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DISCLAIMER

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Solidification of SRNL High Activity Drain Waste: Feasibility Study

Authors: L. N. Oji, A. D. Cozzi and C. A. Langton

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Immobilization Technology Section
Savannah River National Laboratory
Aiken, SC 29808

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1.0 SUMMARY

Solidification/stabilization of Savannah River National Laboratory (SRNL) high activity drain (HAD) liquid waste at the point of generation was evaluated and determined to be feasible and relatively easy to implement with inorganic reagents. Testing was conducted with water, a non radioactive simulant, a non radioactive spiked simulant (spiked with Resource Conservation and Recovery Act (RCRA) metals) and actual radioactive waste from three SRNL laboratory modules. "At the source" solidification of the SRNL HAD waste was successfully demonstrated. Inorganic solidification/stabilization reagents are recommended based on the testing to date.

Various solidification/stabilization reagents and mixtures of reagents were tested. A sorbent mixture consisting of ordinary Portland cement and silicate filter aid media, Harbolite™ (perlite) or Celite™ (diatomaceous earth), resulted in waste forms with the wicking and cementation properties that met the simple processing and cured property requirements. These reagent blends were used to solidify actual SRNL HAD waste.

In these reagent mixtures the silicate filter aids behave as:

1) absorbents,
2) "wicking" agents, which allow the quick dispersing of the liquid waste into the cement-silicate matrix, and
3) pozzolans*, which react with $Ca(OH)_2$ in the hydrated Portland cement to form additional calcium silicate hydrate binder phases with extended curing (months).

In most cases, the resulting final waste form was a self-supporting solid material. For most HAD liquid waste streams, no pH adjustment is required before stabilization with the Portland cement-silicate sorbent mixture. With the right sorbent mixture-to-HAD waste combination the solidification process takes place in under five minutes and no mechanical mixing is required.

The resulting final waste form passed toxicity characteristic leaching procedure (TCLP) test for all the RCRA metals tested, excluding mercury, barium and silver which were not part of the RCRA metals evaluated.

In addition, testing was performed to optimize dispersion of the liquid in a container (high density plastic polyethylene bottle) with the solidification reagents. Glassware for this purpose was designed and tested. The dispersing device performed adequately. However, optimization of the wicking component in the reagent mixtures solved the dispersion problem without the need for a liquid dispersing device and/or mixing.

Based on the positive results described in this report, the study should be expanded to include additional laboratory waste stream treatment studies and comparative cost analysis for the

* A siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties.

sorbent components. Limited trial implementation of the solidification/stabilization technology is recommended for SRNL HAD waste. Additional funding and technical support are required from both SRNL Engineering and ITS/WPT personnel.

2.0 INTRODUCTION

2.1 Background

A variety of aqueous waste streams are generated daily at the Savannah River National Laboratory (SRNL) in research and development activities designed to support both SRS and outside work. The predominant source of the high activity drain (HAD) waste generated in the laboratory comes from the dissolution and analysis of Tank Farm and the DWPF samples. Post analytical and characterization sample returns from the Analytical Development Section (ADS) are stored until a sufficient quantity of the waste is accumulated for neutralization and eventual discharge to the SRS drain system. These aqueous waste streams are classified into two distinct radioactive categories:

1. Low activity waste, which is discharged down the low activity drain (LAD) and,
2. High activity waste, which is discharged down the HAD.

Both of these waste streams are potentially mixed waste due to the presence of RCRA regulated metals. Both waste streams are collected and stored at SRNL in the mixed waste storage tanks as low activity waste (LAW) and high activity waste (HAW). Periodically, the LAW is shipped to the Effluent Treatment plant (ETP) for treatment and disposal and the HAW is shipped to H-Area for disposal in the SRS Tank Farm.

2.2 Objective

The objective of this study was to demonstrate feasibility of "at the source" solidification of HAD waste and disposal of the resulting solid waste form in E-Area as an alternative to the current practice.

Solidification/stabilization is one of four technologies currently being evaluated as alternatives to the current disposal practice. The other technologies are: steam reforming, microwave drying/high temperature treatment, and ion exchange.

This work complies with the work scope requested by A. Zagrodnik of SRNL Engineering.

2.3 Approach

The solidification/ stabilization tests performed in this study included the following:

- Screening tests to evaluate the effectiveness of commercially available inorganic sorbents or mixture of sorbents in the stabilization of water colored with food dye.
- Identification of the most effective inorganic material or mixtures for water stabilization.
- Evaluation of the selected inorganic sorbents or sorbent mixtures above for use in stabilization of a typical non radioactive high activity drain (HAD) simulant and HAD simulant spiked with RCRA metals, and
- Demonstration of solidification/stabilization performance of the selected sorbents above with "actual" waste (radioactive waste) from SRNL.

Initially only organic materials were considered as potential sorbents for the laboratory liquid waste but were eliminated in subsequent testing because of the potential for generation of flammable gases (hydrogen) during radiolysis and decomposition of organic-based sorbent materials (polymers)[1].

2.4 Waste Form Acceptance Criteria

Some of the test parameters used to evaluate each sorbent mixture liquid waste solidification efficiency included:

- Volume changes with the introduction of liquid waste into the sorbent mixture
- Temperature changes indicating exothermic reactions
- The time required to uniformly disperse the liquid waste into the sorbent mixture without physical agitation or mixing
- The formation of a single monolith at end of the solidification/stabilization
- Final waste form characteristics as determined from information on microstructure (Scanning electron microscope (SEM)), X-ray diffraction (XRD) and toxicity leaching characteristics (TCLP) for regulated transition metals.

Solidification tests involving RCRA spiked solutions were performed at Universal Treatment Standard levels for:

- cadmium (0.11 mg/L)
- selenium (1mg/L)
- arsenic (5 mg/L)
- beryllium(1.22 mg/L)
- lead (0.75 mg/L)
- thallium(0.2 mg/L)
- vanadium(1.6mg/L)

The spike solution did not contain mercury or silver. After solidification the solids formed from both simulant (with and without RCRA metal spikes) and real waste tests (radioactive waste) were characterized for TCLP (TCLP leachates analyzed for RCRA metals), SEM and XRD.

The “real waste solutions” solidified in these tests were obtained from:

- Archived Tank 50H samples (500 mL) from Laboratory B-126/130,
- Actinide-rich salt waste from Laboratory B-126/130 (500 mL),
- Laboratory B-111 (140 mL)-mixed acid and peroxide fusion dissolution of Defense Waste Processing Facility (DWPF) glass.

The first two radioactive samples above were all caustic salt solutions (pH > 11) while the third sample was moderately acidic with pH < 5. With pH < 1 the HAD simulant solution used in these tests was highly acidic.

3.0 EXPERIMENTAL

The materials evaluated as prospective solidifying and stabilization agents for solidifying/stabilizing the SRNL HAD liquid wastes are shown Table 1.

Table 1. Solidification/Stabilization Reagents Tested.

