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RETENTION: Permanent

STABILIZATION OF HIGH AND LOW SOLIDS CONSOLIDATED INCINERATOR FACILITY (CIF) WASTE WITH SUPER CEMENT

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Date: September 30, 1999

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Stabilization of High and Low Solids Consolidated Incinerator Facility (CIF) Waste with super Cement

by

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STABILIZATION OF HIGH AND LOW SOLIDS CONSOLIDATED INCINERATOR FACILITY (CIF) WASTE WITH SUPER CEMENT (U)

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SUMMARY

The Consolidated Incinerator Facility (CIF) at the Savannah River Site (SRS) burns low-level radioactive waste and mixed waste as a method of treatment and volume reduction. The CIF generates secondary waste, which consists of ash and off-gas scrubber solution. Currently the ash is stabilized/solidified in the Ashcrete process with Portland cement. The scrubber solution (blowdown) is sent to the SRS Effluent Treatment Facility (ETF) for treatment as waste water. In the past, the scrubber solution was also stabilized/solidified in the Ashcrete process as blowcrete and will continue to be treated this way for listed waste burns and scrubber solutions that do not meet the Effluent Treatment Facility (ETF) Waste Acceptance Criteria (WAC).

CIF has a need to upgrade/modify the secondary waste treatment stabilization process for ash and blowdown to give a waste form with better waste acceptance characteristics, increase production rate, and modify equipment so that there is less downtime/maintenance.

The Mixed Waste Focus Area (MWFA) had a list of stabilization technologies that were evaluated for possible deployment at CIF. Magnesium Phosphate Ceramic (CeramicreteTM) and Slag Cement (Super CementTM) technologies were chosen from the list as the best possible alternatives to Portland cement to stabilize ash and scrubber solution (blowdown) waste streams and were evaluated in this study.

One ash and blowdown waste stream solidified in this study was generated from incineration of radioactive diatomaceous earth filters (High Solids). A second ash and blowdown (Low Solids) waste stream solidified was generated from burning Purex waste and low level solid waste containing trace amounts of plutonium.

Waste Acceptance Criteria (WAC) used to evaluate solid waste forms generated are a minimum compressive strength of 500 psi, no leaching of hazardous metals above RCRA limits, no bleed water after 24 hours, a set time of less than 1 days, and a permeability of less than 1×10^{-8} cm/sec. The SRS performance assessment model which qualified solid waste forms for trench land disposal required the 1×10^{-8} cm/sec permeability limits. Permeability was measured using a falling head method. Simulant permeabilities obtained with the falling head method were cross checked by centrifuge method analysis.

The CeramicreteTM solidification of High Solids ash and blowdown part of this study is detailed in a previous report.¹ CeramicreteTM waste forms had unacceptable permeabilities and those containing blowdown exhibited crystallization cracking

problems. For these reasons CeramicreteTM solidification of Low Solids incinerator waste was not pursued.

High Solids Super CementTM ash with setting agent solid waste forms pass acceptance criteria except for permeability. Initially High Solids Super CementTM ash waste forms did not pass setting requirements. This problem was remedied by adding calcium hydroxide setting agent as a formulation modification. Super Cement is not acceptable for solidification of High Solids 30 wt % blowdown solution waste forms because of permeability problems. The permeability of the waste form made with High Solids 10 wt % blowdown solution (unconcentrated) could not be determined because the sample was cracked.

Super CementTM ash Low Solids waste forms pass SRS acceptance criteria but waste forms made with blowdown (at all concentrations) fail permeability requirements.

High Solids ash stabilized with Portland cement meet SRS acceptance criteria including permeability. The highest blowdown concentration for the High Solids waste that can be stabilized with Portland cement and meet all acceptance criteria is 10 wt % total solids (which is unconcentrated blowdown). Waste forms made with blowdown above this concentration do not meet permeability requirements.

Low Solids Portland Cement ash solid waste forms meet all acceptance requirements while Low Solids Portland Cement blowdown solid waste forms (at all concentrations) fail permeability requirements.

Super CementTM is unsuitable for use to stabilize High Solids ash because it does not meet permeability requirements. Super CementTM is not acceptable for 30 wt % blowdown solution waste forms because of permeability problems. It is acceptable to stabilize Low Solids ash but not blowdown (because blowdown waste forms do not meet permeability requirements). Other disadvantages to using Super CementTM is that it is a more complicated process than Portland cement and it would require expensive plant modifications.

Portland cement is suitable to stabilize High Solids ash and blowdown up to 10 wt % total solids (unconcentrated blowdown). This technology also meets all acceptance requirements for Low Solids ash but fails permeability requirements for stabilizing Low Solids blowdown at any concentration.

Most of the waste forms for High and Low Solids are close to the 1×10^{-8} cm/sec permeability requirements for trench disposal of solidified waste forms. The performance assessment model used to generate these requirements will be evaluated again to see if samples that are more permeable might still result in waste forms that have acceptable leaching characteristics. If a more permeable sample is acceptable, Super CementTM or Portland cement applications could be increased.

INTRODUCTION

High Solids ash and scrubber solution waste streams were generated in the past at the incinerator facility at SRS by burning M area radioactive diatomaceous filter rolls which contained small amounts of uranium, and listed solvents (F and U). Low Solids ash and scrubber solution is currently being generated from incineration of a radioactive Purex waste containing small amounts of plutonium and other radionuclides.

Disposal plans for the CIF Ashcrete and Blowcrete depend on whether the waste burned in the incinerator is listed hazardous/mixed, characteristically hazardous/mixed, or radioactive. At the present time, SRS does not have an on-site disposal facility for listed hazardous/mixed waste even if the waste is treated and the resulting waste form passes the TCLP leaching requirements. An example of this type of waste/waste form is the High Solids Ashcrete and Blowcrete resulting from burning the M-Area Filter Paper Take-up Rolls.

The stabilized waste drums generated in this campaign are stored in M-Area. Off-site disposal at Envirocare is the preferred disposal option. Disposal of Low Solids ashcrete is by trench disposal after waste acceptance have been meet (compression, leaching, permeability).

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

This report details solidification activities using selected Mixed Waste Focus Area (MWFA) technologies with the High and Low Solids waste streams. 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 depends on waste form performance, process flexibility, process complexity, and cost of equipment and/or raw materials.

Low Solids waste was tested with only Super CementTM technology since the CeramicreteTM technology had permeability and waste form cracking problems when used in previous High Solids studies. Portland Cement reference samples with High and Low Solids incinerator waste were also generated for comparison with other solid waste form results.

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. 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.

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EXPERIMENTAL METHOD

Super CementTM and Portland cement solid waste forms were made with scrubber solution, ash, and a combination of ash and scrubber solution. All samples were mixed by hand stirring with a spatula in a plastic beaker for 10 minutes. The samples were cast as cylinders with a diameter of approximately 3 cm and heights varying from about 0.75 cm to 5 cm. Bleed water observations were conducted during the first three days of curing. After 28 days of curing compression testing was performed with a penetrometer. Samples were then cut from the solid waste forms with a hack saw and sent to an outside laboratory for RCRA metals leach tests.

Characterization data of the High Solids and Low Solids ash and blowdown used to make the solid waste forms are presented in Appendix 1.

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

Property	Acceptance Criteria
Bleed water	0 volume after 24 hours
Set time	Less than 1 day
Mixability	low viscosity
Processibility	Minimal number of components

Table II. Acceptance Criteria for Cured Waste Forms

Property	Acceptance Criteria
Compressive Strength	> 500 psi
Permeability	$< 1 \times 10^{-8}$ cm/s
RCRA metal leachability	Regulatory Limit (ppm)
As	5
Hg	0.025
Ba	7
Cr	0.86
РЬ	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 Standards.²

Compressive strength is usually performed by using a mechanical press to crush samples. The amount of force needed to cause the sample to fail is recorded and related to the area. In order to minimize the spread of contamination a method was developed to estimate compressive strength based on resistance to penetration with a Gilson penetrometer.

