High Solids Consolidated Incinerator Facility (CIF) Wastes Stabilization with Ceramicrete and Super Cement

by

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**HIGH SOLIDS CONSOLIDATED INCINERATOR FACILITY (CIF) WASTES
STABILIZATION WITH CERAMICRETE AND SUPER CEMENT (U)**

JUNE 1, 1999

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SUMMARY

The Consolidated Incinerator Facility (CIF) at the Department of Energy Savannah River Site (SRS) burns low level radioactive and mixed waste. Ash and scrubber system waste streams are generated during the incineration process and are currently solidified with Portland cement. Magnesium Phosphate Ceramic (Ceramicrete™) and Slag Cement (Super Cement™) technologies were tested to evaluate their effectiveness to stabilize High Solids ash and scrubber solution (blowdown) waste streams, which are generated from incineration of radioactive diatomaceous earth filters. Waste Acceptance Criteria (WAC) used to evaluate solid waste forms generated are compressive strength, leaching of hazardous metals, bleed water, set time, and permeability. These criteria were used to generate the following summary statements.

- Ceramicrete™ solid waste forms made with scrubber solution, ash, and a combination of scrubber solution and ash meet the Waste Acceptance Criteria (WAC) of compressive strength > 500 psi, leaching levels for arsenic, mercury, barium, chromium, lead, selenium, silver, and cadmium less than the 40 CFR 268.48 Universal Treatment Standards, no bleed water after 24 hours, and a set time of less than 24 hours.
- The Ceramicrete™ blank, which should have the best permeability of the Ceramicrete™ samples prepared, had a permeability of 1×10^{-4} cm/s which does not meet the WAC requirement of 10^{-8} cm/s.
- After curing for 3 to 4 months Ceramicrete™ samples made with scrubber solution and ash exhibited cracking and visible crystal formation. The deterioration was caused by the formation of potassium chloride, sodium phosphate hydrate, and sodium calcium sulfate formation. Ceramicrete™ is not recommended for sodium chloride wastes because of the cracking and crystal formation observed with waste forms made with ash and scrubber solution.
- Super Cement™ solid waste forms made with scrubber solution and ash/scrubber solution combinations met the compressive strength, leaching, bleed water, permeability, and setting requirements of the WAC.
- Super Cement™ solid waste forms made with only ash passed all WAC requirements except the setting requirement. Modification of the formulation by adding calcium hydroxide or Portland cement resulted in a waste form that meets the setting requirement.
- Ash waste loadings up to 50 % by weight were achieved with Ceramicrete™ waste forms and up to 66.7 wt % were achieved with Super Cement™ waste forms which are greater than current plant Portland cement waste loadings of 31.8 %.
- Blowdown waste loadings up to 28 wt % were achieved with Ceramicrete™ waste forms and up to 43.1 wt % were achieved with Super Cement™ waste forms which

are less than current plant Portland cement waste loadings of 46 wt %. The waste loadings of blowdown waste forms for both CeramicreteTM and Super CementTM are actually greater than the plant waste loadings because samples in this study were concentrated up to 20 and 30 wt % total solids. The 46 wt % waste loading for the plant Portland cement is based on using blowdown solution with 10 wt % total solids because currently the plant has no equipment to concentrate the blowdown waste.

INTRODUCTION

High Solids ash and scrubber solution waste streams were generated at the incinerator facility at SRS by burning radioactive diatomaceous filter rolls which contained small amounts of uranium, and listed solvents (F and U). This report details solidification activities using selected Mixed Waste Focus Area (MWFA) technologies with the High Solids waste streams.

Solidification of a Low Solids ash and scrubber solution generated from incineration of a radioactive Purex waste containing small amounts of plutonium and other radionuclides will be covered in a final report due 9/30/99. Low Solids waste will be tested with Portland and Super CementTM technologies since the CeramicreteTM technology has permeability and waste form cracking problems.

Currently the waste solidification section of the incinerator uses Portland cement. SRS is modifying and upgrading the waste solidification part of the incinerator process to optimize solid waste form loadings, improve solid waste form characteristics, increase through put, and reduce equipment down time.

CeramicreteTM and Super CementTM technologies were chosen as the best possible replacement solidification candidates for the waste streams generated by the SRS incinerator from a list of several suggested Mixed Waste Focus Area technologies. These technologies were tested, evaluated, and compared to the current Portland cement technology being employed. Recommendation of a technology for replacement will depend on whether the technologies are superior to the current Portland cement technology in respect to meeting the WAC, have higher waste loadings, and are not prohibitively expensive in implementation or raw materials cost.

CeramicreteTM technology was developed at Argonne National Laboratory for the treatment of various low-level mixed wastes.¹ Setting is the result of an acid-base reaction which occurs at ambient temperature according to the following reaction given in Equation 1.²

Starting materials used in this study were prepared at Argonne National Laboratory specifically for this testing. The manufacture of the MgO was engineered to produce slow reaction with the KH₂PO₄. CeramicreteTM is the mixture of MgO and

KH_2PO_4 in stoichiometric quantities which when mixed with the stoichiometric amount of water will produce the hydrated product on the right side of Equation 1.