Inorganic materials	Commercial Source	Comments
Harbolite™ (perlite)	Harbolite Corporation	For only the 200, 700 and 900 categories of Habolite Silicate
Techflow™ 2000X		Filter Aid Silicate
Amorphous sodium aluminosilicate		Silicate
Synthetic nitrated sodalite		Silicate
Synthetic gibbsite		Silicate
Synthetic zeolite A		Silicate
Celite™ diatomaceous earth	Cellulite Corporation	Filter Aid Silicate
Stardust™	Paradigm International, Inc.	Silicate
Vermicilite		Expanded micaceous silicate
Petroset™	Fluid Tech, Inc.	Treated Clay + Portland cement
Fly ash	South Eastern Fly Ash Company	
Portland cement	Lafarge	
Ceramicrete™	Argonne National Laboratory	Magnesium phosphate cement
Bentonite clay		Clay
Attapulgite clay		Clay
Slag grade 100	Holcim company	Chemical reducing reagent
Calcium phosophate		Hydroxyapatite
Spill-X-A™ and Spill-X-C™	ANSUL, Inc.	Organic spill control reagent + neutralization reagents
Liquid waste solidifier	Arcus Absorbents, Inc	Reference organic polymer

3.1 Water – Reagent Tests

In the initial part of the study, each of the above materials was independently evaluated for the uptake of liquid waste. Screening tests were performed using a one-to-one basis by weight of red dyed-water and each material. The screening tests were performed in 50-mL glass vials as shown in Figures 1A and 1B.

A: Complete absorption of equal mass of water containing red food dye was only observed with the silicate wicking agents (Test 79).

B: Neat Portland cement failed to completely wick an equal weight of water (Tests 22 and 23). Portland cement plus silicate wicking agents sorbed an equal weight of water (Tests 17 and 21).

Figure 1. Preliminary screening tests with inorganic sorbents using red-colored water.

3.2 Simulant- Reagent Tests

In the second phase of the screening tests, those inorganic materials which showed potential were blended to improve the waste form processing properties. The best results were obtained from mixtures of two inorganic components (Portland cement and a siliceous wicking agent). These sorbent mixtures were further evaluated using water and a non radioactive HAD simulant provided by the Immobilization Technology Section through the SRNL mobile laboratory.

The composition of the HAD simulant solution is shown in Table 2. The simulant was actual non radioactive laboratory waste resulting from digesting glass and dried sludge samples in

acid or base. It consisted of 8L of mixed acid ($HF/HNO_3/HCl/H_3BO_3$ acids), 8L of aqua regia (HCl/HNO_3 acids), and 8L of residuals from sodium peroxide/sodium hydroxide fusion (Na_2O_2/NaOH/HCl).

Table 2. HAD simulant and RCRA spike solution compositions.

HAD Component	Concentration, mg/L
Ag*	0.131
Al	45.2
As*	<0.120
B	541
Ba*	0.454
Ca	17.6
Cd*	<0.010
Cr*	0.478
Cu	1.43
Fe	106
K	14.9
Li	166
Mg	10.4
Mn	16.4
Na	2750
Ni	3.44
P	0.376
Pb*	<0.020
S	1.65
Se*	<0.120
Si	150
Sr	0.125
Ti	1.95
Zn	1.59
Zr	2.67
F^-	1460
Cl^-	6500
NO_3^-	21300

* RCRA D-Coded Characteristically Hazardous Components.

Screening tests with the simulated HAD waste consisted of pouring the waste into 50-mL poly-bottles pre-loaded with the blended reagents. See Figures 2A and 2B. Sorbent mixtures containing the clays, Portland cement and the silicate minerals gave better results than other mixtures of inorganic materials from Table 1. The Portland cement (PC) and silicate blends were measured in proportions as follows: 70% PC and 30% silicate wicking agent by weight. The amount of simulant was 1.5 times the weight of the sorbent mixture. Equal weights of waste simulant and reagent mixture were used for tests using diatomaceous earth.

A: Complete solidification of simulant observed for blends with silicates (# 59 and 75) and not with pure Portland cement or any of the other clays (# 72, 73 and 74). The silicates alone formed only a pasty (#60, 61, and 66) material with the simulant.

B: Complete solidification of simulant was observed with sorbent mixtures of Portland cement and Harbolite™, sodium aluminosilicate and diatomaceous earth.

Figure 2. Screening tests with HAD simulant using two-component sorbent mixtures.

3.3 Simulant - Reagent Scale-Up Testing

The non radioactive simulant was used in initial scale-up testing. Occasionally one may run into some liquid waste with unique fluid properties which makes it difficult to disperse them into the sorbent mixtures without employing mechanical mixing techniques such as stirring. To minimize any type of stirring and to enhance wetting and contact between the liquid phase and the sorbent material, a multi-pore funnel concept for this special case was adopted. One of the SRNL designed and fabricated device (a multi-pore funnel) is shown in Figures 3A and 3B. The multi-pore funnel was successfully used to introduce and distribute the liquid waste into the sorbent mixture container. This and other similar trial delivery funnels (not shown) were fabricated in SRNL glassblowing and apparatus development laboratory from standard borosilicate glass. The funnel end of the multi-pore funnel, which fits into the sorbent mixture container, bears six protruding holes located around the surface of the base with gas venting slots at the neck portion of the funnel. This glass-funnel delivery system ensured that the liquid to be solidified was evenly delivered and distributed over the upper portion of the sorbent mixture in the container without saturating one part of the sorbent mixture.

A: Multi-pore funnel with six different delivery holes.

B: The multi-pore funnel mounted on a one-liter poly-bottle.

Figure 3. Multi-pore funnel assembly.

3.4 RCRA Spiked Simulant – Reagent Tests

Testing with the non radioactive simulant was also expanded to include spiking simulant sample sizes of 100-120 mL with RCRA metals and other hazardous constituents typical of the HAD waste. TCLP extractions and leachate analyses were performed by the SRNL-ADS on these waste forms to evaluate the potential for treating characteristically hazardous mixed HAD waste by ambient temperature solidification/stabilization technology. The TCLP extraction and analytical methods used in this study are documented as either ADS procedure 2512 or 2572[2].

3.5 Actual HAD Waste Solidification/Stabilization

The final task in this feasibility study involved evaluating solidification/stabilization of actual radioactive HAD waste. The most promising reagent mixtures and proportions were selected for testing. Combination of PC and Harbolite™ (perlite), and PC plus Celite™ (diatomaceous

earth) were tested. Actual waste solidification/stabilization tests were performed in 250 and 1000-mL high density polyethylene poly-bottles.

4.0 RESULTS and DISCUSSION

4.1 Screening Tests with Water

Screening tests with water were used as a quick way to identify potential reagents. These tests indicated that no one reagent provided all of the properties necessary to produce a satisfactory waste form. In particular, portland cement did not wick liquid fast enough to eliminate the need for physical mixing. The clays did not sorb quickly and resulted in a plastic, paste-like waste form. The silicate filter aids and reagents often exhibited drainable liquid and never solidified into a free standing waste form (see Figure 1A).

The screening tests did indicate that mixtures of Portland cement and silicate reagents produced acceptable waste forms. Some of the clays and Portland cement absorbed water with the formation of self-supporting solids only when the water loadings were less than one-to-one by weight. At about one-to-one by mass loading with water, Portland cement formed a liquid and a solid phase after 24 hours of contact. Dispersing or "wicking" of water into porous silicate reagents was relatively fast compared to the clays.

