BENCH SCALE TESTS FOR THE CHEMICAL STABILIZATION/SOLIDIFICATION OF WELDON SPRING SITE SLUDGE AND QUARRY SOILS

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ABSTRACT

Bench scale testing for chemical stabilization/solidification (CSS) of the contaminated materials at the U. S. Department of Energy (DOE) Weldon Spring Site (WSS) has progressed from initial solidification studies to stabilization studies to optimization of the CSS formula. These endeavors will culminate in a pilot plant scheduled for operation late in 1993. Unique to the project are the types of contaminants to be treated by CSS, the development of two final product forms, and possible waste pretreatment requirements. Not only will CSS be used to treat sludge with both metal and radioactive contamination but it will also be used for nitroaromatic contaminated soils generated during ordnance production in World War II. The sludge, which is contained in four raffinate pits (ponds), is the result of lime neutralization of acid extraction waste streams from the refining of uranium metal at the WSS site from 1957-1966.

The sludge has a consistency ranging from a thin pudding to peanut butter depending on the percent water and how the sludge is handled. As pretreatment of the sludge, flocculating agents will likely be added to dredged sludge to aid in settling and thickening. Through the addition of binders and soil to the dewatered sludge, either a CSS grout or a soil-like material will be generated as the final product. This paper presents the sequence and results of the initial off-site studies and the continuing on-site bench scale testing.

INTRODUCTION

The WSSRAP is located 30 miles west of St. Louis, Missouri, and is the result of both the U. S. Department of the Army's (DOA) operation of an ordnance plant from 1941 to 1946, and the Atomic Energy Commission's (AEC) operation of a uranium production plant from 1957 to 1966. The DOA property consisted of 17,000 acres of which the AEC plant later occupied 220. The DOA demolished ordnance plant structures and performed some degree of soil remediation prior to AEC constructing the uranium production plant. The closing of the AEC plant in 1966 left behind residual nitroaromatic soil contamination and over 40 buildings and four raffinate pits containing up to 16 feet of radioactive sludge.

In 1986, under DOE contract No. DOE-AC05-86OR21548, the Project Management Contractor (PMC), MK-Ferguson Company with Jacobs Engineering Group, Inc. as an integrated subcontractor, began developing the site remedial action plan for this superfund site.

The plan included studying possible options for treating a combination of waste. Nitroaromatic contaminants (TNT, DNT, and nitrobenzene) are found predominately in soils dumped into an abandoned quarry located approximately 4 miles from the processing site. The total amount of quarry soil requiring treatment is 57,000 cubic yards (c.y.) with 7,000 c.y. containing the higher nitroaromatically contaminated soils and the remainder containing low levels of both radiological and nitroaromatic waste. Radiological contamination (uranium, thorium, and radium) is highest at the chemical processing site in the four raffinate pits containing over 200,000 c.y. of sludge, and an estimated 50,000 c.y. of clay bottom and dikes of the four pits. The raffinate pit sludges are thixotropic and appear when first extracted from the pits to look like a fairly solid peanut butter. Upon stirring, the sludge samples transform into a pudding consistency.

Initiated during the feasibility studies, tests were begun to determine if chemical stabilization/solidification was a viable treatment method for the wastes. The sequence of the studies utilizes the logic stated by J.R. Conner in a recent paper on treatability studies (1). The first step is identifying a stabilization/solidification matrix which provides the physical characteristics required since these are the easiest tests to perform. Those samples which give adequate strength are then subjected to leaching tests to prove chemical stabilization. If leachability tests meet regulatory limits, further optimization studies are performed to provide flexibility in operation of the system. Finally, confirmation tests are performed on larger samples to provide data for scale up to a full size plant. Confirmation tests will be performed in a pilot plant scheduled for operation during 1993. The bench scale tests leading up to the pilot plant are discussed in this paper.