Super CementTM technology uses a cement binder of alkali activated slag cement. The cement consists of glassy blast furnace slag, and additives for TCLP improvement, dispersion, and pH adjustment. In this study two types of Super CementTM were used with different particle size. Since the Super CementTM formulation information is proprietary, specific details will not be released in this report without clearance from the manufacturer, ADTECHS Corp./JGC Corp.

EXPERIMENTAL

CeramicreteTM and Super CementTM solid waste forms were made with scrubber solution, ash, and a combination of ash and scrubber solution. The waste forms were then cured for 28 days and tests performed to determine if waste acceptance criteria were met.

Waste Form Acceptance Criteria

Acceptance criteria for the solid waste forms which include leachability, bleed water, compression testing, and permeability are listed in Tables I, II. Waste loading, mixing properties, and data on whether waste forms meet acceptance criteria will be compared to the current Portland cement solidification technology now used at the SRS incinerator for solidification of waste.

Table I. Acceptance Criteria for Freshly Prepared Waste Forms

<u>Property</u>	<u>Acceptance Criteria</u>
Bleed water	0 volume after 24 hours
Set time	Less than 3 days (shorter time preferred)
Mixability	low viscosity
Processibility	Minimal number of components

Table II. Acceptance Criteria for Cured Waste Forms

<u>Property</u>	<u>Acceptance Criteria</u>
Compressive Strength	> 500 psi
Permeability	< 10^{-8} cm/s
RCRA metal	Regulatory Limit (ppm)
As	5
Hg	0.025
Ba	7
Cr	0.86
Pb	0.37
Se	0.16
Ag	0.3
Cd	0.69

Note: RCRA metal regulatory leaching ppm limits are from 40CFR 268.48 Universal Treatment Standards³

High Solids Off Gas Scrubber Solution (Blowdown) Characterization

Characterization of the incinerator blowdown is given in Table III. The quench system is operated to produce blowdown containing close to 10 % total solids. The suspended solids of the blowdown used in this study were 1.5 % and contained mostly SiO_2 and $\text{Zn}(\text{OH})_2$. Dissolved solids results from analyses on plant samples were 8.2 % and are usually NaCl and Na_2SO_4 . The pH of the blowdown was 8.77 and the water content 90.3 %.

Table III. Scrubber Solution (Blowdown) Characterization

Component	(mg/liter)
Aluminum	541.5
Calcium	600.3
Iron	545.3
Magnesium	178.0
Sodium	32126.8
Fluoride	639.0
Formate	<10.0
Chloride	19,618.0
Nitrite	230.0
Nitrate	274.0
Phosphate	260.0
Sulfate	40247.0
Oxalate	<10.0

High Solids Ash Characterization

High Solids ash characterization of the incinerator ash is given in Table IV.

Table IV. High Solids Ash Characterization

Based on X-ray diffraction the ash contained :

Cristobalite; SiO_2

Silicon oxide; SiO_2

Anorthoclase; $(\text{NaK})(\text{AlSi}_3\text{O}_8)$

Magnetite; Fe_3O_4

Hematite; Fe_2O_3 .

The ash was wet quenched and contained 45 +/- 15 % quench water. Ash used in this study was drained of excess water which resulted in a water content of about 25%. The pH of the water in contact with the ash was 10.55.

Preparation of Ceramicrete™ Waste Forms

Ceramicrete™ waste forms were prepared by reacting calcined magnesium oxide with potassium phosphate under aqueous conditions and mixing with either the ash or scrubber solution or mixtures of ash and scrubber solution for 20 minutes then pouring into a plastic mold to set. The binder contains MgO and KH_2PO_4 in a mixture ratio of 9.4 grams to 32.0 grams respectively. During mixing, 0.08 grams of SnCl_2 and 0.04 grams of Na_2S were added for 100 grams of waste form generated to improve RCRA metal leaching characteristics. This process was repeated with different proportions of ash, scrubber solution, and combinations of ash and scrubber solution. The test matrix of waste forms composition is given in Table V.

The scrubber solution was evaporated before solidification to achieve higher salt waste loadings (up to 30 wt % total solids) in the waste form while maintaining the same amount of water. The samples were cured in sealed containers for 28 days. After removing the waste form from the molds the samples were divided for compressive strength and analytical testing.