Waste Processing Technology (WPT) personnel at SRTC were requested to use an ELE Permeameter, which was available in the CIF Laboratory to perform the permeability measurements. This instrument is similar to the one described for ASTM D2434-68. In ASTM D2434-68 a constant low pressure head (constant head test) is used to determine permeability of high permeability materials such as sand or gravel. The ELE instrument is a modified version of this method called a falling head test.

Two non radioactive mixtures were prepared with Portland cement and a 10 and 30 wt % NaCl solution for the purpose of learning to use the ELE instrument and to obtain samples to send to UFA Ventures for permeability comparison testing using the centrifuge method. No offsite laboratories were equipped to handle permeability testing of radioactive samples.

The falling head method of determining permeability is based on Darcy's Law. An ELE permeameter, Model K-670A, was used in these experiments. A picture of the permeameter apparatus is given in Figure 1. A technique was developed to glue the disk-shaped samples into the ELE sample holder. The apparatus consists of a tank, tank manometer, inlet pressure gauge, outlet pressure gauge, pressure regulator, isolation valves, sample holder, two sample holder heads, connection tubing, and a sample head manometer. Water is forced from the tank through the sample and into a buret at the sample head outlet. The time that it takes to push a known amount of water through the sample is recorded. A schematic of the experimental apparatus is given in Figure 2.

The permeability is calculated using the following equation:

K = (QxL)/(AxH) = Permeability (cm/sec) whereh = (h1 + h2)/2 (cms)V = V2 - V1 (cm³)T = T2 - T1 (sec)Q = V/T = water flow rate (cm³/sec)L = length of the sample (cms)A = area of sample (cm²)H = (P_{in} - P_{out})x70.31 + h (cms)

h1 is the measured distance in centimeters between the top of the tank manometer level and the top of the sample holder manometer when the permeameter is open to the atmosphere before the analysis is performed. h2 is the measured distance in centimeters between the top of the tank manometer level and the top of the sample holder manometer when the permeameter is open to the atmosphere after the analysis is performed. V is the change in volume of the sample manometer (V2 - V1) from the beginning to the end of time interval, T = T2 - T1. P_{in} and P_{out} units are pounds per square inch (psi). The 70.31 is a factor to convert psi to centimeters in the H equation. Appendix 2 contains permeability calculations.

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The permeability results using the Falling Head method were compared to results obtained by UFA Ventures with an open flow Centrifuge method on duplicate samples to verify the accuracy of the Falling Head Method. The centrifuge method is effective because it allows the operator to set the variables in Darcy's Law. Darcy's Law states that the fluid flux equals the permeability times the fluid driving force. The driving force is fixed by imposing an acceleration on the sample through an adjustable rotation speed. The flux is fixed by setting the flow rate into the sample with an appropriate constant flow pump and dispersing the flow front evenly over the sample. Thus, the sample reaches the steady state permeability, which is dictated by that combined flux and driving force.



Figure 1. Permeameter manufactured by ELE

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Figure 2. Permeameter Schematic

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A UFA instrument consists of an ultracentrifuge with a constant, ultra-low flow pump that provides fluid to the sample surface through a rotating seal assembly and microdispersal system. The apparatus can reach accelerations of up to 20,000 g, temperatures can be adjusted from – 20 degrees to 150 degrees C. Effluent from the sample is collected in a transparent, volumetrically calibrated chamber at the bottom of the sample assembly. A diagram of the centrifuge internal parts is shown in Figure 3 and a picture of the instrument is shown in Figure 4.

Preparation of Super CementTM Waste Forms

Super CementTM waste forms were prepared according to Table III and Component Proportions given in Table IV. Super CementTM Low Solids waste form compositions are given in Table V and Component proportions in Table 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 additives are not listed in any Table in this report.

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.

The Super CementTM from Japan by ADTECHS Corp./JGC Corp. containing blended silicon oxide was used in this study.

Preparation of Portland Cement Waste Forms

Portland cement formulations were determined by an algorithm used by the plant to make solid waste forms. See appendix 3 for plant algorithm information.

Ingredients in the High Solids Portland cement formulations prepared for this study are listed in Table III. The weight per cents of different components in the High Solids formulations are shown in Table IV. Ingredients in the Low Solids Portland cement formulations prepared for this study are listed in Table V. The weight per cents of different components in the Low Solids formulations are shown in Table VI.



Figure 3. Centrifuge Internal Parts



Figure 4. Picture of UFA Centrifuge

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Table III. High Solids Waste Forms Composition

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<u>No.</u>	Sample Descrip.	PC Wt (g)	SC Wt (g)	Add. H ₂ O Wt (g)	Scrub. Soln. 10wt% (g)	Scrub. Soln. 20wt% (g)	Scrub. Soln. 30wt% (g)	Dry Ash (g)	Other Comps (g)
1	Portland Cem. With 10 Wt % Solids Scrub. Sol	86.8 In.	-	-	40.0	-	-	-	-
2	Portland Cem. With 30 Wt % Solids Scrub. So	84.2 oln.	-	-	-	-	61.0	-	-
3	Portland Cem. With ash	44.2	-	39.8	-	-	-	23.8	-
4	Portland Cem. With 10 wt % Solids Scrub. Sol and ash	76.4 In.	-	1.7	33.3	-	-	5.0	-
5	Portland Cem. With 30 wt % Solids Scrub. Soln. and ash	60.2	-	1.7	-	-	33.3	5.0	-
6	Super Cem. Blank	-	62.0	45.7	-	-	-	-	1.9
7	Super Cem. 5wt%Ca(OH) ₂ in ash and Ca(OH) ₂ mix	-	50.0	42.5	-	-	-	37.5	2.5
8	Super Cem. 25wt%Ca $(OH)_2$ in ash and Ca $(OH)_2$ mix	-	40.0	46.8	-	-	-	37.5	12.5
9	Super Cem. 25wt% PC in ash and PC mi	12.5 x	40.0	52.5	-	-	-	37.5	-
10	Super Cem. 5wt% NaCl in ash and NaCl 1	- mix	45.0	37.1	-	-	-	37.5	7.6

<u>No.</u>	Sample Descrip.	PC Wt (g)	SC Wt (g)	Add. H ₄ O Wt (g)	Scrub. Soln. 10wt% (g)	Scrub. Soln. 20wt% (g)	Scrub. Soln. 30wt% (g)	Dry Ash (g)	Other Comps (g)
11	Portland Cem. 10 wt% NaCl simulant	100.0	-	41.5	-	-	-	-	4.6
12	Portland Cem. 30 wt% NaCl simulant	100.0	-	41.5	-	-	-	-	17.8
13	Super Cem. 30 wt% Solids Scrub. Soln.	-	52.5	-	-	-	43.1	-	8.5
14	Super Cem. 10 wt% Solids Scrub. Soln.	-	56.5	-	41.5	-	-	-	8.0

Table III. High Solids Waste Forms Composition Continued

Table III notes: 1) The wt % scrubber solution refer to the concentration of total solids in the solution. 2) Initially the ash contained close to 25 weight % water. The ash amount is reported in this table on a dry basis and the ash water included in the additional water column. 3) Samples 7,8,9,10 contain a % of additive to try and improve setting

Table IV. High Solids Waste Form Component Proportions

No.	Sample Descrip.	Port. Cem. (wt %)	Sup. Cem. wt%)	Add. Water (wt <u>%</u>)	S. Soln. Solids (wt %)	Dry Ash (wt%)	Other Comp. (wt %)	<u> W/C</u>
1	Portland Cem. With 10 Wt % Solids Scrub. So	68.4 In.	-	-	31.6	-	-	0.42
2	Portland Cem. With 30 Wt % Solids Scrub. So	58.0 In.	-	-	42.0	-	-	0.51
3	Portland Cem. With ash	41.0	-	36.9	-	22.1	-	0.90
4	Portland Cem. With 10 wt % Solids Scrub. So and ash	65.6 In.	-	1.5	28.6	4.3	-	0.46