Certain silicates materials (perlite, sodium aluminosilicate, and diatomaceous earth), Portland cement and clays (attapulgite, bentonite and petroset) were selected for further testing with the HAD simulant. It is worth noting that some of the materials in Table 1(petroset, slag 100 and fly-ash) when contacted with the red food colored water efficiently removed the organic food dye color from the resulting matrix. The liquid phase of the resulting mixture was devoid of red coloration.

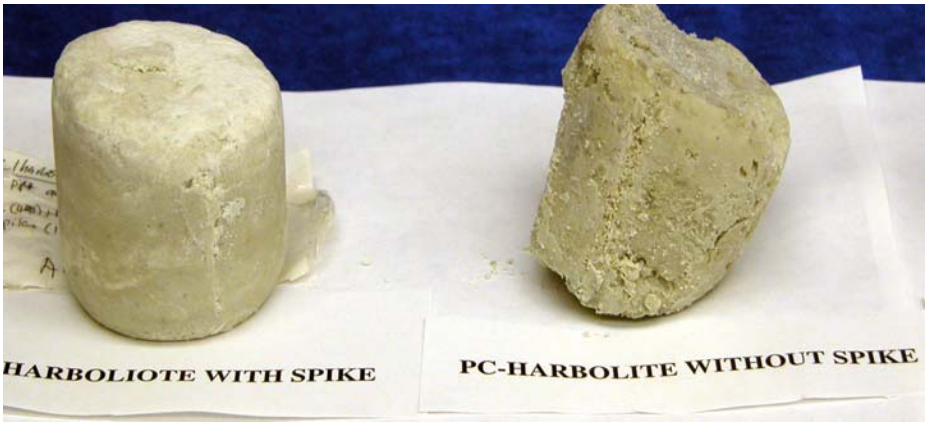
4.2 Tests with Simulants and Sorbent Mixtures

Screening tests of individual reagents and mixtures of reagents plus the HAD simulant resulted in the elimination of the clays (attapulgite, bentonite and petroset) as prospective waste form ingredients because of poor distribution or wicking of the simulant, inability to absorb sufficient amounts of the simulant and inability to form a hard solid final waste form after 24 hours. The only materials from Table 1 above which met most of the required conditions as mentioned above for stabilization were mixtures of Portland cement, the silicates including sodium aluminosilicate and sodalite, and diatomaceous earth.

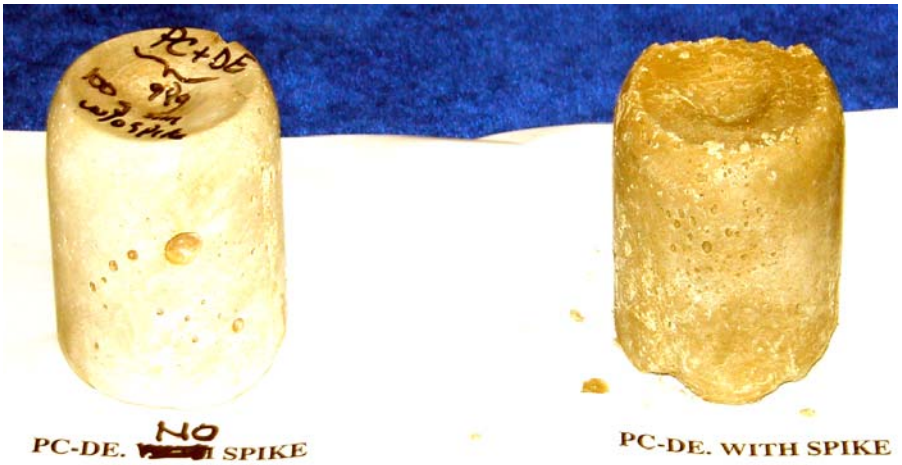
Tests with two component blends of Portland cement and any of the silicates, Harbolite™ (perlite) and Celite™ (diatomaceous earth), provided the most promising results with the HAD stimulant (see Figure 4). Temperature increase measured in these blended reagent waste forms containing the simulated HAD waste were minimal (generally less than 1^{o}C) and the volume changes were normally less than the initial volume of the sorbent mixtures. Over 24 hours, these waste forms solidified and were generally hard due to the hydration of the cement in the mixture.

These blended reagents were also used to solidify simulant spiked with RCRA metals. The RCRA spike had no impact except for one sample containing Portland cement and Harbolite™

Grade 635, which failed to solidify when RCRA metals were added. Other grades of Harbolite™, -200, -700 and -900, worked well with and without the RCRA spike.



A: Waste forms made with spiked or unspiked simulant and a mixture of PC and Harbolite™.



B: Waste forms made with spiked and unspiked simulant and PC plus diatomaceous earth.

Figure 4. Final waste forms produced with Portland cement and silicate blends after 48 hours; pH of the simulated waste was < 1.

4.3 Solidification/Stabilization of Real Waste with Sorbent Mixtures

Three actual waste samples (archived Tank 50H sample, actinide waste from B-126/130, and radioactive blended analytical-returns from B-143) were solidified/stabilized for disposal as solid waste. Blends of Portland cement and Harbolite Grade 900 were used. The volumes of the three actual HAD waste samples solidified were 500-mL (550 g), 500 mL (550 g) and 140 (153 g) mL, respectively. The solidification reagent mixture consisted of premixed Harbolite™ (375 g) and Portland cement (85 g). These reagents were placed in a poly-bottle. Because no mechanical mixing was required, each real waste was poured into the poly-bottles containing the sorbent mixtures without the use of the multi-pour funnel described earlier.

The solidification/stabilization mixture wicked in the real waste solution to form a solid waste form without standing or drainable water in less than three minutes from moment the pouring

was initiated. After 24 hours, most of the material was hardened, with the exception of excess sorbent mixtures which had not come into contact with the liquid waste (see Figures 5 through 7). Figure 8A shows the top surface layer of one of these waste forms immediately after introducing the liquid waste into the container. Figure 8B shows the same surface after three minutes. After three minutes there is almost a complete wetting of the reagents at the upper layer. In all the solidification tests with real HAD waste the temperature changes were small and volume changes were relatively small.

A: A typical radioactive HAD waste to be solidified, pH>11.

B: A typical self-supporting post-solidification waste form produced.

Figure 5. Final waste form produced with caustic radioactive waste: note excess unwetted sorbent mixture on the waste form.

A: Top layer of solid form produced after complete wetting of the sorbent mixture.

B: Self supporting real waste form produced after 24 hours.

Figure 6. Self supporting real waste form produced after 24 hours.

Figure 7. Real waste solidification. Final waste form as seen from the bottom with excess unwetted sorbent mixture powder (caustic waste stream).

A: Photo taken immediately after pouring of real waste into sorbent mixture powder.

B: Photo showing complete wetting of sorbent mixture after 3 minutes.

Figure 8. Solidification of HAD "real waste" with sorbent mixture. Complete wetting of sorbent powder after three minutes of contact with liquid.

A limited post-TCLP analysis of the leachate from the three real waste samples (archived Tank 50H sample, actinide waste from B-126/130, and radioactive blended analytical-returns from B-143) for total uranium gave a uranium content of 27, 22.7 and 96 mg/L, respectively. The total strontium characterization of these three radioactive sample leachate also gave the following values, 22.6, 18.4 and 119 mg/L, respectively.