Table V. Ceramicrete™ Test Matrix

Sample Number	Ash Wt (g)	Added H ₂ O Wt (g)	Blow down 10 wt % Solids(g)	Blow down 20 wt % Solids(g)	Blow down 30 wt % Solids(g)	Binder Wt (g)	Class F Fly ash Wt (g)
1	0	12.6	0	0	0	41.4	50
2	0	0	10	0	0	71.2	0
3	0	0	25	0	0	73.8	0
4	0	0	0	36.1	0	93.8	0
5	40	11.2	0	0	0	49.0	0
6	50	6.5	0	0	0	43.5	0
7	60	2.6	0	0	0	38.4	0
8	50	12.6	0	0	0	49.4	0
9	50	6.5	0	0	0	43.5	0
10	16.5	0	25	0	0	66.4	0
11	45	0	15	0	0	60.7	0
12	48	0	0	16	0	55.6	0
13	15	0	15	0	0	56.0	0
14	6.7	0	33.3	0	0	74.2	0
15	4.0	0	40.0	0	0	74.1	0
16	7.0	0	35.0	0	0	66.5	0
17	20	0	0	0	20	47.6	0
18	30	0	0	0	10	63.3	0
19	6.7	0	0	0	33.3	99.1	0
20	6.7	0	0	33.3	0	111.6	0

Notes for Table V:

- 1) Binder contains MgO and KH_2PO_4 mixture ratio of 9.4 grams to 32.0 grams.
- 2) .08 grams of SnCl_2 and .04 grams of Na_2S were added during mixing for each 100 grams of waste form generated to improve RCRA metal leaching characteristics.
- 3) Sample # 9 has no SnCl_2 or Na_2S
- 4) Total water content of the waste form = added water + BD water + ash water

Preparation of Super CementTM Waste Forms

Super CementTM waste forms were prepared according to Test Matrix VI. The water to cement ratio ranged from 0.5 to 1. Details concerning hardening, dispersing, and TMT15 agents are proprietary and will not be disclosed without ADTECHS Corp./JGC Corp. permission. Because the reagent details are proprietary the weight of Super CementTM and other additives are not listed in Test Matrix V. However, the total sample weight is listed so that the waste weight per cent can be easily seen.

Sodium sulfide and an organic reagent (TMT15) were added to the initial mix to improve leaching characteristics for toxic metals such as As, Se, Cr, and Pb. A dispersing reagent was added to samples containing ash to aid in dispersing the binder particles and fine ash particles.

Super CementTM waste form ingredients were mixed for 10 minutes. The sequence of mixing is to:

- 1) add waste
- 2) add TMT15 and sodium sulfide
- 3) add dispersing agent
- 4) add hardening agent
- 5) add Super CementTM.

Two different kinds of Super CementTM were used in this study (American and Japanese Super CementTM). The American Super CementTM had to be blended by adding powdered silicon oxide to blast furnace slag produced by KOCH Chemical Company. The Super CementTM from Japan by ADTECHS Corp./JGC Corp. does not need blending because it already contained silicon oxide.

Table VI. Super CementTM Test Matrix

Sample Number	SRS Ash Wt (g)	Added H ₂ O Wt (g)	Blow down 10 wt % Solids(g)	Blow down 20 wt % Solids(g)	Blow down 30 wt % Solids(g)	Total Sample Wt (g)
21	0	40.0	0	0	0	109.6
22	0	0	41.5	0	0	106
23	0	0	40.0	0	0	101.9
24	0	0	0	42.0	0	104.2
25	0	0	0	40.0	0	92.8
26	0	0	0	0	42.1	103.1
27	40	10.0	0	0	0	112
28	60	0	0	0	0	113.4
29	60	0	0	0	0	98.1
30	40.0	0	0	0	0	60
31	40.0	0	0	0	0	77.8
32	40.0	0	0	0	0	99
33	20.0	0	20.0	0	0	103.1
34	30.0	0	10.0	0	0	94.3
35	6.7	0	33.3	0	0	103.6
36	20	0	0	20	0	94.6
37	30.0	0	0	10	0	92.5
38	6.7	0	0	33.3	0	96.3
39	20	0	0	0	20	92.3
40	30	0	0	0	30	110.5
41	6.7	0	0	0	33.3	97.2

Note for Table VI:

All samples were made with American Super CementTM except for sample 39 and 40.

When none of the Super Cement™ solid waste forms made with ash set in 24 hours the formula was modified as given in Table VII.

Table VII. Super Cement™ Formula Modification

Sample Number	NaCl (g)	Ca(OH) ₂ (g)	P. Cem. (g)	S. Cem. (g)	Ash (g)	Water (g)	Waste Loading Wt %
42	0	2.5	0	50	50	30.0	37.8
43	0	12.5	0	40	50	34.3	36.6
44	0	0	12.5	40	50	40.0	35.1
45	7.6	0	0	45	50	24.6	39.3

Note: All samples in Table VII were made with Japanese type Super Cement™.

RESULTS

Freshly Prepared Waste Form Results

A substantial amount of bleed water was observed in Ceramicrete™ waste forms made with scrubber solution Samples 2,4 (Table V) but was absorbed after 24 hours of set time.

Table VIII. High Solids Ceramicrete™ Freshly Prepared Waste Form Criteria Evaluation

<u>Waste form Type</u>	<u>Set Time</u> <u>< 1 day</u>	<u>Bleedwater</u> <u>after 24 hrs.</u>	<u>Good</u> <u>Mixability</u>	<u>Easily</u> <u>Processed</u>
Ash	yes	no	yes	yes
Scrubber solution	yes	no	yes	yes
Ash and scrubber solution	yes	no	yes	yes

Super Cement™ solid waste forms made from only scrubber solution and a ash-scrubber solution combination using the original formulation set within 24 hours but waste forms made with ash using the original formulation did not.