INITIAL LABORATORY TEST WORK

The original physical test work performed by T.M. Gilliam and C.L. Francis at Oak Ridge National Laboratories (ORNL) in 1989 (2) developed a formula for CSS treatment of raffinate pit sludge samples. Three binder (reagent) blends were mixed with the sludge to make CSS grout. The three blends included:

- 20 wt % Type II Portland cement + 80 wt % Class F fly ash
- 40 wt % Type II Portland cement + 60 wt % Class F fly ash
- 60 wt % Type II Portland cement + 40 wt % Class F fly ash.

Raffinate pit sludge was mixed with these three basic blends at ratios of 0.4, 0.6, and 0.8 g/g (grams of dry-solids binder per gram of waste). The 0.8:1 binder to sludge ratio was so stiff, the sludge was diluted to 20 percent solids before mixing with the binder. Another screening test was run using Class C fly ash alone with the three ratios.

This original screening indicated that a mixing ratio of 0.6 binder to 1.0 sludge with the binder containing 40 weight % Type II Portland cement with 60 weight % ASTM Class F fly ash was optimal. The 28 day unconfined compressive strengths for the CSS treated raffinate pits 1-4 ranged from 500-600 psi which are an order of magnitude above the strength anticipated for design criteria at WSS.

The testing at ORNL also established the following physical performance criteria for the WSS:

- No drainable water within 28 days.
- Unconfined compressive strength of 60 psi.
- Resistance to thermal cycling.

WTG TEST WORK

Additional test work was initiated at the Waste Technologies Group (WTG) laboratories in the summer of 1991. The study included a series of tasks performed on composite samples taken from each of the four raffinate pits, from the quarry, and from surface locations next to the raffinate pits. Three laboratory tasks were defined for investigating chemical stabilization of the CSS product, applicability of CSS to nitroaromatic contaminated soils, and optimization of the ORNL formula. (A fourth test was identified but not implemented which dealt with investigating additives in the event that the original formula did not pass toxic characterization leaching procedure [TCLP] criteria.)

Task 1 — Baseline

Task 1 included baseline analyses to establish total concentrations for a broad list of contaminants with a primary goal of providing concentrations of the elements of concern. These contaminants of concern included metals (arsenic, barium, cadmium, chromium, lead, nickel, selenium), radionuclides (uranium and thorium), and nitroaromatics (DNT, TNT, and nitrobenzene).

In addition to the baseline analysis requested in the bid specification, total analyses for volatile organics, herbicides, and pesticides were also performed. The TCLP criteria requires analysis of the leachates for these components unless they are known not to be present. The concentration results were low enough to make it impossible to fail TCLP criteria, given the 20:1 dilution factor introduced by the method. This allowed the test program to eliminate the expense and time associated with testing for these components in future TCLP leachates.

Following baseline analysis, those samples which did not contain the maximum levels of the contaminants of concern as seen in historical data were spiked to raise the levels. Both raffinate pit sludges and the nitroaromatic soils were spiked with their respective prime elements. Arsenic trioxide, barium nitrate, cadmium nitrate, sodium chromate, lead nitrate, nickel nitrate, selenium dioxide, 2,4,6 TNT, 2,4 DNT, 1,3,5 TNB, and nitrobenzene were selected as the spiking compounds for these contaminants. The spiked samples were then tested for TCLP results to obtain a conservative baseline prior to treatment.

Results of the TCLP tests on the spiked samples (Table I) indicated that raffinate pits 1 and 3 failed the TCLP for arsenic, raffinate pit 3 for cadmium and raffinate pit 4 for barium while the quarry soils failed for nitrobenzene and 2,4 DNT.

Along with the addition of metals and nitroaromatics, radionuclides were also spiked. The bid specification listed seven radioisotopic contaminants of concern, U-234, U-238, Th-228, Th-230, Th-232, Ra-226, and Ra-228 for spiking purposes. Since there are no criteria for these contaminants in the TCLP it was decided that their only influence would be to alter the chemical matrix of the samples. Of the radioisotopes listed, only U-238 and Th-232 had analyzed specific activities low enough in concentration to require spiking. As a result, it was decided to spike the samples only with natural uranium and thorium in the form of uranyl nitrate and thorium nitrate.