4.4 SEM Microstructure and XRD Characterization of Waste Forms

Mixtures of Portland cement and Harbolite™ Grade 900 and Celite™ (spherical porous wicking agents) were used to solidify simulated HAD waste. Samples for microstructural analysis were collected from the solidified/cemented waste forms. The samples selected for analysis were completely wetted so no unreacted reagents were present at the bottom of the container.

Fractured-surface microstructures of three of the samples are illustrated in secondary electron images in Figures 9-11. Qualitative compositional information obtained from energy dispersive x-ray (EDX) analyses of portions of the sample is also presented in Figures 9-11.

Sample PC+DE, containing Portland cement, diatomaceous earth and simulated HAD waste, clearly show the cementitious binder surrounding "cellular" diatoms Figure 9 (a) and (b). The Celite™ material used in this study appears to have undergone low temperature processing/drying based on the presence of cristobalite, an elevated temperature form of SiO_2 which makes up the diatom skeleton.

At low magnification, the larger diatoms were pulled out of the sample as indicated by the numerous spherical depressions on the fractured surface. See Figure 9 (a). Diatoms surrounded by cementitious material are shown in Figure 9 (b). The EDX compositional information indicates that the binder consists of inter grown calcium silicate and calcium aluminate sulfate and chloride particles.

Samples PC-HARB and PC-HARB+Spike contained Portland cement, perlite, and simulated HAD waste with and without a contaminant RCRA spike, respectively. The perlite used in these tests is a heat treated (fully heat expanded) volcanic glass. In the natural form it contains water. Upon processing (heating) the water expands to form spherical lightweight microporous particles. Perlite is pozzolanic in cement waste forms. The silica and alumina in the perlite react with water and calcium hydroxide.

The microstructures of the two Portland cement-Harbolite™ waste forms are similar as indicated in Figures 10-11 (A and B). They also resemble the microstructure of the Portland cement-Celite waste form, since these three samples used spherical wicking agents as a major component and since the reaction products of the cement are essentially the same based on x-ray diffraction phase data. The C-S-H gel is the bulk of the undifferentiated material in the matrix which binds the spherical particles together. The needle and platelets with discrete planar surfaces are the crystalline phases: ettringite (sulfate salt), hydrocalumite (chloride salt), portlandite (calcium hydroxide), and nitrantine (sodium nitrate) detected in the XRD patterns (see Figures 12 to 14). Equant grains are typical of unreacted cement and are often multiphase.

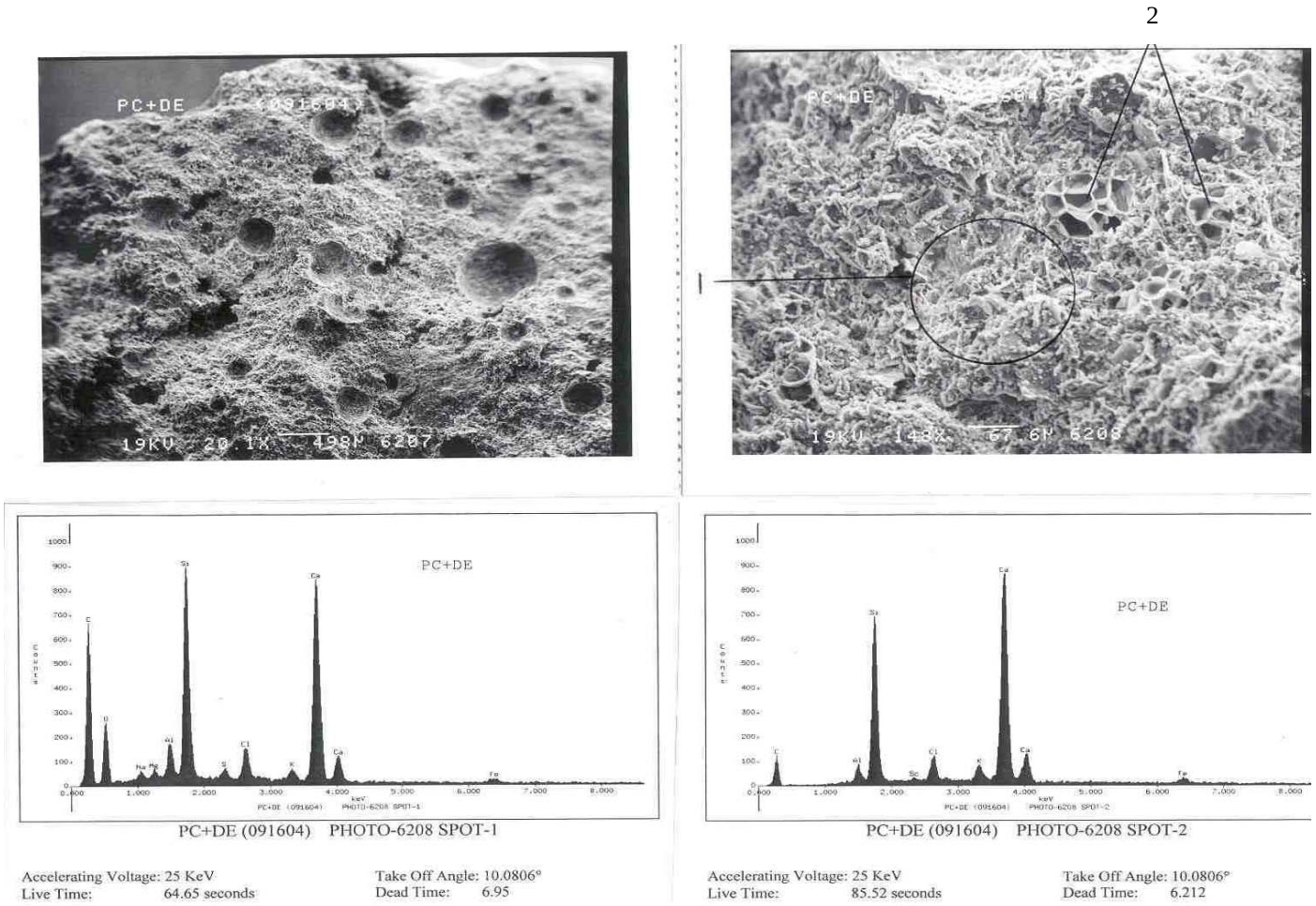


Figure 9. Microstructure of sample PC + DE + simulated HAD waste. SEM secondary electron images of a fractured surface (top) and energy dispersive x-ray qualitative analyses of two areas.