The formulation modification of adding enough calcium hydroxide to the ash so that the calcium hydroxide is 25 wt % of the ash and calcium hydroxide mixture then treating with Super Cement™ resulted in a waste form that set within time requirements. Use of only 5 % by weight calcium hydroxide with ash and calcium hydroxide mixture and Super Cement™ treatment did not give a waste form that set within time requirements.

Formulation modification by adding Portland cement to the ash so the Portland cement is 25 % by weight of the Portland Cement and ash mixture followed by Super Cement™ treatment also gave waste forms that set with time constraints. The modification of adding 25 % by weight of NaCl in an ash and NaCl mixture then Super Cement™ treatment resulted in a waste form that did not set.

An overview of High Solids Super Cement™ Freshly Prepared Waste Forms is given in Table IX.

Table IX. High Solids Super Cement™ Freshly Prepared Waste Form Criteria Evaluation

<u>Waste form Type</u>	<u>Set Time</u> <u>< 1 day</u>	<u>Bleedwater</u> <u>after 24 hrs.</u>	<u>Good</u> <u>Mixability</u>	<u>Easily</u> <u>Processed</u>
Ash	no	no	yes	yes
Scrubber solution	yes	no	yes	yes
Ash and scrubber solution	yes	no	yes	yes
modified Ash	yes	no	yes	yes

Cured Waste Form Results

Compressive strength estimates were determined after 28 days of curing time by using a Penetrometer for Concrete model # HM-78 from the Gilson Company in Worthington, Ohio.

All Ceramicrete™ samples tested with the concrete penetrometer gave compressive strengths greater than 700 psi which exceeds our specification criteria of 500 psi. After prolonged curing crystalline type structures and swelling were observed in waste forms made with both blowdown and SRS ash (See Figure 1). This swelling resulted in cracking which does not meet durability criteria.

Figure 1. Ceramicrete™ waste form made with ash and scrubber solution

See Table X for an overview of Ceramicrete™ Cured Waste Form Test Results.

Table X. High Solids Ceramicrete™ Cured Waste Form Criteria Evaluation

<u>Waste form Type</u>	<u>> 500 psi Compressibility</u>	<u><10⁻⁸ cm/s permeability</u>	<u>Leachability limits met</u>
Blank waste form	yes	no	not applicable
Ash	yes	not tested	yes
Scrubber solution	yes	not tested	yes
Ash and scrubber solution	yes	not tested	yes

Compressive strengths of Super Cement™ waste forms made with scrubber solutions and a combination of scrubber solutions and ash were > 700 psi which meets acceptance criteria. Waste forms made with ash using the original formulation gave unacceptable compression results of < 500 psi.

Table XI. High Solids Super Cement™ Cured Waste Form Criteria Evaluation

<u>Waste form Type</u>	<u>> 500 psi Compressibility</u>	<u><10⁻⁸ cm/s permeability</u>	<u>Leachability limits met</u>
Blank waste form	yes	yes	not applicable
Ash	no	not tested	yes
Scrubber solution	yes	not tested	yes
Ash and scrubber solution	yes	not tested	yes
Modified Ash	yes	not tested	not tested

Scanning Electron Microscopy and X-ray Diffraction Results

The microstructure of the ash and waste forms made from the High Solids ash and scrubber solution were examined by scanning electron microscopy (SEM). Qualitative elemental analyses of these materials was obtained by energy dispersive x-ray analysis (EDX).

SEM of only the high solids ash indicates a very porous structure and EDX analyses shows the presence of Si, Fe, Al, Ca, and K. SEM of the Ceramicrete™ waste forms revealed a matrix phase consisting of short needle shaped crystals of $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}$ which were interlocked to form a solid coherent matrix. The needles are intergrown and the overall microstructure is relatively porous. The elemental profiles confirm the presence of sodium, sulfate, and chloride which could be distributed in pore spaces or the matrix of the waste form.

SEM micrographs of a Ceramicrete™ waste form containing ash and 30 wt % total solids scrubber solution displayed cracking, expansion, and crystal growth. KCl was detected in an elemental scan. Since the potassium was present as a component of the binder and the Cl was introduced from the waste, reaction between the cured binder, original binder components, and the scrubber solution has occurred. The sample structure is very porous and open. With prolonged curing there is more crystallization to a phase containing more potassium than in the fresh waste form.

X-ray diffraction analyses of the Ceramicrete™ waste forms reveals crystalline phases. Distinct peaks are seen for the binding magnesium potassium phosphate phase. MgO, which functions as a filler material in the matrix, also shows up as peaks in X-ray diffraction patterns.