Spiked samples from the four raffinate pits and the quarry soil were mixed according to the ORNL formula with 0.6 parts of binder (60 Class C flyash/40 Portland II cement) and 1.0 part contaminated material. TCLP tests were then performed on the CSS samples following a 14 day cure and a 28 day cure. As seen in Table I, the TCLP results for the CSS treated materials indicated that none of the samples tested would be classified as toxic waste per the TCLP criteria (3).

The nitroaromatic contaminated quarry soils added an unanticipated reaction occurrence. Following mixing of the spiked (e.g. 2% TNT) quarry soil samples with the cement/fly ash formula, the curing cubes began emitting a red or pinkish condensate on the surface of the cube. After searching literature and contacting several consultants, it was feared that by mixing the TNT into a basic solution, a new unstable intermediary compound had formed which upon drying, could potentially be shock sensitive. Because the TCLP tests require grinding of the product in the initial phase, there was some concern for safety. These curing quarry soil samples were placed in containers of water while further investigations were conducted. Arrangements were made to prepare identical specimens at Hercules Incorporated, Rocket Center, WV, and explosivity tests were performed. All three sensitivity tests provided results indicating that the samples were not sensitive nor explosive (4).

While the sensitivity tests were being run, an additional nitroaromatic contaminated quarry soil was sampled and spiked with nitrobenzene. The sample was not spiked with TNT to 2% concentration because the original total analysis showed 2,772 ppm. Compared to the average TNT concentrations in the quarry soils of 260 ppm, the TNT level was felt to be adequate for testing. Likewise, since the 2,4 DNT at 19 ppm was similar to the historical maximum of 29 ppm and well above the historical average of 8.1 ppm, the sample used was not spiked for 2,4 DNT. When this second sample was mixed with cement and flyash, no red liquid appeared. Curing continued and TCLP tests were performed. Shown in Table II, the test results indicated that all samples passed the TCLP test criteria.

Task 2 — Optimization

The second task included in the WTG study involved optimization of the original formula to produce either a pourable grout product or a soil-like product. The pourable grout will be used in filling voids of rubble placed in the disposal cell while the soil-like product will be compacted in the cell similar to other contaminated but untreated soils. This also provided

TABLE I

WSS Raffinate Pit Samples - Analytical Results With and Without CSS Treatment

Sample	As ppm	Ba ppm	Cd ppm	Cr ppm	Pb ppm	Se ppm
TCLP Limits	5.0	100	1.0	5.0	5.0	1.0
Pit 1 Baseline Analysis	194	87	7	16	42	13
Pit 1 Spiked	648	143	11	37	242	73
Pit 1 Spiked TCLP	8.84	0.38	0.127	0.003	<0.02	0.05
Pit 1 CSS 28 day TCLP	0.03	0.91	0.003	0.126	<0.02	0.03
Pit 2 Baseline Analysis	583	73	7	26	256	0
Pit 2 Spiked	955	76	14	164	358	30
Pit 2 Spiked TCLP	1.68	0.24	0.035	<0.003	<0.02	0.072
Pit 2 CSS 28 Day TCLP	0.04	0.58	<0.002	0.006	<0.02	<0.04
Pit 3 Baseline Analysis	253	139	4	31	89	0
Pit 3 Spiked	916	288	278*	30	556	70
Pit 3 Spiked TCLP	6.6	0.37	3.24	<0.003	<0.055	0.219
Pit 3 CSS 28 Day TCLP	0.22	1.44	0.003	0.03	<0.018	0.061
Pit 4 Baseline Analysis	26	492	0	16	52	0
Pit 4 Spiked	409	7505	8	22	152	32
Pit 4 Spiked TCLP	0.178	120	0.18	<0.003	0.692	<0.023
Pit 4 CSS 28 Day TCLP	0.017	10.9	<0.002	0.013	<0.018	0.034