No	Sample Descrip.	Port. Cem. (wt %)	Sup. Cem. <u>wt%)</u>	Add. Water (wt %)	S. Solr Solids (wt %)	n. Dry Ash (wt%)	Other Comp. (wt %)	<u>W/C</u>
5	Portland Cem. With 30 wt % Solids Scrub. So And ash	60.1 In.	-	1.7	33.2	5.0	-	0.42
6	Super Cem. Blank	-	56.6	41.7	-	-	1.7	0.74
7	Super Cem. 5wt%Ca(OH) ₂ in ash and Ca(OH) ₂ mix	-	37.7	32.1	-	28.3	1.9	0.85
8	Super Cem. 25wt%Ca(OH) ₂ in ash and Ca(OH) ₂ mix	-	29.2	34.2	-	27.4	9.2	1.2
9	Super Cem. 25wt% PC in ash and PC m	8.8 ix	28.1	36.8	-	26.3	-	1.0
10	Super Cem. 5wt% NaCl in ash and NaCl 1	- nix	35.4	29.2	-	29.5	5.9	0.82
11	Portland Cem. 10 wt% NaCl simulant	68.4	-	2 8.4	-	-	3.2	0.42
12	Portland Cem. 30 wt% NaCl simulant	62.8	-	26.0	-	-	11.2	0.42
13	Super Cem. 30 wt% Solids Scrub. Soln.	-	50.4	-	41.4	-	8.2	0.57
14	Super Cem. 10 wt% Solids Scrub. Soln.	-	53.3	-	39.2	-	7.5	0.66

Table IV. High SolidsWaste Form Component Proportions Continued

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Table IV notes: 1) The wt % scrubber solution refers to the concentration of total solids in the solution. 2) Initially the ash contained close to 25 weight % water. The ash amount is reported in this table on a dry basis and the ash water included in the water column. 3) W/C is water to cement ratio

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Table V. Low Solids Waste Forms Composition

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<u>No.</u>	Sample Descrip.	PC Wt (g)	SC Wt (g)	Add. H ₂ O Wt (g)	Scrub. Soln. 1wt% (g)	Scrub. Soln. 10wt% (g)	Scrub. Soln. 20wt% (g)	Scrub. Soln. 30wt% _(g)	Scrub. Soln. 40wt% (g)	Dry Ash (g)	Other Comps (g)
15	Portland Cem.1 Wt Solids Scr Soln.	136.9 % ub.	-	-	63.1	-	-	-		-	-
16	Portland Cem.30 W Solids Scr	101.2 7t % rub. Solr	- 1.	-	-	-	-	60.0	-	-	-
17	Portland Cem. 10 wt Scrub. Soln	130.2 : %	-	-	-	60.0	-	-	-	-	-
18	Portland Cem.40 Wt Solids Scrub. Soli	86.7 : % n.	-	-	-	-	-	-	60.0	-	-
19	Portland Cem. with wet as	77.5 h	-	80.7	-	-	-	-	-	41.8	-
20	Portland Cem. with wet as	140.0 h	-	80.7	-	-	-	-	-	41.8	-
21	Portland Cem. Plant Ashcrete	225.0	-	168.0	-	-	-	-	-	14.4	-
22	Super Cem.20 wt % Solids Scrub. Solr	- S 1.	77.0	-	-	-	60.0	-	-	-	11.8
23	Super Cem.10 wt % Solid Scrub. Soli	- · S 1.	81.7	-	-	60.0	-	-	-	-	11.6

<u>No.</u>	Sample Descrip.	PC Wt (g)	SC Wt (g)	Add. H ₂ O Wt (g)	Scrub. Soln. 1wt% (g)	Scrub. Soln. 10wt% (g)	Scrub. Soln. 20wt% (g)	Scrub. Soln. 30wt% (g)	Scrub. Soln. 40wt% (g)	Dry Ash (g)	Other Comps (g)
24	Super Cem. 30 wt % Solids Scrub. Soln.	-	73.1	-	-	-	-	6 <u>0</u> .0	-	-	11.9
25	Super Cem.40 wt % Solids Scrub. Soln.	-	72.3	-	-	-	-	-	60.0	-	12.0
26	Super Cem. 1wt % Solids Scrub. Soln.	-	62.0	-	40.0	-	-	-	-	-	8.0
27	Super Cem. Wet Ash with Setting agent	-	40.0	12.5	i -	-	-	-	-	37.5	17.1
28	Super Cem. Wet Ash no setting age	- ent	40. 0	15.0)	-	-	-	-	45.0	11.8

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Table V. Low Solids Waste Forms Composition Continued

Table V notes: 1) Wt % scrubber solution refer to the concentration of total solids in the solution. 2) Initially the ash contained close to 25 weight % water. The ash amount is reported in this table on a dry basis and the ash water included in the additional water column.

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Table VI. Low Solids Waste Form Component Proportions

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<u>No</u>	Sample Descrip.	Port. Cem. (wt %)	Sup. Cem. wt%)	Add. Water (wt %)	S. Soln. Solids (wt %)	Dry Ash (wt%)	Other Comp. (wt %)	<u>W/C</u>
15	Portland Cem.1 Wt % Solids Scrub. Sol	68.5 n.	-	-	31.5	-	-	0.44
16	Portland Cem. With 30 Wt % Solids Scrub. Sol	62.8 In.	-	-	37.2	-	-	0.40
17	Portland Cem. 10 wt % Scrub. Soln	68.5	-	-	-	31.6	-	0.40

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NT.	Sample	Port. Cem.	Sup. Cem.	Add. Water	S. Soln. Solids	Dry Ash	Other Comp.	WC
<u>No.</u>	Descrip.	(wt %)	(Wt%)	(Wt %)_	_(Wt %)	(Wt%)	(WL %)	<u></u>
18	Portland Cem. 40wt Scrub. Soln	59.1	-	-	40.9	-	-	0.47
19	Portland Cem. With wet ash	38.7	-	40.4	-	20.9	-	1.04
20	Portland Cem. with wet ash	53.3	-	30.7	-	15.9	-	0.58
21	Portland Cem. Plant Ashcrete	55.2	-	41.2	-	3.5	-	0.75
22	Super Cem. With 20 wt % Solids Scrub. So	- In.	51.8	-	40.3	-	7.9	0.62
23	Super Cem. With 10 wt % Solids Scrub. So	 ln.	53.3	-	39.1	-	7.6	0.66
24	Super Cem. 30 wt % Solids Scrub. So	- In.	50.4	-	41.4	-	8.2	0.58
25	Super Cem. 40wt% Solids Scrub. Soln.	-	50.1	-	41.6	-	8.3	0.50
26	Super Cem. 1wt% Solids Scrub. Soln.	-	56.4	-	· 36.4	-	7.2	0.64
27	Super Cem. Wet Ash with setting agent	-	37.4	11.7	-	35.0	16.0	0.31
28	Super Cem. Wet Ash no setting agent	-	35.8	13.4	-	40.3	10.6	0.37

Table VI. Low Solids Waste Form Component Proportions Continued

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Table VI notes: 1) Scrubber solution solids refers to the concentration of total solids in the solution. 2) Initially the ash contained close to 25 weight % water. The ash amount is reported in this table on a dry basis and the ash water included in the water column. 3) W/C is water to cement ratio

RESULTS

Processing Properties

High Solids Super CementTM Processing Properties are given in Table VII.

Table VII. High Solids Super CementTM Processing Properties Evaluation

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

Super CementTM High Solids waste forms made from only scrubber solution and a ashscrubber solution combination using the original formulation set within 24 hours. Waste forms made with only ash using the original formulation did not set after 24 hours.

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 CementTM 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 CementTM 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 CementTM 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 CementTM treatment resulted in a waste form that did not set.

Low Solids Super CementTM Processing Properties are given in Table VIII.