The Ceramicrete™ matrix when prepared with tap water is $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ with trace amounts of MgO. When the same stoichiometrically proportional starting materials are mixed with High Solids scrubber solution an impure (XK) $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ phase and magnesium aluminum phosphate hydrate phase are formed. These phases were detected in X-ray diffraction patterns and in SEM/EDX elemental scans as struvite and montgomeryite. Struvite, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$, is not possible since the system does not contain ammonia, therefore the impure magnesium phosphate hydrate probably contains potassium. The other phase, montgomeryite, is probably also impure.

X-ray diffraction analysis of the ash-blowdown waste form after curing for 3 months indicated sodium phosphate hydrates, sylvine, potassium chloride, and sodium calcium sulfate. (See Appendix 3) The ash and blowdown waste react with the matrix phase magnesium potassium phosphate 6 hydrate to form the new phases which result in expansion, cracking, and sample deterioration.

Components found in Ceramicrete™ samples for the blowdown are:

$\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$

SiO_2 -silicon oxide

MgO-magnesium oxide.

Components in Ceramicrete™ samples made with the SRS ash and blowdown are:

$\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$

MgO-magnesium oxide

$\text{Ca}_4\text{MgAl}_4(\text{PO}_4)_6(\text{OH})_4 \cdot 12\text{H}_2\text{O}$ -Montgomeryite

The Ceramicrete™ blank with Coal ash components were $\text{KMgPO}_4 \cdot 6\text{H}_2\text{O}$ and SiO_2 .

SEM of the Super Cement™ waste forms indicate the presence of Ca and Si which is probably from the high solids ash. X-ray diffraction analyses of Super Cement™ waste forms reveals highly amorphous characteristics with few crystalline structures but does indicate calcite which is probably contributed by the incinerator waste.

Permeability Results

Permeability testing was conducted using Permeameter Model # K-670A purchased from ELE International in Lake Bluff, Illinois of the non radioactive blank samples of each technology to determine the best projected permeability for each technology. Portland Cement waste forms were prepared with 10 and 30 wt % NaCl solution which were also analyzed. A picture of the permeameter is given in Figure 2 on the next page.

Permeability results are summarized in Table XII. The data and calculations for these permeability determinations are given in Appendix 2.

Table XII. Waste Form Permeability

<u>Description</u>	<u>Permeability (cm/s)</u>
Ceramicrete™ Blank	1×10^{-4}
Portland Cement made with 10 % NaCl simulant	$< 1 \times 10^{-10}$
Portland Cement made with 30 % NaCl simulant	3×10^{-9}
Super Cement™ Blank	$< 1 \times 10^{-10}$

Figure 2. Permeameter manufactured by ELE

Leaching Results

A sample of ash submitted for TCLP without solidification passed all SRS leachability limits. The following are the analytical results for SRS High Solids ash TCLP:

Hg	Ag	As	Ba	Cd	Cr	Pb	Se
<DL	<DL	0.099	0.243	0.011	0.046	0.023	0.032

Initially blowdown solution contained:

Mercury	< .01 ppm
Silver	<0.025 ppm
Arsenic	2.56 ppm
Barium	0.12 ppm
Cadmium	0.211 ppm
Chromium	2.11 ppm
Lead	0.325 ppm
Selenium	0.65 ppm

Only selenium was outside SRS TCLP limits which are based on 40CFR 268.48 Universal Treatment Standards (UTS). For the eight RCRA metals the limits are:

Mercury	0.025 ppm
Silver	0.3 ppm
Arsenic	5 ppm
Barium	7 ppm
Cadmium	0.69 ppm
Chromium	0.86 ppm
Lead	0.37 ppm
Selenium	0.16ppm

Toxicity Characteristic Leaching Procedure (TCLP) results are given in Table XIII for selected representative CeramicreteTM waste forms made with SRS incinerator waste. The concentrations of the hazardous metals in the leachate meet SRS TCLP limits. Stabilization of heavy metal contaminants is due to chemical stabilization by reactions between the contaminants and the phosphates, followed by microencapsulation of the stabilized contaminants within the waste form matrix.

Table XIII. TCLP Results for Ceramicrete™ Waste Forms (mg/liter)

Sample	Hg	Ag	As	Ba	Cd	Cr	Pb	Se
1	<DL	<DL	.406	<DL	<DL	.014	<DL	.084
2	<DL	<DL	.082	<DL	<DL	.115	<DL	.028
4	<DL	<DL	.099	<DL	<DL	.016	<DL	<DL
5	<DL	<DL	.067	<DL	<DL	.016	<DL	<DL
7	<DL	<DL	.068	<DL	<DL	.008	<DL	<DL
10	<DL	<DL	.069	<DL	<DL	.005	<DL	<DL
12	<DL	<DL	.089	<DL	<DL	.011	<DL	.048
18	<DL	<DL	<DL	<DL	<DL	.025	<DL	.027
19	<DL	<DL	<DL	<DL	<DL	.019	<DL	<DL

<DL means less than the detectable limit. These limits are CrDL=.0056, AsDL=.045, SeDL=.0045, BaDL=.0051, CdDL=.0044, AgDL=.0073, PbDL=.0159, HgDL=.00035

All Ceramicrete™ samples pass WAC leaching requirements for RCRA metals. Sample 1 is a blank containing no ash or scrubber solution only coal ash. Waste forms in samples 2,4 (see matrix in Table IV) made with blowdown show a decrease in all chemical species. The selenium level in the blowdown which initially exceeded limits is within compliance after solidification. The waste forms in samples 5,7 made with SRS ash show a decrease in chemical species leaching. A decrease in leaching was also seen for samples 10, 12 made with both 10 wt % blowdown and SRS ash and samples 18, 19 made with ash and 30 % blowdown.