* Maximum cadmium value was biased by factor of 100 (historical data misinterpretation)

TABLE II

WSS Quarry Soil Samples Analyitical Results With and Without CSS Treatment

Sample	Analysis		
Quarry Soil	Nitrobenzene ppm	2,4 DNT ppm	2,4,6, TNT ppm
Historical Maximum	133	29	20,055
Spiked To	133	19*	2,772*
Spiked TCLP	3.0	0.95	---
CSS 28-Day Cure, TCLP	0.81	0.017	---
TCLP Limits	2.0	0.13	---

*Not spiked to historical maximums.

a range of mixing ratios for operator flexibility. Raffinate pit 3 (spiked) was selected for this optimization segment because of its high levels of contamination and because pit 3 is the largest pit, containing over two-thirds of the sludge. The matrix of samples developed for testing included ratios set at 0.2, 0.4, and 0.6 binder to 1.0 part of raffinate pit 3 sludge. Additionally, surface soils were mixed in ratios of 0, 0.2, 0.4, 0.6, 0.8, and 1.0 to 1 part of raffinate pit sludge. The resultant eighteen samples were visually classified into either monolithic (pourable grout) or soil-like. Of these 18 samples, four monolithic and four soil-like samples were tested for TCLP compliance and strength characteristics.

Table III presents the results for arsenic, selenium, and the unconfined compressive strengths for these eight samples and shows the effects associated with addition of more soil and less binder. All samples passed TCLP tests, and all monolithic grout samples had unconfined compressive strengths above 100 psi. The soil-like material will undergo compaction in the cell along with untreated soil (not requiring treatment). Therefore, the unconfined compressive strengths compare favorably with strengths seen in compacted soil.

For the grout product, it is felt that the mixing ratio of 0.6 binder to 1.0 sludge can be lowered to 0.4 binder to 1.0 sludge without violating either strength or TCLP criteria. For the soil-like product, the mixing of soil to sludge in the ratio of 1:1 with only 0.2 part binder to 1 part sludge is also viable and will compact well.

Task 3 --- Detailed Leachability Tests

The third task tested samples for long-term leachability using the ANSI 16.1 procedure. One grout sample and one soil-like sample from Task 2 were tested along with the quarry grout sample from Task 1. Total uranium leached was used to calculate the leach index for the sludge grout and soil-like product. For the sample of treated quarry soil, 2,4 dinitrotoluene was used to calculate the leach index. Calculated values for the leach index on leachate uranium were 15 and 14 for the grout and soil-like product, respectively. The index calculated for 2,4 DNT in the quarry soil was 15. The leach indexes obtained are several orders of magnitude higher than those required by the regulatory agencies for low-level

TABLE III
Raffinate Pit 3 Optimization Tests

Test Matrix Monolithic Product	Binder/sludge Ratio	Soil/sludge Ratio	As* ppm	Se* ppm	Unconfined Compressive Strength psi
OP-I-3	0.6	0.4	0.64	0.08	335
OP-II-1	0.4	0	1.25	0.05	185
OP-II-2	0.4	0.2	1.80	0.07	225
OP-II-3	0.4	0.4	3.73	0.11	125
Soil-like Product					
OP-II-4	0.4	0.6	2.93	0.09	60
OP-II-6	0.4	1.0	0.35	0.10	43
OP-III-5	0.2	0.8	2.96	0.16	32
OP-III-6	0.2	1.0	3.05	0.17	36

* Prior to mixing, arsenic was spiked to 1005 ppm, selenium to 77 ppm.

radioactive waste disposal (shallow land burial) and therefore, provide a greater margin of safety.

Additional analyses on the leachate provided information on potential chemical components of the leachate which could cause clogging of the leachate collection system of the proposed disposal cell. Some of these parameters included calcium, iron, magnesium, nickel, potassium, sodium, alkalinity, chloride, flouride, nitrate, phosphorus, sulfate, and pH. Results indicated that whether the cations are present in the leachate as soluble species that may precipitate or as colloidal materials, in both cases the potential exists for the formation of very small particulate material. Therefore, any leachate collection system should be designed to pass small particulate material.