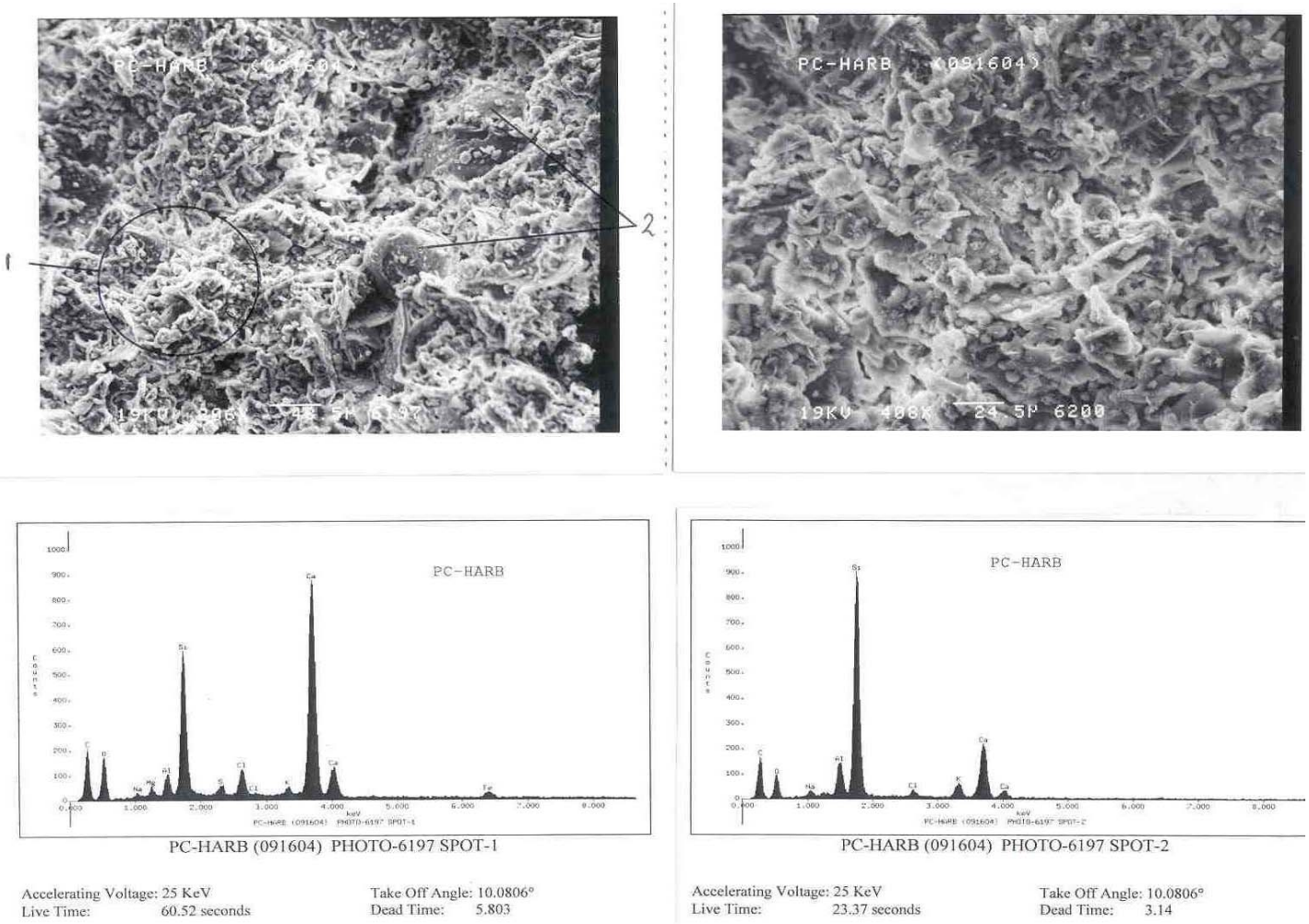


Figure 10. Microstructure of sample PC + HARB + simulated HAD waste. SEM secondary electron images of a fractured surface (top) and energy dispersive x-ray qualitative analyses of two areas.

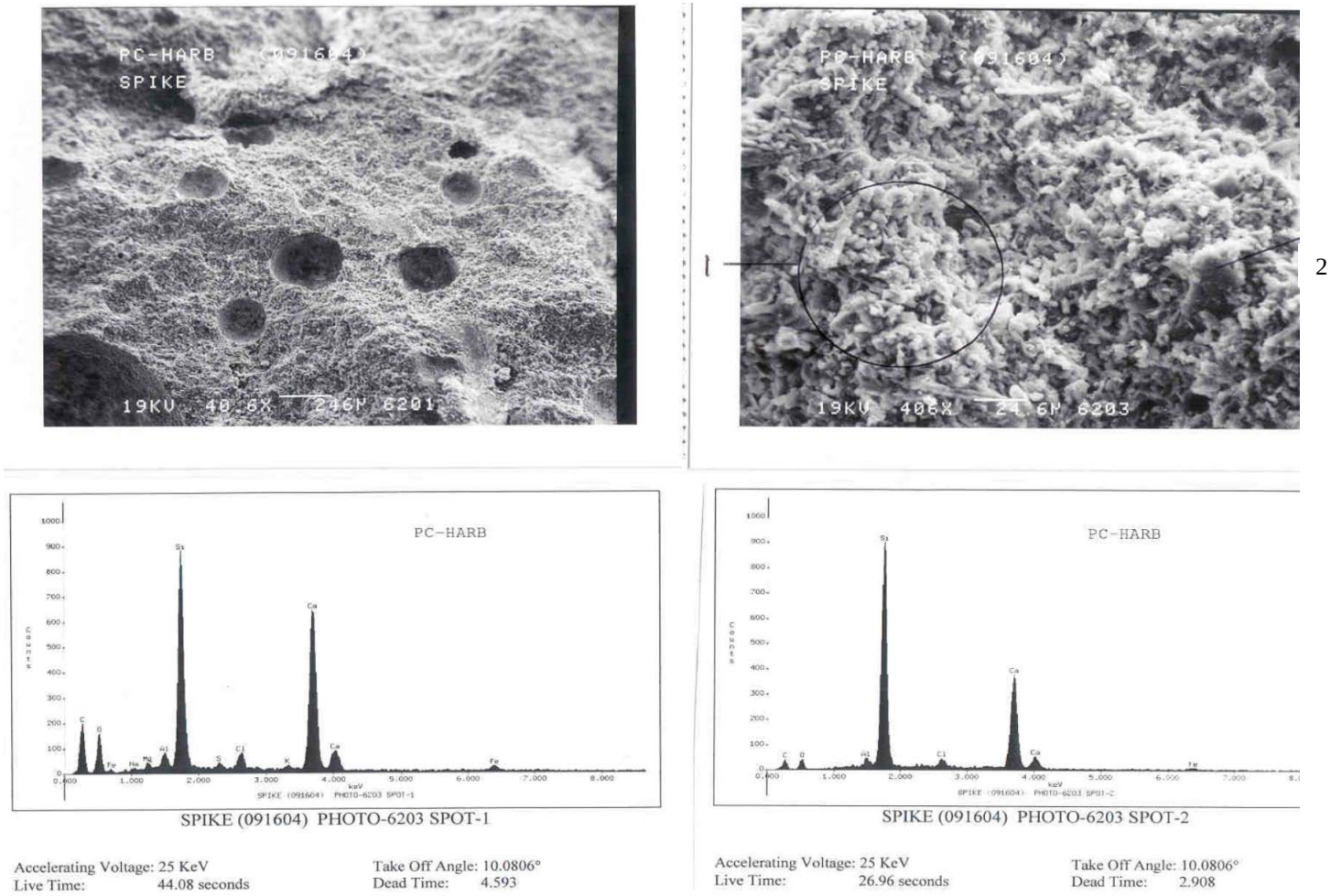


Figure 11. Microstructure of sample containing PC + HARB + spiked simulated waste. SEM secondary electron images of a fractured surface (top) and energy dispersive x-ray qualitative analyses of two areas.