14010 1111. 1.011 00.	nus ouper con		Griepermee =	
	Set Time	Bleedwater	Good	Easily
Waste form Type	<u>< 1 day</u>	<u>after 24 hrs.</u>	<u>Mixability</u>	Processed
Ash	yes	no	yes	yes
Scrubber solution	yes	no	yes	yes
Ash and scrubber solution	yes	no	yes	yes
Modified Ash	ves	no	yes	yes

Note: A bleed water problem was observed with the Low Solids Portland cement ash waste forms made for comparison testing but not in the Low Solids Super Cement ash waste forms.

Cured Waste Form Properties

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.

Compressive strengths of High Solids Super CementTM waste forms made with scrubber solutions and a combination of scrubber solutions and ash were > 700 psi which meets acceptance criteria. High Solids Super CementTM waste forms made with ash using the original formulation gave unacceptable compression results of < 500 psi but waste forms made with calcium hydroxide reagent pass compression requirements.

High Solids Super CementTM cured properties are listed in Table IX.

Table IX. High Solids Super Cement TM Cured Properties Evaluation						
	> 500 psi	$<1x 10^{\circ} \text{ cm/s}$	Leachability			
Waste form Type	Compressibility	permeability	<u>limits met</u>			
Blank waste form	yes	yes	not applicable			
Ash	no	yes	yes			
Scrubber solution	yes	no	yes			
Ash and scrubber solution	yes	not tested	yes			
Modified Ash	yes	no	yes			

Table VIII. Low Solids Super CementTM Processing Properties Evaluation

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Compressive strengths of Low Solids Super CementTM 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 also gave acceptable compression results of > 700 psi.

Table X. Low Solids Super CementTM Cured Waste Form Criteria Evaluation

Waste form Type	> 500 psi <u>Compressibility</u>	<1x 10 ^{-°} cm/s permeability	Leachability limits met
Ash, no Ca(OH) ₂	yes	no	yes
Scrubber solution	yes	no	yes
Ash and scrubber solution	yes	not tested	yes
Ash, with Ca(OH) ₂	yes	yes	yes

Permeability Results

Two non radioactive mixtures were prepared with Portland cement and a 10 and 30 wt % NaCl solution for the purpose of learning to use the ELE instrument and to obtain samples to send to UFA Ventures for permeability testing using the centrifuge method. These formulations were cast into several sample containers which were sealed for curing.

The non radioactive simulant samples made with 10 and 30 wt % NaCl were used to establish a correlation between the falling head and whole body centrifuge permeability results. Results obtained by the centrifuge method were one order of magnitude higher (10x more permeable) than those obtained by the falling head method. This correlation was used to estimate centrifuge permeability results because radioactive samples could not be analyzed using this method. Therefore in Tables XI through XIV the falling head permeability values were measured and the centrifuge permeability values were calculated. Since the centrifuge method is the worst case scenario it was decided to use the predicted centrifuge results in determining whether samples met permeability acceptance criteria.

Permeabilities of High Solids Portland cement sample were determined for comparison with High Solids Super cement sample permeabilities and are given in Table XI.

The highest High Solids blowdown concentration that can be stabilized with Portland cement is 10 wt % total solids. High Solids ash stabilized with Portland cement gives a centrifuge permeability which meets SRS acceptance requirements.

	H	Falling Head		Est. Centrif.	
Sample	Sample H	Permeability	E-Area	Permeability	E-Area
Number	Description	(cm/s)	WAC	(cm/s)	WAC
11	Simulant with 10 wt % NaCl solution	<1.7x10 ⁻¹⁰	Pass	1.7x10°	Projected Pass
12	Simulant with 30 wt % NaCl solution	2.9x10 ⁻⁹	Pass	3.1x10 ⁻⁸	Projected Fail
1	blowcrete with 10 wt % solids scrub. solutio	6.2x10 ⁻¹⁰	Pass	6.2x10°°	Projected Pass
2	blowcrete with 30 wt % solids scrub. solutio	7.5x10° ∞n	Pass	7.5x10*	Projected Fail
3	ashcrete	6.2x10 ⁻¹⁰	Pass	6.2x10 ⁻⁹	Projected Pass

Table XI. High Solids Portland Cement Waste Form Permeabilities

High Solids Super cement sample permeabilities are given in Table XII.

Table XII. High Solids Super Cement Waste Form Permeabilities

		Falling Head		Est. Centrif.	
Sample	e Sample	Permeability	E-Area	Permeability	E-Area
Numbe	r Description	(cm/s)	WAC	(cm/s)	WAC
8	ashcrete 25wt%Ca(OH) ₂ in ash and Ca(OH) ₂ mi	4.8x10 ⁻⁹ x	Pass	4.8x10 ⁻⁸	Projected Fail
13	blowcrete with 30 wt % solids scrub. solut	4.6x10 ⁻⁷	Fail	4.6x10 ⁻⁶	Projected Fail
14	blowcrete with 10 wt % solids scrub. solut	8.0x10 ⁻⁷	Unknov	vn 8.0x10°	Unknown

Centrifuge permeabilities for High Solids Super Cement waste forms made with ash and blowdown at 30 wt % concentrations do not meet SRS requirements. Sample 14 seemed

to be cracked which could give an erroneous permeability value.

Low Solids Portland Cement permeability test results are summarized in Table XIII:

Sample	Sample	Falling Head	E-Area	Est. Centrif. Permeability	E-Area
Number	r Description	(cm/s)	WAC	(cm/s)	WAC
15	Purex blow crete with 1 wt % solids scrub. solution	2.0x10° on	Pass	2.0x10 ⁻⁸	Projected Fail
18	Purex blow crete with 40 wt % solids scrub. solution	8.5x10° on	Pass	8.5x10*	Projected Fail
19	Purex ashcrete	<4.2x10 ⁻¹⁰	Pass	<4.2x10 ⁻⁹	Projected Pass
21	CIF Plant Purex	<7.4x10 ⁻¹⁰	Pass	<7.4x10 ⁻⁹	Projected Pass

Table XIII. Low Solids Portland Cement Waste Form Permeabilities

The 10x correlation was used to estimate that Low Solids Portland cement Ashcrete centrifuge method results would meet permeability requirements. Low Solids Portland cement blowcrete made with 1 and 40 wt % scrubber solution centrifuge permeability results does not meet SRS requirements.

Low Solids Super CementTM permeability results are given in Table XIV.

Table XIV. Low Solids Super CementTM Permeabilities

		Falling Head		Est. Centrif.	
Sam	ole Sample	Permeability	E-Area	Permeability	E-Area
Num	ber Description	(cm/s)	WAC	(cm/s)	WAC
27	ashcrete with setting agent	6.7x10 ⁻¹⁰	Pass	6.7x10 ⁻⁹	Projected Pass
28	ashcrete no setting agent	1.6x10 ⁻⁹	Pass	1.6x10 ⁻⁸	Projected Fail

		Falling Head		Est. Centrif.	
Sample	Sample	Permeability	E-Area	Permeability	E-Area
Number	Description	(cm/s)	WAC	(cm/s)	WAC
25	blowcrete with 40 wt % solids scrub. soli	7.5x10 ⁻⁷ ution	Fail	7.5x10 ⁻⁶	Projected Fail
23	blowcrete with 10 wt % solids scrub, soli	1.5x10°	Pass	1.5x10 ^{-s}	Projected Fail

Table XIV. Low Solids Super CementTM Permeabilities Continued

Centrifuge permeabilities for Super CementTM waste forms made with all concentrations of blowdown fail to meet acceptance criteria. Ashcrete Super CementTM waste forms made without the setting agent fail permeability requirements but ashcrete with setting agent passes.

Compressive Strength

Compressive strengths of all samples tested except for High Solids Super CementTM ashcrete without calcium hydroxide additive were greater than 700 psi using the penetrometer method.