CURRENT ON-SITE TESTING

Additional work has been implemented at Weldon Spring to take into account other system needs and optimizations. Delivery of the raffinate pit sludge to the treatment plant begins with excavation of the material. Due to the potential for radon release, water needs to be maintained on the four pits during sludge removal to blanket radon emissions. The method of sludge removal currently envisioned is a cutter head dredge mounted on a barge. The dredge, however, will introduce additional water into the sludge. The dredged slurry could be as much as 85% water, up from the 60-75% in-situ water. This additional water would produce a weak product or could require significant additional binder to solidify the sludge. Therefore, reducing the water percentage is highly desirable but difficult. Because the sludge is so fine grained, gravity settlement of the slurried sludge would require extremely large settling basins and/or a great deal of time. From an operational standpoint, additives could be mixed into the dredged sludge to more quickly reduce the amount of excess water. Routinely used by the mining/milling industry, flocculants can be added to aid in settlement of fine particles and thus reduce the percentage of water in the slurry.

During June 29 through July 16, 1992, flocculation-settling tests were performed on raffinate pit 3 and 4 sludges to determine the optimal flocculent and concentration for flocculation of raffinate slurry. The following 18 flocculants were screened for their relative effectiveness in flocculating pit 3 and 4 raffinate slurries with roughly 15 percent solids:

- Allied Colloids
  - Percol - 351
- Calgon Corp.
  - WT - 2640
  - CA - 250L
  - POL-E-Z 7736
- American Cyanamid
  - SuperFloc - 204
  - SuperFloc - 208
  - SuperFloc - 210
  - SuperFloc - 212
- Mazer Chemical
  - MaFloc - 720
  - MaFloc - 721
  - MaFloc - 900
- Nalco Chemical Co.
  - No. 7127
  - No. 7148
  - No. 7741
  - No. 7744
  - No. 7769
  - No. 7774
  - No. 7778

For both pits 3 and 4, Nalco 7769, a slightly anionic polyacrylamide, performed the best with respect to the clarity of the supernatant and density of the settled flocculants. Other flocculants, however, also performed well for both pits. These included Percol - 351, MaFloc - 720, Nalco No. 7774, and SuperFloc - 212.

Initial flocculation/settling tests on relatively small sludge slurry samples (1 to 2 kilograms) mixed in graduated cylinders indicated fairly high flocculent usage (1,200 to 2,000 ppm). Further testing in October 1992 on much larger sludge slurry samples (45 to 55 kilograms) mixed in plastic barrels, however, showed flocculent addition in the range of 200 ppm or roughly 3 pound flocculant per ton of dry solids. The lower rate of flocculent usage is well within the normal range of flocculent consumption in industrial processes. The use of flocculants as well as settling, thickening, and dewatering of the slurried sludge will be further defined during future bench scale and pilot plant scale tests.

Stabilized sludge using Class C flyash, leaner binder ratios, and flocculated sludge is currently being tested for TCLP criteria. Although penetrometer resistance tests on the most recently formulated CSS grouts indicate adequate strength, unconfined compressive strength tests must be performed. Given the compounds contained in the best performing flocculants at the concentrations used, the addition of flocculants is not expected to interfere with meeting TCLP limits.

CONCLUSIONS

Through the various stages of bench-scale testing, the treatment of wastes by chemical stabilization/solidification at the WSS has evolved to the pilot plant stage. The basic formula developed initially by physical testing and verified chemically by the TCLP test has been optimized for use with a broader range of wastes, operation parameters and final product forms. Both nitroaromatic and radioactively contaminated materials at the WSS can be stabilized and solidified to produce both a grout or a soil-like product. Pretreatment of dredged sludge involving flocculants appears to be an initial step in the sludge dewatering process. Each step has built upon the last to provide meaningful and documentable results for the implementation of the CSS treatment at the Weldon Spring Site Remedial Action Project.

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