4.5 Mineralogy

The phases present in three HAD waste forms were determined using x-ray diffraction analyses. Powder patterns are shown in Figures 12-14. Results are summarized in Table 3. All three samples contained a large amount of non crystalline (amorphous) material characteristic of the calcium silicate hydrate (C-S-H) gel in hydrated portland cement. In addition, crystalline reaction products (hydrocalumite, ettringite, and portlandite) and unreacted cement phases (alite +/- larnite) were detected in all three waste forms. Unreacted diatomaceous earth (cristobalite) was detected in the sample containing Celite™. Unreacted Harbolite™ (perlite) is assumed to be amorphous since it was not detected. Sodium nitrate from the waste solution was detected in one of the samples.

4.6 TCLP Leaching Data

TCLP leaching data for a control sample prepared with unspiked simulant and two waste form samples prepared with Portland cement, a wicking agent (diatomaceous earth or perlite), and the non radioactive spiked simulant are provided in Tables 4 to 6. All of the TCLP results were well below the limits for characteristically hazardous waste and are therefore not hazardous waste. The concentrations of all of the potential contaminants that were analyzed in the leachates were also below the Universal Treatment Standard (UTS) limits.

Stabilization factors were calculated for each contaminant of concern that was analyzed in the TCLP leachate. The stabilization factors were calculated by assuming that 100 % of each contamination of concern (COC) in the waste form was leached and dividing this value by the amount actually leached.

The assumption was also made that the spike was the only source of the COCs. Stabilization factors are listed in Tables 4 and 5. The calculated stabilization factors ranged from 7 for Se to 35,000 for Pb for the PC + Harbolite™ waste form. Similar values of 6 for Se to 28,000 were calculated for the PC + Celite™ waste form. These values indicate that the solidification/stabilization technology evaluated for the spiked simulated HAD waste significantly reduced the leachability of these contaminants of concern.

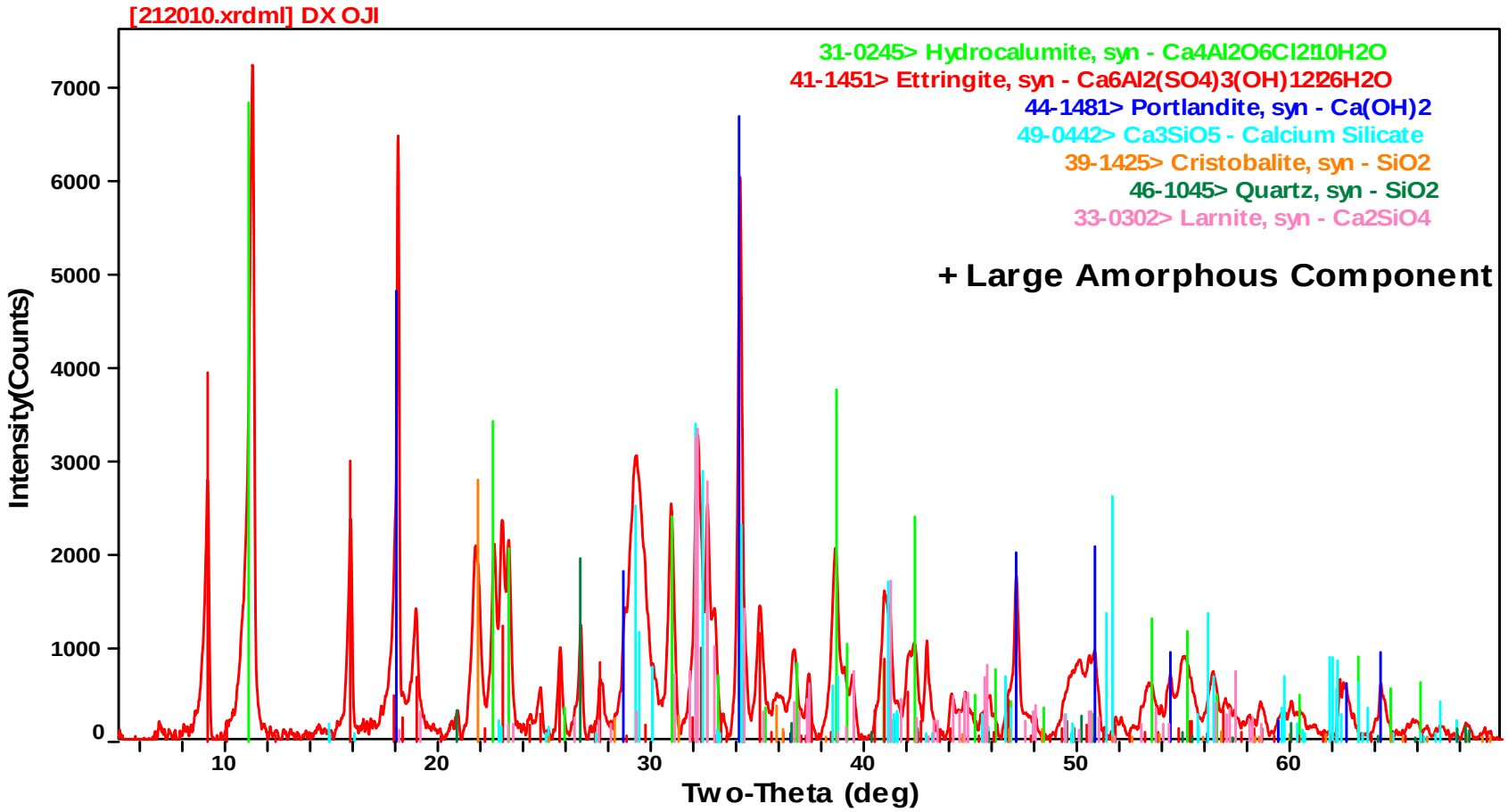


Figure 12. X-ray diffraction powder pattern of solidified simulated HAD waste. This sample contains: Portland cement, Celite™ (diatomaceous earth), and non radioactive spiked simulated waste.