Leaching Results

A sample of High Solids ash submitted for Toxicity Characteristic Leaching Procedure (TCLP) testing without solidification passed all SRS leachability limits. The following are the analytical results for SRS High Solids ash TCLP before solidification:

<u>Hg Ag As Ba Cd Cr Pb Se</u> <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

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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

TCLP results are given in Table XV for selected representative High Solids Portland cement waste forms made with SRS incinerator waste. The concentrations of the hazardous metals in the leachate meet SRS TCLP limits.

Table XV.	TCLP Results	for High Solid	s Portland Cement	Waste Forms	(mg/liter)

<u>Nc</u>	<u>. Hg</u>	Ag	As	Ba	Cd	Cr	Pb	Se_	Description
									· · · ·
1	<dl< td=""><td>0.02</td><td><dl< td=""><td>0.98</td><td><dl< td=""><td>0.05</td><td><dl< td=""><td>0.03</td><td>P. Cem.10wt % T. Solids</td></dl<></td></dl<></td></dl<></td></dl<>	0.02	<dl< td=""><td>0.98</td><td><dl< td=""><td>0.05</td><td><dl< td=""><td>0.03</td><td>P. Cem.10wt % T. Solids</td></dl<></td></dl<></td></dl<>	0.98	<dl< td=""><td>0.05</td><td><dl< td=""><td>0.03</td><td>P. Cem.10wt % T. Solids</td></dl<></td></dl<>	0.05	<dl< td=""><td>0.03</td><td>P. Cem.10wt % T. Solids</td></dl<>	0.03	P. Cem.10wt % T. Solids
2	<dl< td=""><td>0.01</td><td><dl< td=""><td>0.47</td><td><dl< td=""><td>0.08</td><td><dl< td=""><td>0.06</td><td>P. Cem.30wt % T. Solids</td></dl<></td></dl<></td></dl<></td></dl<>	0.01	<dl< td=""><td>0.47</td><td><dl< td=""><td>0.08</td><td><dl< td=""><td>0.06</td><td>P. Cem.30wt % T. Solids</td></dl<></td></dl<></td></dl<>	0.47	<dl< td=""><td>0.08</td><td><dl< td=""><td>0.06</td><td>P. Cem.30wt % T. Solids</td></dl<></td></dl<>	0.08	<dl< td=""><td>0.06</td><td>P. Cem.30wt % T. Solids</td></dl<>	0.06	P. Cem.30wt % T. Solids
5	<dl< td=""><td>0.01</td><td><dl< td=""><td>0.65</td><td><dl< td=""><td>0.07</td><td><dl< td=""><td>0.05</td><td>P. Cem.30wt % T. Solids & ash</td></dl<></td></dl<></td></dl<></td></dl<>	0.01	<dl< td=""><td>0.65</td><td><dl< td=""><td>0.07</td><td><dl< td=""><td>0.05</td><td>P. Cem.30wt % T. Solids & ash</td></dl<></td></dl<></td></dl<>	0.65	<dl< td=""><td>0.07</td><td><dl< td=""><td>0.05</td><td>P. Cem.30wt % T. Solids & ash</td></dl<></td></dl<>	0.07	<dl< td=""><td>0.05</td><td>P. Cem.30wt % T. Solids & ash</td></dl<>	0.05	P. Cem.30wt % T. Solids & ash
4	<dl< td=""><td>0.01</td><td><dl< td=""><td>0.87</td><td><dl< td=""><td>0.04</td><td><dl< td=""><td>0.03</td><td>P. Cem.10wt % T. Solids & ash</td></dl<></td></dl<></td></dl<></td></dl<>	0.01	<dl< td=""><td>0.87</td><td><dl< td=""><td>0.04</td><td><dl< td=""><td>0.03</td><td>P. Cem.10wt % T. Solids & ash</td></dl<></td></dl<></td></dl<>	0.87	<dl< td=""><td>0.04</td><td><dl< td=""><td>0.03</td><td>P. Cem.10wt % T. Solids & ash</td></dl<></td></dl<>	0.04	<dl< td=""><td>0.03</td><td>P. Cem.10wt % T. Solids & ash</td></dl<>	0.03	P. Cem.10wt % T. Solids & ash
3	<dl< td=""><td>0.02</td><td><dl< td=""><td>0.81</td><td><dl< td=""><td>0.06</td><td><dl< td=""><td>0.04</td><td>P. Cem. and ash only</td></dl<></td></dl<></td></dl<></td></dl<>	0.02	<dl< td=""><td>0.81</td><td><dl< td=""><td>0.06</td><td><dl< td=""><td>0.04</td><td>P. Cem. and ash only</td></dl<></td></dl<></td></dl<>	0.81	<dl< td=""><td>0.06</td><td><dl< td=""><td>0.04</td><td>P. Cem. and ash only</td></dl<></td></dl<>	0.06	<dl< td=""><td>0.04</td><td>P. Cem. and ash only</td></dl<>	0.04	P. Cem. and ash only

<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 Portland CementTM samples pass leaching requirements for RCRA metals. Waste forms in samples 1,2,5,4 made with blowdown show a decrease in all chemical species except for barium. The selenium level in the blowdown which initially exceeded limits is within compliance after solidification. The waste form in sample 3 made with SRS ash shows a decrease in chemical species leaching except for barium and silver. Chromium and selenium levels in ash sample 3 remained about the same before and after solidification.

All High Solids Super CementTM Samples meet leaching requirements and were covered in a previous MWFA report¹. Super CementTM waste form samples 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.

High Solids Super CementTM sample made with only ash showed a decrease in chemical species except for barium which remained relatively constant. Samples made with a

combination of ash and blowdown showed a leaching decrease in chemical species except for barium which showed an increase.

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

Hg	Ag	As	Ba	Cd	Cr	Pb	Se
.0035	.0015	0.039	0.251	0.018	0.042	0.012	0.0054

Initially blowdown solution contained:

Mercury	<dl< th=""></dl<>
Silver	<0.003 ppm
Arsenic	0.024 ppm
Barium	0.085 ppm
Cadmium	0.032 ppm
Chromium	0.009 ppm
Lead	0.037 ppm
Selenium	<0.015 ppm

No heavy metal concentration was outside SRS TCLP limits which are based on 40CFR 268.48 Universal Treatment Standards.

Toxicity Characteristic Leaching Procedure (TCLP) results are given in Table XVI for selected representative Low Solids waste forms made with SRS incinerator waste.

The concentrations of the hazardous metals in the leachate meet SRS TCLP limits.