TCLP results are given in Table XIV. for selected representative Super Cement™ waste forms made with SRS incinerator waste. The concentrations of the hazardous metals in the leachate meet SRS requirements.

Table XIV. TCLP Results for Super Cement™ Waste Forms (mg/liter)

Sample	Hg	Ag	As	Ba	Cd	Cr	Pb	Se
22	<DL	<DL	<DL	.344	<DL	<DL	<DL	<DL
26	<DL	<DL	<DL	.172	<DL	<DL	<DL	.039
32	<DL	<DL	<DL	.182	<DL	<DL	<DL	<DL
35	<DL	<DL	<DL	.322	<DL	<DL	<DL	.027
38	<DL	<DL	<DL	.262	<DL	<DL	<DL	<DL
41	<DL	<DL	<DL	.206	<DL	<DL	.005	.035

All Super CementTM Samples meet WAC leaching requirements. Super CementTM waste form samples 22 and 26 made with scrubber solution showed a decrease in chemical species except for barium which showed an increase possibly from the Super CementTM changing barium bound in the blowdown in a non leachable form to a leachable form.

Super CementTM sample 32 made with only ash showed a decrease in chemical species except for barium which remained relatively constant. Samples 35, 38, and 41 made with a combination of ash and blowdown showed a leaching decrease in chemical species except for barium which showed an increase.

Waste Loading Results

The typical Portland cement plant waste loadings are 31.8 wt % for ash and 46.1 wt % for scrubber solution. Plant formulations are based on previous work performed by Don Fisher at SRS.^{4,5} The calculations for plant waste loadings are given in Appendix 1.

CeramicreteTM Waste Loadings are given in Table XV.

Table XV. CeramicreteTM Waste Loadings

Sample Number	Wt%		
	Wt% Bd	SRS Ash	Blowdown (BD) Total Solids Wt %
1	0	0	0
2	12	0	10
3	25.3	0	10
4	28.0	0	20
5	0	33	0
6	0	42	0
7	0	51	0
8	0	43.1	0
9	0	50.0	0
10	23	15	10
11	12.4	37.3	10
12	13	40	20
13	17.4	17.4	10
14	29.2	5.9	10
15	33.9	3.4	10
16	32.3	6.5	10
17	22.8	22.8	30
18	12.8	38.3	30
19	33.3	6.7	30
20	30.9	6.2	20

Super Cement™ waste loadings are given in Table XVI.

Table XVI. Super Cement™ Waste Loadings

Sample Number	Wt% Bd	Wt%	
		SRS Ash	Blowdown (BD) Total Solids Wt %
21	0	0	0
22	39.2	0	10
23	39.3	0	10
24	40.3	0	20
25	43.1	0	20
26	40.8	0	30
27	0	35.7	10
28	0	52.9	0
29	0	61.2	0
30	0	66.7	0
31	0	51.4	0
32	0	40.4	0
33	19.4	19.4	10
34	10.6	31.8	10
35	32.1	6.5	10
36	21.1	21.1	20
37	10.8	32.4	20
38	34.6	7.0	20
39	21.7	21.7	30
40	27.1	27.1	30
41	34.3	6.9	30

Notes for Tables XV and XVI:

- 1) Wt % Bd is the amount in grams of the blowdown or scrubber solution divided by the total weight of the sample that was incorporated in the waste form.
- 2) BD Total Solids Wt % is the concentration of the blowdown or scrubber solution that was incorporated in the waste form.

Waste loadings for Ceramicrete™ and Super Cement™ samples made with only scrubber solution were slightly less than those for the plant. Samples were made with 20 and 30 wt % scrubber solution which is not performed at the SRS incinerator currently. These concentrations were run because an evaporator is planned as part of plant modifications.

Higher waste loadings by weight were achievable with waste forms made with only ash for both the CeramicreteTM and Super CementTM technologies than that currently used by the incinerator. The waste loadings by volume conversions from waste loadings by weight for both Super CementTM and CeramicreteTM will be about the same since the densities of each type of waste form are similar. The waste form densities were:

Table XVII. Waste Form Densities

<u>Sample description</u>	<u>Density (g/ml)</u>
Super Cement TM and ash	1.9
Super Cement TM and scrubber solution	1.8
Ceramicrete TM and ash	1.8
Ceramicrete TM and scrubber solution	1.7

Conclusions

CeramicreteTM had high compressive strength and effectively stabilized hazardous contaminants in the high solids ash and scrubber solution (blowdown) wastes through chemical reaction and microencapsulation. Super CementTM samples also had high compressive strength and stabilized hazardous contaminants in high solids incinerator waste.