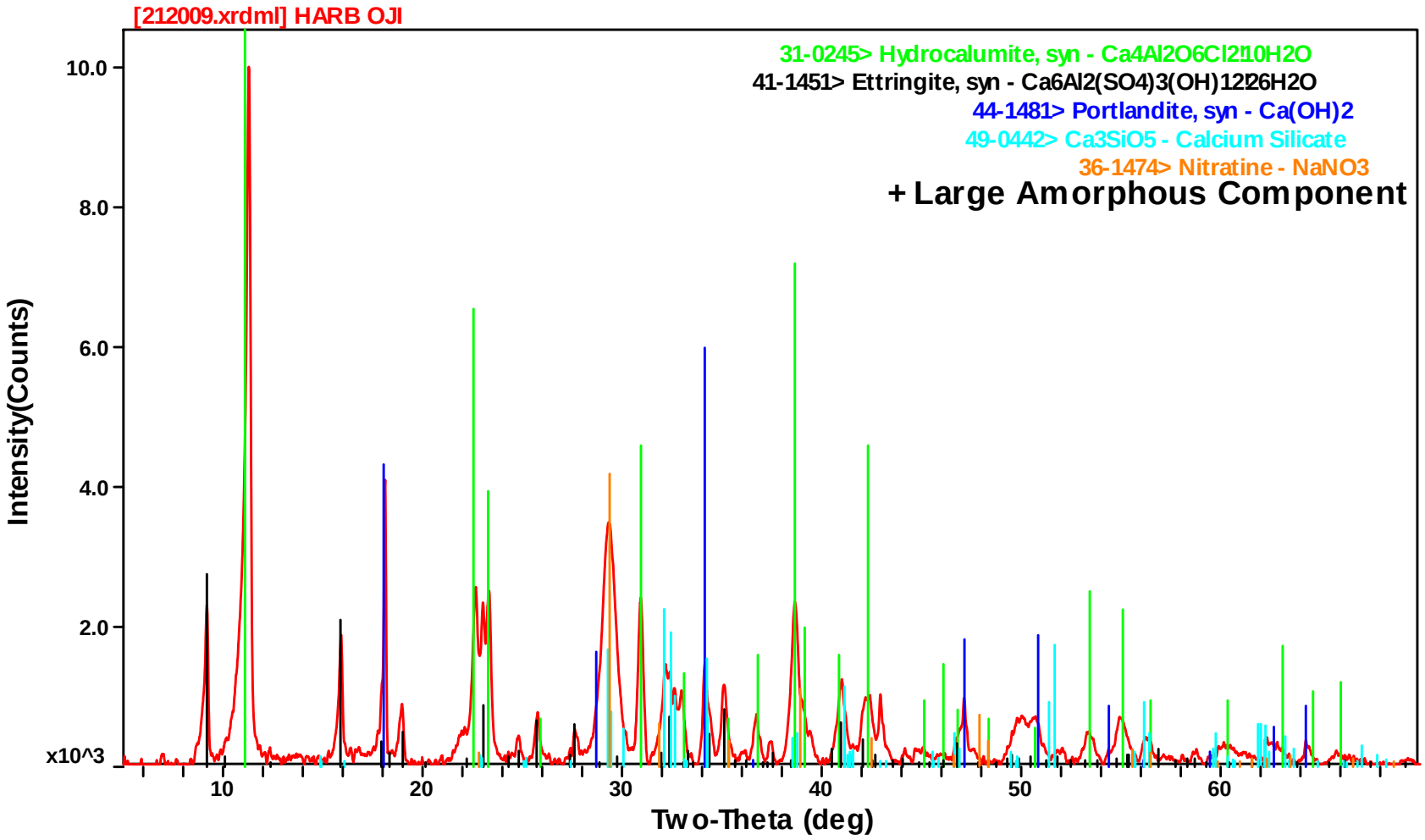


Figure 13. X-ray diffraction powder pattern of simulated HAD waste. This sample contains: Portland cement, Harbolite™ (perlite) and non radioactive spiked simulated waste.

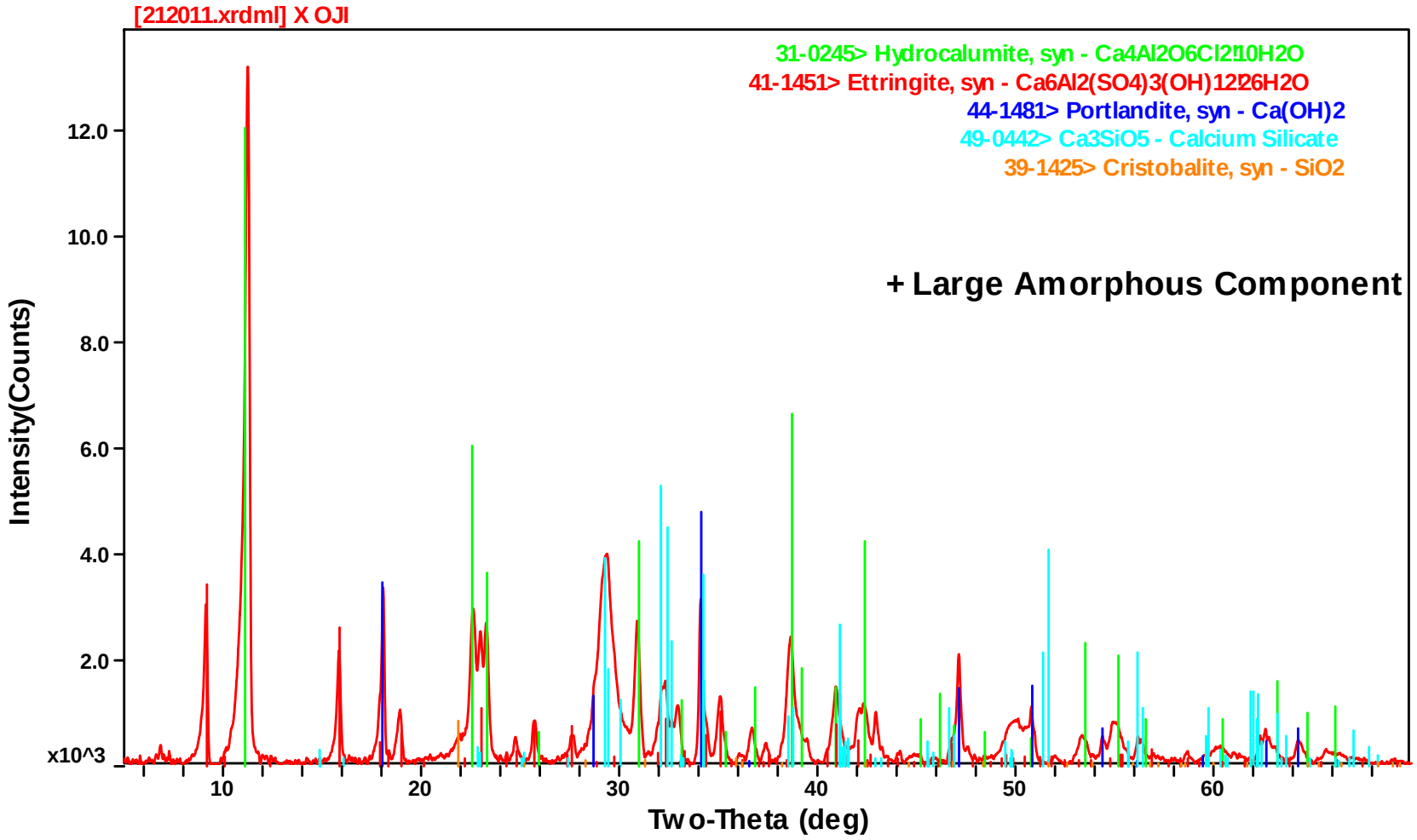


Figure 14. X-ray diffraction powder pattern of solidified simulated SRNL HAD waste. This sample contains: Portland cement, Harbolite™ (perlite) and non radioactive simulated waste.

Table 3. Summary phases present in the SRNL solidified HAD simulant samples.