Table AVI. TOLA ROSULS TO LOW BOILD Waster Office (Mg/MeA/										
<u>No</u>	<u>. Hg</u>	Ag	As	Ba	Cd	Cr	Pb	Se	Description	
26	<dl< td=""><td>0.02</td><td><dl< td=""><td>0.66</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.03</td><td>S. Cem. 1wt%T. Solids</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.02	<dl< td=""><td>0.66</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.03</td><td>S. Cem. 1wt%T. Solids</td></dl<></td></dl<></td></dl<></td></dl<>	0.66	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.03</td><td>S. Cem. 1wt%T. Solids</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.03</td><td>S. Cem. 1wt%T. Solids</td></dl<></td></dl<>	<dl< td=""><td>0.03</td><td>S. Cem. 1wt%T. Solids</td></dl<>	0.03	S. Cem. 1wt%T. Solids	
23	<dl< td=""><td>0.02</td><td><dl< td=""><td>0.88</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.04</td><td>S. Cem. 10wt%T. Solids</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.02	<dl< td=""><td>0.88</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.04</td><td>S. Cem. 10wt%T. Solids</td></dl<></td></dl<></td></dl<></td></dl<>	0.88	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.04</td><td>S. Cem. 10wt%T. Solids</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.04</td><td>S. Cem. 10wt%T. Solids</td></dl<></td></dl<>	<dl< td=""><td>0.04</td><td>S. Cem. 10wt%T. Solids</td></dl<>	0.04	S. Cem. 10wt%T. Solids	
25	<dl< td=""><td>0.01</td><td><dl< td=""><td>0.16</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.05</td><td>S. Cem. 40wt%T. Solids</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.01	<dl< td=""><td>0.16</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.05</td><td>S. Cem. 40wt%T. Solids</td></dl<></td></dl<></td></dl<></td></dl<>	0.16	<dl< td=""><td><dl< td=""><td><dl< td=""><td>0.05</td><td>S. Cem. 40wt%T. Solids</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>0.05</td><td>S. Cem. 40wt%T. Solids</td></dl<></td></dl<>	<dl< td=""><td>0.05</td><td>S. Cem. 40wt%T. Solids</td></dl<>	0.05	S. Cem. 40wt%T. Solids	
27	<dl< td=""><td>0.02</td><td>0.08</td><td>0.58</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>S. Cem. Ash with set agent</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.02	0.08	0.58	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>S. Cem. Ash with set agent</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>S. Cem. Ash with set agent</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>S. Cem. Ash with set agent</td></dl<></td></dl<>	<dl< td=""><td>S. Cem. Ash with set agent</td></dl<>	S. Cem. Ash with set agent	
28	<dl< td=""><td>0.02</td><td>0.09</td><td>0.75</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>S. Cem. Ash no set agent</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.02	0.09	0.75	<dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>S. Cem. Ash no set agent</td></dl<></td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td><dl< td=""><td>S. Cem. Ash no set agent</td></dl<></td></dl<></td></dl<>	<dl< td=""><td><dl< td=""><td>S. Cem. Ash no set agent</td></dl<></td></dl<>	<dl< td=""><td>S. Cem. Ash no set agent</td></dl<>	S. Cem. Ash no set agent	
17	<dl< td=""><td>0.02</td><td><dl< td=""><td>1.01</td><td><dl< td=""><td>0.03</td><td><dl< td=""><td><dl< td=""><td>P. Cem. 10 wt % T. Solids</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.02	<dl< td=""><td>1.01</td><td><dl< td=""><td>0.03</td><td><dl< td=""><td><dl< td=""><td>P. Cem. 10 wt % T. Solids</td></dl<></td></dl<></td></dl<></td></dl<>	1.01	<dl< td=""><td>0.03</td><td><dl< td=""><td><dl< td=""><td>P. Cem. 10 wt % T. Solids</td></dl<></td></dl<></td></dl<>	0.03	<dl< td=""><td><dl< td=""><td>P. Cem. 10 wt % T. Solids</td></dl<></td></dl<>	<dl< td=""><td>P. Cem. 10 wt % T. Solids</td></dl<>	P. Cem. 10 wt % T. Solids	
20	<dl< td=""><td>0.02</td><td><dl< td=""><td>0.91</td><td><dl< td=""><td>0.03</td><td><dl< td=""><td><dl< td=""><td>P. Cem. ash</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<>	0.02	<dl< td=""><td>0.91</td><td><dl< td=""><td>0.03</td><td><dl< td=""><td><dl< td=""><td>P. Cem. ash</td></dl<></td></dl<></td></dl<></td></dl<>	0.91	<dl< td=""><td>0.03</td><td><dl< td=""><td><dl< td=""><td>P. Cem. ash</td></dl<></td></dl<></td></dl<>	0.03	<dl< td=""><td><dl< td=""><td>P. Cem. ash</td></dl<></td></dl<>	<dl< td=""><td>P. Cem. ash</td></dl<>	P. Cem. ash	
18	<dl< td=""><td>0.01</td><td><dl< td=""><td>0.27</td><td><dl< td=""><td>0.16</td><td><dl< td=""><td>0.05</td><td>P. Cem. 40 wt % T. Solids</td></dl<></td></dl<></td></dl<></td></dl<>	0.01	<dl< td=""><td>0.27</td><td><dl< td=""><td>0.16</td><td><dl< td=""><td>0.05</td><td>P. Cem. 40 wt % T. Solids</td></dl<></td></dl<></td></dl<>	0.27	<dl< td=""><td>0.16</td><td><dl< td=""><td>0.05</td><td>P. Cem. 40 wt % T. Solids</td></dl<></td></dl<>	0.16	<dl< td=""><td>0.05</td><td>P. Cem. 40 wt % T. Solids</td></dl<>	0.05	P. Cem. 40 wt % T. Solids	
19	<dl< td=""><td>0.02</td><td><dl< td=""><td>1.23</td><td><dl< td=""><td>0.04</td><td><dl< td=""><td>0.04</td><td>P. Cem. ash</td></dl<></td></dl<></td></dl<></td></dl<>	0.02	<dl< td=""><td>1.23</td><td><dl< td=""><td>0.04</td><td><dl< td=""><td>0.04</td><td>P. Cem. ash</td></dl<></td></dl<></td></dl<>	1.23	<dl< td=""><td>0.04</td><td><dl< td=""><td>0.04</td><td>P. Cem. ash</td></dl<></td></dl<>	0.04	<dl< td=""><td>0.04</td><td>P. Cem. ash</td></dl<>	0.04	P. Cem. ash	
15	<dl< td=""><td>0.02</td><td><dl< td=""><td>0.79</td><td><dl< td=""><td>0.06</td><td><dl< td=""><td>0.05</td><td>P. Cem. 1 wt % T. Solids</td></dl<></td></dl<></td></dl<></td></dl<>	0.02	<dl< td=""><td>0.79</td><td><dl< td=""><td>0.06</td><td><dl< td=""><td>0.05</td><td>P. Cem. 1 wt % T. Solids</td></dl<></td></dl<></td></dl<>	0.79	<dl< td=""><td>0.06</td><td><dl< td=""><td>0.05</td><td>P. Cem. 1 wt % T. Solids</td></dl<></td></dl<>	0.06	<dl< td=""><td>0.05</td><td>P. Cem. 1 wt % T. Solids</td></dl<>	0.05	P. Cem. 1 wt % T. Solids	

Table XVI. TCLP Results for Low Solids Waste Forms (mg/liter)

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All Low Solids Super CementTM samples meet SRS leaching requirements. Low Solids Super CementTM samples 26, 23, 25 made with different concentrations of blowdown showed a decrease in leaching for RCRA metals except for silver and barium. Low Solids Ash Super CementTM samples showed a decrease in RCRA metals except for arsenic and barium. All Low Solids Portland cement samples made with blowdown and/or ash meet SRS leaching requirements. The leaching of metals decreased from the original blowdown and ash except for silver, barium, and selenium.

Waste Loading Results

The typical Portland cement plant waste loadings are 23.9 wt % for ash (on a dry ash basis) and 46.1 wt % for scrubber solution. Plant formulations are based on previous work performed by Don Fisher at SRS.^{3,4}

High Solids Super CementTM waste loadings are given in Table XVII.

Table XVII. High Solids Super Cement[™] Waste Loadings

	Wt%	
Wt%	SRS	Blowdown (BD)
Bd	Ash	Total Solids Wt %
0	28.3	0
0	27.4	0
0	26.3	0
0	29.5	0
41.4	0	30
39.2	0	10
	Wt% Bd 0 0 0 41.4 39.2	Wt% Wt% Wt% SRS Bd Ash 0 28.3 0 27.4 0 26.3 0 29.5 41.4 0 39.2 0

Low Solids Super CementTM waste loadings are given in Table XVIII.

Table XVIII. Low Solids Super CementTM Waste Loadings

		Wt%	
Sample	Wt%	SRS	Blowdown (BD)
Number	Bd	Ash	Total Solids Wt %
22	40.3	0	20
23	39.1	0	10
24	41.4	0	30
25	41.6	0	40
26	36.4	0	1
27	0	35.0	0
28	0	40.3	0

Notes for Tables XVII and XVIII:

- 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 (scrubber solution) that was incorporated in the waste form.
- 3) Wt % SRS ash is on a dry basis

Waste loadings for High Solids Super CementTM samples made with ash were higher than Portland cement. Waste loadings for High Solids Super CementTM samples made with only scrubber solution were slightly less than those for the plant. Samples were made with 10 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. Since the blowdown used was concentrated the actual waste loadings will be greater than that achieved by the plant.