Viscosity of the CeramicreteTM is less than traditional Portland cement and should require less mixing torque. The viscosity of Super CementTM samples is comparable to samples made with Portland cement. Bleed water was observed initially for both the CeramicreteTM and Super CementTM made with blowdown but was absorbed after 24 hours. With waste forms made with blowdown and ash, crystallization as well as swelling seems to occur with CeramicreteTM samples. This phenomenon does not occur with Super CementTM.

CeramicreteTM waste forms exhibited high compressive strength 28 days after preparation but exhibited some physical deterioration after 3 to 4 months of curing. The deterioration was caused by waste and matrix reaction which form potassium chloride, sodium potassium hydrates, and sodium calcium sulfates. The formation of these salt phases resulted in expansion and cracking of the samples. Consequently, CeramicreteTM is not recommended for sodium chloride wastes.

Permeability of a blank made with only CeramicreteTM and no SRS ash or blowdown (best case scenario) were in the range of 1×10^{-4} cm/s which does not meet the current SRS permeability of 10^{-8} cm/s. A blank made with Super CementTM gave acceptable permeability measurements of $<1 \times 10^{-10}$ cm/s.

The CeramicreteTM waste forms generated with SRS ash and blowdown passed acceptance criteria for leachability, bleed water, and compression testing but do not seem to meet the SRS permeability acceptance criteria or durability requirements.

Setting problems with the Super CementTM waste forms made with only ash were overcome by adding calcium hydroxide or Portland cement to the ash before mixing with Super CementTM and water.

Waste forms made with Super CementTM meet all SRS acceptance criteria and have a higher waste loading for ash than the current Portland cement technology employed. Samples made with scrubber solution were slightly less than the waste loading of Portland cement. The actual waste loadings of blowdown waste forms for both CeramicreteTM and Super CementTM are actually greater than the plant waste loadings because samples in this study were concentrated up to 20 and 30 wt % total solids whereas the plant blowdown concentration is only 10 wt % total solids.

Super CementTM is a viable alternative to the current Portland cement solidification of SRS incinerator wastes. Issues that need to be addressed before recommending Super CementTM over the Portland cement technology are the cost of any plant modifications to use Super CementTM technology, cost of Super CementTM, cost of new additives, and the cost (if necessary) to license the technology from ADTECHS Corp./JGC Corp.

Quality Assurance

Quality Assurance testing was conducted in accordance with SRS procedures. Results are recorded in Laboratory Notebook WSRC-NB-96-633. The Task Technical Plan and Task Quality Assurance Plan are documented in WSRC-RP-98-01361 Rev. 0.

TCLP analyses were performed using the Toxic Characteristic Leaching Procedure EPA method 1311.

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References

¹D. Singh, A.S. Wagh, J.C. Cunnane, J.L. Mayberry, "Chemically Bonded Phosphate Ceramics for Low-Level Mixed-Waste Stabilization," J. Environ. Sci. Health, A32 (2), 527-541 (1997).

²A.D. Wilson and H.W. Nicholson, Acid-base cements, Cambridge Univ. Press (1993).

³40 CFR 268.48, Code of Federal Regulations 40, "Protection of Environment" Section 268.48.

⁴D.L. Fisher, 1995, "CIF Blowdown Stabilization: Formula Development Report (U)," WSRC-TR-95-00114, March 9, 1995.

⁵D.L. Fisher, 1996, "CIF Ashcrete Mixture Limits (U)," WSRC-TR-96-0169, June 14, 1996.

Appendix 1.

Waste Loadings Calculations for Portland Cement

Calculations

Comparison of waste loadings was performed by first determining the algorithm used by the plant to make Portland cement waste forms. For waste forms made with ash the algorithm is

$$y = .05582x^4 - .51808x^3 + 1.8576x^2 - 3.5521x + 4.162$$

Where x = water to ash ratio and y = slurry to cement ratio

This is used for x values greater than or equal to 1 and values less than or equal to 3.25. Optimally the plant tries to achieve an x value of 1.25.

For our case the ash contained 25 grams of water in 100 grams of ash. Since this is not a 1.25 ratio water must be added to the ash (in this case 100 grams). Doing this gives $x = 1.25$ and using the equation we find $y = 1.748$.

The amount of cement needed for mixing is found by dividing the slurry weight by y :
 $200 \text{ grams of slurry} / 1.748 = 114.4 \text{ grams of Portland cement needed.}$

The plant typical ash waste loading is therefore

$$100 \text{ grams of ash} / 314.4 \text{ grams total mix} \times 100 = 31.8 \% \text{ ash}$$

Waste Loadings for plant Portland cement made with scrubber solution uses the formulation of water/cement = .415/1.

