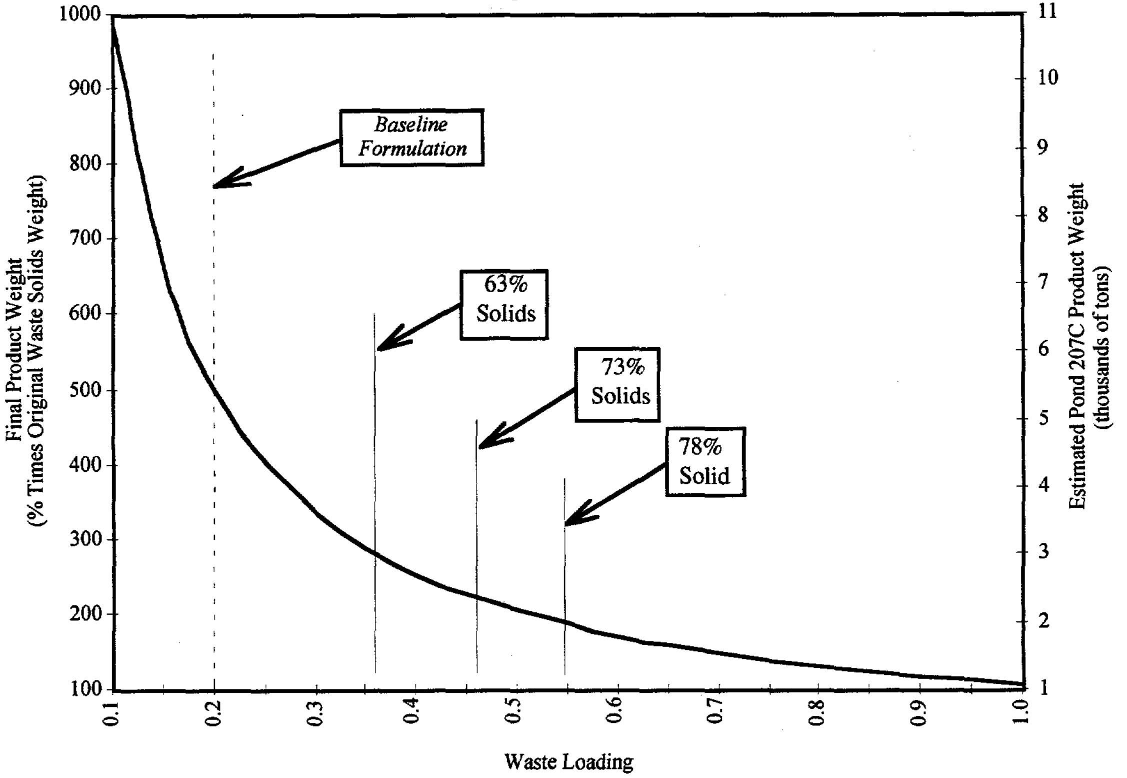
The results are discussed in three separate sections, Waste Loading, Solidification, and Stabilization, below.

WASTE LOADING

S/S Process:

Volume reductions with increased waste loading was achieved as predicted and are shown in Figure 15.

Figure 15:
Product Weight vs. Waste Loading



SOLIDIFICATION

Based on the EPA definition of solidification (USEPA, 1982) and a UCS ≥ 50 psi, satisfactory solidification was achieved at every waste loading tested in Phases II and III of this investigation. The physical characteristics of the final waste forms are discussed below.

STABILIZATION

The stabilization results of this study are 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.

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. 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, chloride and carbonate.

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. Cadmium fixation was 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, Figure 13.

Roy et al. (1993) studied S/S of a synthetic electroplating sludge containing Cr, Ni, Cd, and Hg and varying concentrations of NaOH. They suggested that physical encapsulation was the primary mechanism of solidification/stabilization. Kindness et al. (1994) offer two possible chemical fixation mechanisms for chromium. One is the substitution of Cr(VI) in place of Al(III) in the calcium aluminates present in hydrated cements. The other is the chemical reduction of Cr(VI) to Cr(III) (Kindness et al., 1994).

The decreasing fixation of nickel with increased waste loading observed in the present study is consistent with expectations based on a physical encapsulation mechanism. 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. 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 Mat'l Env Res, 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.

Percent Fixation: Bio-S/S Process

Cadmium and silver fixation was virtually complete at all waste loadings investigated. However, nickel fixation was much higher (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 it has significant detrimental effects on physical encapsulation. A possible cause of the loss of physical encapsulation is the large increase in biosolids with the bio-S/S process, which may increase the matrix porosity.

Increased fixation of chromium at higher waste loadings was evident with the bio-S/S process, as with the S/S process. If the biomass incorporated into the waste matrix has a significant water content, and that water is unavailable for reaction. 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.

Predicted Process Performance with Pond 207C Waste:

The present investigation 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 investigation.

In this section an attempt will be made to predict the performance of the processes investigated as 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 (1992) reported results at similar waste loading.

Halliburton (1992) tested two process formulations similar to that used as the experimental control in this investigation. These are referred to as Batch 18 and 24 in the "Treatability Study Report and Process Formulation Report for Pond 207C and Clarifier, Revision 0" (Halliburton, 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 18.

Table 18:
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 19 (following page), in terms of TCLP CCWE for the target contaminants. Predictions were made with Equation 5.

The contaminant silver was not included in Table 19 because silver was below detectable concentrations for all samples tested in this investigation and by Halliburton (1992) (except for a single anomalous detection in this investigation). 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 19 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, of about 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 at about 20% Waste Loading values for cadmium and nickel used in Equation 5 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.

$$\left(\frac{\textit{CCWE w / Pond 207C @}\sim\textit{20\% Waste Loading}}{\textit{Present Study CCWE @}\sim\textit{20\% Waste Loading}}\right)\left(\begin{array}{l}\textit{Present Study CCWE}\\ \textit{@ Higher Waste Loading}\end{array}\right)=\left(\begin{array}{l}\textit{Predicted CCWE w / Pond207C}\\ \textit{@ Higher Waste Loadings}\end{array}\right) \qquad (5)$$

Table 19:
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

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.

CONCLUSIONS

- 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, a slight increase in final product UCS and no significant improved in stabilization of metals. An assumption in the pretreatment was Cr(VI) was not reduced in the bioprocess, which is not true under all bioprocess operating conditions.
- 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 investigators 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.

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