Waste loadings for Low Solids Super CementTM were higher than Portland cement for samples made with ash and slightly lower than samples made with blowdown.

CONCLUSIONS

Portland cement and Super Cement[™] waste forms meet set time, bleed water, mixability, compression, and leaching requirements for High and Low Solids. High Solids Portland cement centrifuge permeability is acceptable for 10 wt % total solids scrubber solution but fails at higher concentrations. High Solids Portland cement permeabilities of ash waste forms meet SRS criteria.

High Solids Super CementTM ash or scrubber solution (at 30 wt % solids) waste forms fail permeability criteria. 10 wt % scrubber solution High Solids Super CementTM waste form permeability could not be determined because of cracking of the sample. Low Solids Portland cement and Super CementTM ash waste forms pass permeability requirements but waste forms made with all concentrations of scrubber solution fail for both technologies.

The viscosity of High Solids Super CementTM samples is comparable to samples made with Portland cement. Bleed water was observed initially for Super CementTM made with blowdown but was absorbed after 24 hours.

From a processibility stand point Super CementTM will present more problems than Portland cement because of additional reagents (hardening, TMT15, sodium sulfide) that need to be added. Portland cement uses only the cement mix and water with no plant modifications.

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Setting problems with the High Solids 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.

High Solids waste forms made with Super CementTM meet all SRS acceptance criteria except permeability and have a waste loading similar to 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 Super CementTM is 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.

Solid waste forms made with scrubber solution are thought to be more permeable because of the effect of excess salt. The phenomenon occurs because water flowing through the solid waste form dissolves away the salt and thereby opens the porosity. In addition, the salts affect the water/cement ratio required to obtain processable mixtures. The higher the water to cement ratio the higher the porosity and permeability. The combination of salt and uncombined water can cause additional pore space if it is washed out which results in increased permeability.

There are no clear advantages to using Super CementTM instead of Portland cement for Low Solids waste at this time other than the Super CementTM ash waste forms do not have bleed water problems like Portland cement ash waste forms. Portland cement ash waste form bleed water is taken care of in the plant by adding Portland cement to react with the bleed water. Super CementTM and Portland cement Low Solid waste forms made with scrubber solution both fail permeability criteria which eliminates the possibility of solidifying this secondary waste stream.

Portland cement High Solids ash waste forms and 10 wt % scrubber waste forms pass permeability criteria but 30 wt % scrubber waste forms do not. Permeability requirements are not met for any of the High Solids Super CementTM ash or 30 wt % scrubber waste forms and could not be determined for 10 wt % scrubber waste forms. At this time, permeability is not a requirement for disposing of High Solids solid waste forms. Since disposal is not by trench burial at SRS this may not be an issue. If permeability is not an issue for High Solids waste forms then either technology will be acceptable for solidification.

RECOMMENDATIONS

Super CementTM does not have clear advantages over Portland cement and requires additional expense to incorporate. Neither technology creates a waste form with acceptable permeability when concentrated scrubber solutions are stabilized. This is a potential issue if the plant desires to stabilize concentrated solutions from a new evaporator to be added in the near future.

Most of the waste forms for both the High and Low Solids meet the acceptance criteria except for permeability. The high salt in the concentrated scrubber solution apparently causes waste forms with unacceptable permeabilities. Most of the permeability values of blowdown marginally fail to meet acceptance criteria.

Permeability is one of the parameters in a performance assessment model, which predicts leaching to the environment. If the plant needs to solidify concentrated high or low solids scrubber solution and dispose of the solid waste forms in trenches (trench disposal requires meeting permeability criteria at this time) the performance assessment model should be evaluated again to see if the permeability limit can be lowered to around 1×10^{-6} cm/sec and still achieve acceptable leaching levels.

Another possibility to try and solve the permeability problem is to modify the Portland and Super CementTM formulation to deal with the high salt problem in the blowdown.

QUALITY ASSURANCE

Quality Assurance testing was conducted in accordance with SRS procedures. Results are recorded in Laboratory Notebook WSRC-NB-96-633. The Technical Task Plan and Quality Assurance Plan are documented in WSRC-RP-99-01361⁵.

Centrifuge analyses performed by UFA Ventures have been accepted to ASTM D18.21 Subcommittee on Ground Water.

ACKNOWLEDGEMENTS

This work was done as part of the DOE Office of Science and Technology, Mixed Waste Focus Area program (TTP SR1-8-MW-44).

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- 2. 40 CFR 268.48, Code of Federal Regulations 40, "Protection of Environment" Section 268.48.
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- 4. D.L. Fisher, 1996, "CIF Ashcrete Mixture Limits," WSRC-TR-96-0169, June 14, 1996.
- 5. B. W. Walker, "Technical Task Plan for Mixed Waste Focus Area (MWFA) Evaluation of Salt Waste Treatment Technologies," WSRC-RP-98-01361, March 6, 1998.

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Appendix 1.

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Characterization of Incinerator Waste

High Solids Off Gas Scrubber Solution (Blowdown) Characterization

Characterization of the incinerator blowdown is given below. 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 SiO₂ and Zn(OH)₂. Dissolved solids results from analyses on plant samples were 8.2 % and are usually NaCl and Na₂SO₄. The pH of the blowdown was 8.77 and the water content 90.3 %.

<u>Component</u>	(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; (NaK)(AlSi₃O₈) Magnetite; Fe₃O₄ Hematite; Fe₂O₃.

The ash was wet quenched and contained $45 \pm 15\%$ 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.

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Low Solids Off Gas Scrubber Solution (Blowdown) Characterization

Soluble solids were 1 % (wt./vol.). Insoluble solids were 0.2 % (wt./vol.). Most of the solids (>99%) were soluble in a hot 30 wt % NaOH solution. The bulk of the insolubles are likely alumina, silica, and probably titanium dioxide. There was no detectable soluble mercury. The density of the blow down was 1.01 g/ml and the pH was 7.5.

Gross alpha was 539 dpm/ml Gross beta was 240 dpm/ml Gross gamma was 154 dpm/ml Tritium was 1302 dpm/ml

Gamma Contributors

Component
-
K-40
Co-60
Cs-137
Eu-154
Am-241

<u>Component</u>	<u>(mg/liter)</u>	<u>Component</u>	(mg/liter)
-	-	-	-
Silver	<0.003	Manganese	0.712
Aluminum	<0.060	Molybdenum	0.776
Arsenic	0.024	Sodium	2459
Boron	7.75	Nickel	0.075
Barium	0.085	Lead	0.037
Beryllium	< 0.0004	Selenium	<0.015
Calcium	39.16	Antimony	10.64
Cadmium	0.032	Silicon	69.5
Chromium	0.009	Strontium	0.065
Cesium	<10	Thorium	<0.50
Copper	1.66	Titanium	< 0.001
Iron	0.252	Thallium	< 0.015
Potassium	92.53	Uranium	< 0.15
Magnesium	12.26	Vanadium	0.091
Zinc	2.43	Zirconium	< 0.035
Chloride	988	Sulfate	2050
Carbonate	105		

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Low Solids Ash Characterization

The ash was wet quenched and contained 45 ± 15 wt. % quench water. Ash used in this study was drained of excess water which resulted in a water content of about 25 wt. %. The pH of the water in contact with the ash was 10.6.

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<u>Component</u>	(mg/liter)	Component	(mg/liter)
\ <i>f</i>	0.0042	Colonium	0.255
wercury	0.0042	Selemum	0.255
Silver	0.226	Antimony	29.7
Arsenic	6.96	Thallium	0.416
Barium	238	Copper	646
Beryllium	0.266	Iron	6400
Cadmium	2.57	Manganese	153
Chromium	16.9	Sodium	5450
Nickel	87.4	Titanium	3.9
Lead	44.8	Zinc	846
Cobalt	3.43		

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Appendix 2.