The plant scrubber solution contains approximately 10 % wt total solids. For 100 grams of scrubber solution there is 90 grams of water. The amount of cement needed would therefore be 216.9 grams for this sample. A typical plant waste loading for scrubber solution is $100 \text{ grams of scrubber solution} / 216.9 \text{ grams of total mix} \times 100 = 46.1 \%.$

Appendix 2.

Permeability Calculations for Waste Forms

Calculations

1) Ceramicrete Blank Permeability

L = length of sample = .396 cm

D = diameter of sample = 2.66 cm

R = .5 x D = 1.33

A = $3.14 r \times r = 5.5836 \text{ cm}^2$

Manometer height 1 = h1 = 12.5

Manometer height 2 = h2 = 10.2

Average manometer height = h = $(h1 + h2)/2 = 11.35 \text{ cm}$

Pressure gauge 1 reading = P1 = 10 psig

Pressure gauge 2 reading = P2 = 0 psig

H = $(P1 - P2)70.31 + h = (10 - 0)70.31 + 11.35 = 714.45$

Q = volume collected/collection time = $54.52 \text{ cm}^3/60 \text{ seconds} = .9087 \text{ cm}^3/\text{s}$

Permeability = K = $QL/AH = (.9087)(.396)/(5.5836)(714.45) = 1 \times 10^{-4} \text{ cm/s}$

2) Portland cement made with 10 % NaCl simulant Permeability

L = length of sample = .793 cm

D = diameter of sample = 3.075 cm

R = .5 x D = 1.54

A = $3.14 r \times r = 7.42 \text{ cm}^2$

Manometer height 1 = h1 = 2 cm

Manometer height 2 = h2 = 3 cm

Average manometer height = h = $(h1 + h2)/2 = 2.5 \text{ cm}$

Pressure gauge 1 reading = P1 = 10 psig

Pressure gauge 2 reading = P2 = 0 psig

H = $(P1 - P2)70.31 + h = (10 - 0)70.31 + 2.5 = 705.6$

Q = volume collected/collection time = $0 \text{ cm}^3/12 \times 3600 \text{ seconds} = 0 \text{ cm}^3/\text{s}$

Solve for Q if K = $1 \times 10^{-10} \text{ cm/s}$

If Permeability = K = $QL/AH = (Q)(.793)/(7.42)(705.6) = 1 \times 10^{-10} \text{ cm/s}$

Q = .0036 mls/hr (this is probably the smallest flowrate that can be detected with the permeameter therefore the permeability of the sample is less than $1 \times 10^{-10} \text{ cm/s}$)

3) Portland cement made with 30 % NaCl simulant Permeability

L = length of sample = .863 cm

D = diameter of sample = 3.113 cm

$R = .5 \times D = 1.56$

$A = 3.14 r \times r = 7.61 \text{ cm}^2$

Manometer height 1 = $h_1 = 1.5 \text{ cm}$

Manometer height 2 = $h_2 = 2.5 \text{ cm}$

Average manometer height = $h = (h_1 + h_2)/2 = 2 \text{ cm}$

Pressure gauge 1 reading = $P_1 = 10 \text{ psig}$

Pressure gauge 2 reading = $P_2 = 0 \text{ psig}$

$H = (P_1 - P_2)70.31 + h = (10 - 0)70.31 + 11.35 = 714.45$

Q = volume collected/collection time = $.15 \text{ cm}^3 / 2.25 \text{ hrs} = 1.9 \times 10^{-5} \text{ cm}^3/\text{s}$

Permeability = $K = QL/AH = (1.9 \times 10^{-5})(.863)/(7.61)(705.1) = 3 \times 10^{-9} \text{ cm/s}$

4) Super cement Blank Permeability

L = length of sample = .568 cm

D = diameter of sample = 3.13 cm

$R = .5 \times D = 1.57$

$A = 3.14 r \times r = 7.74 \text{ cm}^2$

Manometer height 1 = $h_1 = 2.1 \text{ cm}$

Manometer height 2 = $h_2 = 2.3 \text{ cm}$

Average manometer height = $h = (h_1 + h_2)/2 = 2.2 \text{ cm}$

Pressure gauge 1 reading = $P_1 = 10 \text{ psig}$

Pressure gauge 2 reading = $P_2 = 0 \text{ psig}$

$H = (P_1 - P_2)70.31 + h = (10 - 0)70.31 + 2.2 = 705.3$

Q = volume collected/collection time = $0 \text{ cm}^3 / 12 \times 3600 \text{ seconds} = 0 \text{ cm}^3/\text{s}$

Solve for Q if $K = 1 \times 10^{-10} \text{ cm/s}$

If Permeability = $K = QL/AH = (Q)(.568)/(7.74)(705.3) = 1 \times 10^{-10} \text{ cm/s}$

$Q = .0035 \text{ mls/hr}$ (this is probably the smallest flowrate that can be detected with the permeameter therefore the permeability of the sample is less than $1 \times 10^{-10} \text{ cm/s}$)

Appendix 3.

CeramicreteTM Ash and Blowdown Waste Form XRD

<127401.MD> PBDWA30-1:1 WALKER

<127402.MDI> PBDWA10-5:1 WALKER