Sample No.	Ingredinets	Wt.%	Waste Form Phases (after curing)
DX	Portland Cement	29.8	Hydrocalumite, $Ca_4Al_2O_6Cl_2 \cdot 10H_2O$
	Celite™ (diatomaceous earth)	19.9	Ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$
	Non radioactive spiked simulant	50.3	Portlandite, $Ca(OH)_2$
			Alite, Ca_3SiO_5 (unhydrated cement)
			Larnite, Ca_2SiO_4 (unhydrated cement)
			Cristobalite, SiO_2
			Large amount of amorphous material, C-S-H hydrate
X	Portland Cement	25	Hydrocalumite, $Ca_4Al_2O_6Cl_2 \cdot 10H_2O$
	Harbolite™ (perlite)	12.5	Ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$
	Non radioactive simulant	62.5	Portlandite, $Ca(OH)_2$
			Alite, Ca_3SiO_5 (unhydrated cement)
			Cristobalite, SiO_2
			Large amount of amorphous material, C-S-H hydrate
Harb	Portland Cement	24.8	Hydrocalumite, $Ca_4Al_2O_6Cl_2 \cdot 10H_2O$
	Harborlite (perlite)	12.4	Ettringite, $Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$
	Non radioactive spiked simulant	62.8	Portlandite, $Ca(OH)_2$
			Alite, Ca_3SiO_5 (unhydrated cement)
			Nitratine, $NaNO_3$ (salt precipitated from waste solution)
			Large amount of amorphous material, C-S-H hydrate

Table 4. TCLP results for a waste form containing PC + Harbolite + RCRA spiked simulant.

Element	Spiked Simulant Concentration (mg/L)	Waste form Concentration* (mg/Kg)	TCLP Leachate Concentration (mg/L)	TCLP Limit (mg/L)	UTS Limit (mg/L)	Non RCRA	TCLP Leachate Concentration if 100% Leached (mg/L)	Stabilization Factor Column H ÷Column C
A	B	C	D	E	F	G	H	I
Antimony	1.15	7.12E-06	NA	NA	1.15	NA	0.534	NA
Arsenic	5	3.10E-05	< 0.0550	5.0	5	Pass	2.32	> 42.22
Beryllium	1.22	7.55E-03	NA	NA	1.22	NA	0.567	NA
Cadmium	0.11	6.81E-07	< 0.00154	1.0	0.11	Pass	0.051	> 33.17
Lead	0.75	4.64E-06	< 1.00E-05	5.0	0.75	Pass	0.348	> 34830
Selenium	1	6.19E-06	< 0.0550	1.0	1	Pass	0.464	> 8.44
Thallium	0.2	1.24E-06	3.20E-05	NA	0.2	NA	0.093	2902
Vanadium	1.6	0.99E-06	1.12 E-03	NA	1.6	NA	0.743	663.4
Chromium	NA	NA	0.23	5.0	0.6	Pass	NA	NA

* 60 g sorbent mixture: PC (40 g) + Harbolite (20 g) + 100 g RCRA spiked simulant (1.5 g spike solution added)

Table 5. TCLP results for waste form containing PC + Diatomaceous earth + RCRA spiked simulant.

Element	Spiked Simulant Concentration (mg/L)	Waste form Concentration** (mg/Kg)	TCLP Leachate Concentration (mg/L)	TCLP Limit (mg/L)	UTS Limit (mg/L)	Non RCRA	TCLP Leachate Concentration if 100% Leached (mg/L)	Stabilization Factor Column H ÷Column D
A	B	C	D	E	F	G	H	I
Antimony	1.15	7.12E-06	NA	NA	1.15	NA	0.428	NA
Arsenic	5	3.10E-05	< 0.0550	5.0	5	Pass	1.861	> 33.8
Beryllium	1.22	7.55E-03	NA	NA	1.22	NA	0.454	NA
Cadmium	0.11	6.81E-07	< 0.00154	1.0	0.11	Pass	0.041	> 26.59
Lead	0.75	4.64E-06	< 1.00E-05	5.0	0.75	Pass	0.279	> 27920
Selenium	1	6.19E-06	< 0.0550	1.0	1	Pass	0.372	6.77
Thallium	0.2	1.24E-06	1.20E-05	NA	0.2	NA	0.074	> 6203
Vanadium	1.6	0.99E-06	< 2.00E-04	NA	1.6	NA	0.596	> 2978
Chromium	NA	NA	0.27	5.0	0.6	Pass	NA	NA

** 100 g sorbent mixture: PC (60 g) + diatomaceous earth (40 g) + 100 g of RCRA spiked simulant (1.5 g spike solution added)

Table 6. TCLP leaching results for waste form* containing PC + Harbolite + unspiked simulant (Control Sample).**

Element	Spiked Simulant Concentration (mg/L)	TCLP Leachate Concentration (mg/L)	TCLP Limit (mg/L)	UTS Limit (mg/L)
A	B	D	E	F
Antimony	0		NA	1.15
Arsenic	0	< 0.0550	5.0	5
Beryllium	0		NA	1.22
Cadmium	0	< 0.00154	1.0	0.11
Lead	0	1.00E-05	5.0	0.75
Selenium	0	< 0.0550	1.0	1
Thallium	0	< 1.00E-05	NA	0.2
Vanadium	0	< 2.00E-04	NA	1.6
Chromium	0	0.24	5.0	0.6

*** 60 g sorbent mixture (PC(40 g) + Harbolite (20 g)) + 100 g simulant.

5.0 CONCLUSIONS

Testing was performed on simulated and actual HAD waste using mostly inorganic solidification reagents with the objective of converting aqueous liquid waste into solid waste that can be disposed of in the SRS E-Area (low-level waste) or WIPP (TRU waste). Testing with simulated HAD waste was successful.

After developing a solidification reagent formulation using water, simulated HAD waste and a spiked HAD simulant, the technology was tested on three different actual HAD waste streams. SRNL Engineering supported disposal of the resulting solidified/stabilized actual HAD waste forms using existing procedures because the waste forms met the requirements for solid waste disposal.

Mixtures of Portland cement and inorganic wicking agents were identified as the most suited for solidification of the SRNL HAD waste. The best wicking agents tested were Harbolite™ (perlite) and Celite™ (diatomaceous earth). The wicking agents eliminated the need for mixing by quickly dispersing of the liquid waste into the stabilization reagents. The resulting final waste forms were self-supporting solids with no drainable liquid.

For most HAD liquid wastes, pH adjustment is not required prior to stabilization with the Portland cement-silicate wicking agent blends. Reagent to waste proportioning was typically 2:3 by weight. The reagent proportions were 2:1 by weight Portland cement to wicking agent. With these proportions, the solidification process took place in under five minutes and no mechanical mixing is required. The volume increase relative to the volume of the waste being solidified was typically a factor of 2 to 2.5 including the volume of the disposal container (poly-bottle).

The resulting final waste forms passed the TCLP test for all the RCRA metals tested, excluding mercury, silver and barium which were not included in the spike provided as part of this study.

6.0 RECOMMENDATIONS

Implement solidification/stabilization technology for SRNL HAD waste on a pilot-scale based on the encouraging results to date.

Stage the implementation so ITS/WPT personnel and SRNL Engineering have sufficient time and funding to work with individual waste generators to customize the stabilization reagents, identify and address unique disposal issues and perform comparative cost analysis for the sorbent components and others.

Finally, allocate additional funding to implement this technology at SRNL.

7.0 QUALITY ASSURANCE

Data obtained from this study reside as records in WSRC-NB-2001-00180.

8.0 REFERENCES

1. L. N. Oji, "Evaluation of Absorbents for Compatibility with Site Generated Hazardous and Mixed Liquid Wastes," WSRC-RP-2001-00966, Rev. 0
2. Modified Toxicity Characteristic Leaching Procedure, ADS-2572, Feb.7, 1998.

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