Permeability Calculations

				Man.	Man.	Man.			Hyd.	Vol.	Coll.	Flow	Hyd.
	L	D	Α	Ht. 1	Ht 2	Ht ave.	P1	P2	Head	Coll.	Time	Rate Q	Cond. K
<u></u>	(cm)	(cm)	(cm2)	cm	cm	cm	psig	psig	cm	cm3	hr	(cm3/s)	(cm/s)
Sample 11													
10wtNaCl	PC LS												
Actual	0.80	3.10	7.54	2.00	3.00	2.50	10.00	0.00	705.60	0.00	12.00	0.00E+00	0.00E+00
Detect	0.80	3.10	7.54	2.00	3.00	2.50	10.00	0.00	705.60	0.05	12.00	1.16E-06	1.74E-10
Sample 12													
30wtNaCl	PC LS												
actual	0.85	3.11	7.59	1.50	2.50	2.00	10.00	0.00	705.10	0.15	2.25	1.85E-05	2.94E-09
detect	0.85	3.11	7.59	1.50	2.50	2.00	10.00	0.00	705.10	0.05	2.25	6.17E-06	9.80E-10
Sample 15													
1wt BD	PC LS												
actual	0.92	2.90	6.60	1.50	1.40	1.45	10.00	0.00	704.55	0.20	5.50	1.01E-05	2.00E-09
detect	0.92	2.90	6.60	1.50	1.40	1.45	10.00	0.00	704.55	0.05	5.50	2.53E-06	4.99E-10
Sample 18													
40wt BD	PC LS												
actual	0.99	3.10	7.54	2.00	1.90	1.95	10.00	0.00	705.05	0.90	5.50	4.55E-05	8.46E-09
detect	0.99	3.10	7.54	2.00	1.90	1.95	10.00	0.00	705.05	0.05	5.50	2.53E-06	4.70E-10
Sample 19													
Ash SRTC	PC LS												
actual	0.81	3.10	7.54	1.00	0.90	0.95	10.00	0.00	704.05	0.00	5.08	0.00E+00	0.00E+00
detect	0.81	3.10	7.54	1.00	0.90	0.95	10.00	0.00	704.05	0.05	5.08	2.73E-06	4.17E-10
Sample 21													
Ash ClF	PC LS												•
actual	1.50	3.20	8.04	1.10	1.00	1.60	10,00	0.00	704.70	0.00	5.00	0.00E+00	0.00E+00
detect	[.] 1.50	3.20	8.04	1.10	1.00	1.60	10.00	0.00	704.70	0.05	5.00	2.78E-06	7.36E-10

Table A2.1 Measurements and Results of Falling Head Permeability Tests.

* 0.05 cm^3 is the minimum detectable volume which can be measured in the graduated buret. The permeability value reported as detectable is based on achieving steady state flow of 0.05 cm^3 (ml) over the run time interval T2 – T1 reported for each sample. For samples having no actual flow (Q) the permeabilities (K) were reported as less than values using the minimum detectable flow as the upper-bound estimate.

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- 11				Man.	Man.	Man.			Hyd.	Vol.	Coll.	Flow	Hyd.
	L	D	Α	Ht. 1	Ht 2	Ht ave.	P1	P2	Head	Coll.	Time	Rate Q	Cond. K
	(cm)	(cm)	(cm2)	cm	cm	cm	psig	psig	cm	cm3	hr	(cm3/s)	(cm/s)
Sample 1													
10wt BD	PC HS												
actual	1.30	3.10	7.54	1.20	1.10	1.15	10.00	0.00	704.25	0.00	5.50	0.00E+00	0.00E+00
detect	1.30	3.10	7.54	1.20	1.10	1.15	10.00	0.00	704.25	0.05	5.50	2.53E-06	6.18E-10
Sample 3													
ash	PC HS												
actual	1.15	3.20	8.04	1.20	0.30	0.75	10.00	0.00	.703.85	0.00	4.57	0.00E+00	0.00E+00
detect	1.15	3.20	8.04	1.20	0.30	0.75	10.00	0.00	703.85	0.05	4.57	3.04E-06	6.18E-10
Sample 2													
30%BD	PC HS												
actual	1.30	3.30	8.55	1.20	0.30	0.75	10.00	0.00	703.85	2.80	0.40	1.94E-03	4.20E-07
detect	1.30	3.30	8.55	1.20	0.30	0.75	10.00	0.00	703.85	0.05	0.40	3.47E-05	7.50E-09
Sample 8													
ash	SC HS												
actual	1.30	3.10	7.54	3.30	2.80	3.05	10.00	0.00	706.15	0.40	5.62	1.98E-05	4.82E-09
detect	1.30	3.10	7.54	3.30	2.80	3.05	10.00	0.00	706.15	0.05	5.62	2.47E-06	6.03E-10
Sample 13													
BD30%	SC HS												
actual	1.10	3.10	7.54	3.30	2.80	3.05	10.00	0.00	706.15	2.00	0.25	2.22E-03	4.59E-07
detect	1.10	3.10	7.54	3.30	2.80	3.05	10.00	0.00	706.15	0.05	0.25	5.56E-05	1.15E-08
Sample 14													
BD10%	SC HS												
actual	1.80	3.00	7.07	0.90	0.50	0.70	10.00	0.00	703.80	2.00	0.25	2.22E-03	8.04E-07
detect	1.80	3.00	7.07	0.90	0.50	0.70	10.00	0.00	703.80	0.05	0.25	5.56E-05	2.01E-08

Note: Sample 14 appears to be cracked which may give an erroneous permeability value.

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				Man.	Man.	Man.			Hyd.	Vol.	Coll.	Flow	Hyd.
	L	D	Α	Ht. 1	Ht 2	Ht ave.	P1	P2	Head	Coll.	Time	Rate Q	Cond. K
· · · · · · · · · · · · · · · · · · ·	(cm)	(cm)	(cm2)	cm	cm	cm	psig	psig	cm	cm3	hr	(cm3/s)	(cm/s)
Sample 25													
BD40%	SC LS												
actual	1.80	3.10	7.54	1.40	1.00	1.20	10.00	0.00	704.30	2.00	0.25	2.22E-03	7.53E-07
detect	1.80	3.10	7.54	1.40	1.00	1.20	10.00	0.00	704.30	0.05	0.25	5.56E-05	1.88E-08
Sample 23													
10%BD	SC LS												
actual	1.60	3.10	7.54	0.30	0.20	0.25	10.00	0.00	703.35	0.10	5.60	4.96E-06	1.50E-09
detect	1.60	3.10	7.54	0.30	0.20	0.25	10.00	0.00	703.35	0.05	5.60	2.48E-06	7.48E-10
Sample 27													
ashwset	SC LS												
actual	1.40	3.10	7.54	1.10	1.00	1.05	10.00	0.00	704.15	0.00	5.50	0.00E+00	0.00E+00
detect	1.40	3.10	7.54	1.10	1.00	1.05	10.00	0.00	704.15	0.05	5.50	2.53E-06	6.66E-10
Sample 28													
ashnoset	SC LS												
actual	0.81	3.10	7.54	1.00	0.90	0.95	10.00	0.00	704.05	0.15	4.00	1.04E-05	1.59E-09
detect	0.81	3.10	7.54	1.00	0.90	0.95	10.00	0.00	704.05	0.05	4.00	3.47E-06	5.30E-10

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Appendix 3.

Plant Algorithm for Waste Loadings

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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 grams of slurry/1.748 = 114.4 grams of Portland cement needed.

The plant typical ash waste loading is therefore

100 grams of wet ash/314.4 grams total mix times 100 = 31.8 % wet ash 75 grams of dry ash/314.4 grams total mix times 100 = 23.9 % dry 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 grams of scrubber solution / 216.9 grams of total mix x 100 = 46.1 %.