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PHOSPHATE BONDED SOLIDIFICATION OF RADIOACTIVE INCINERATOR WASTES

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ABSTRACT

The incinerator at the Department of Energy Savannah River Site burns low level radioactive and hazardous waste. Ash and scrubber system waste streams are generated during the incineration process. Phosphate Ceramic technology is being tested to verify the ash and scrubber waste streams can be stabilized using this solidification method. Acceptance criteria for the solid waste forms include leachability, bleed water, compression testing, and permeability. Other testing on the waste forms include x-ray diffraction and scanning electron microscopy.

OBJECTIVE

The objective of this study is to determine if Phosphate Ceramic Technology can meet SRS acceptance criteria of leachability (using the Toxic Characteristic Leaching Procedure EPA Method 1311 known as TCLP), bleed water, set time, compression testing, and permeability when used to solidify SRS incinerator ash and liquid used to scrub the off gas system (blowdown).

Waste loading, mixing properties, and data on whether waste forms meet acceptance criteria will be compiled and compared to a future study conducted with the current Portland cement solidification technology now used at the SRS incinerator for solidification of waste.

PHOSPHATE CERAMIC TECHNOLOGY

The Phosphate Ceramic technology has been developed at Argonne National Laboratory for the treatment of various low-level mixed wastes.* Acid-base reaction occurs at ambient temperature according to the following reaction given in Equation 1.**

$$MgO + KH_2PO_4 + 5\ H_2O \rightarrow MgKPO_4 \cdot 6H_2O \qquad (1)$$

The material used in this study was prepared at Argonne National Laboratory specifically for this testing. The manufacture of the MgO was engineered to produce slow reaction with the KH_2PO_4. The KH_2PO_4 was added as a powder and mix proportions (including water) controlled to produce a stoichiometric product.

OFF GAS SCRUBBER SOLUTION (BLOWDOWN) CHARACTERIZATION

Characterization of the incinerator blowdown is given in Table I. The 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 $Zn(OH)_2$. Dissolved solids 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 I. Blowdown Characterization

Component	(mg/liter)
Al	541.5
Ca	600.3
Fe	545.3
Mg	178.0
Na	32126.8
Fl	639
Formate	<10
Cl	19,618
Nitrite	230
Nitrate	274
Phosphate	260
Sulfate	40247
Oxalate	<10

SRS ASH WASTE STREAM CHARACTERIZATION

Based on X-ray diffraction the ash stabilized contained Cristobalite, SiO_2; SiO_2,Silicon oxide; Anorthoclase,(NaK)($AlSi_3O_8$); magnetite,Fe_3O_4; and Hematite;Fe_2O_3.

The ash is wet quenched and contains 45 +/- 15 % quench water. The pH of the water in contact with the ash was 10.55. Ash and blowdown used for sample preparation were generated at SRS by incineration of diatomaceous earth filter rolls.

SAMPLE PREPARATION OF WASTE FORMS

Phosphate ceramic waste forms were fabricated by reacting calcined magnesium oxide with potassium phosphate under aqueous conditions (per Equation 1 in the Phosphate Ceramic Technology section) and mixing with the waste 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, .08 grams of $SnCl_2$ and .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, blowdown, and combinations of ash and blowdown.(The test matrix of waste forms composition is given in Table II.)

The blowdown solution was evaporated to achieve higher salt waste loadings 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 II. Test Matrix

Sample Number	SRS Ash Wt Grams	Added H2O Wt Grams	Blow down (Bd)10% Grams	Blow down (20%) Grams	Binder Wt Grams	Coal ash Wt Grams	Wt% Bd	Wt% SRS Ash
1	0	12.6	0	0	41.4	50	0	0
2	0	0	10	0	71.2	0	12	0
3	0	0	0	36.1	93.8	0	28	0
4	40	11.2	0	0	49	0	0	33
5	50	6.5	0	0	43.5	0	0	42
6	60	2.6	0	0	38.4	0	0	51
7	16.5	0	25	0	66.4	0	23	15
8	48	0	0	16	55.63	0	13	40

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. A substantial amount of bleed water was observed in waste forms made with blowdown (Samples 2,3) but was absorbed after 24 hours of set time. All 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.

Scanning electron microscopy was performed on the waste forms. The matrix phase consisted of short needle shaped crystals of $MgKPO_4 \cdot 6H_2O$ which were interlocked to form a solid coherent matrix. The heavy metals are well distributed with no evidence of clustering.

X-ray diffraction analyses of the 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. Major components found in waste forms made from blowdown, ash, and combinations of blowdown and ash are given in Table III.

Table III Waste Form Components from X-ray Diffraction Analyses

Waste Form Type	Major components
Blowdown	$KMgPO_4 \cdot 6H_2O$, SiO_2-silicon oxide, and MgO-magnesium oxide
SRS ash and Blowdown	$KMgPO_4 \cdot 6H_2O$, Struvite-$NH_4MgPO_4 \cdot 6H_2O$, MgO-magnesium oxide, and Montgomeryite-$Ca_4MgAl_4(PO_4)_6(OH)_4 \cdot 12H_2O$
Blank with Coal ash	$KMgPO_4 \cdot 6H_2O$ and SiO_2

Permeability testing using Permeameter Model # K-670A purchased from ELE International in Lake Bluff, Illinois of the non radioactive blank sample gave results of $1x10^{-4}$ cm^2/s.

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

Hg	Ag	As	Ba	Cd	Cr	Pb	Se
<DL	<DL	.099	.243	.011	.046	.023	.032

Initially blowdown solution contained < .01 ppm Hg, <0.025 ppm Ag, 2.56ppm As, .12 ppm Ba, .211 ppm Cd, 2.11 ppm Cr, .325 ppm Pb, .65 ppm Se. Only selenium was outside SRS limits.

Toxicity Characteristic Leaching Procedure (TCLP) results are given in Table IV for waste forms made with SRS incinerator waste. The concentrations of the hazardous metals in the leachate meet SRS requirements. 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 IV. TCLP Results for 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
3	<DL	<DL	.099	<DL	<DL	.016	<DL	<DL
4	<DL	<DL	.067	<DL	<DL	.016	<DL	<DL
6	<DL	<DL	.068	<DL	<DL	.008	<DL	<DL
7	<DL	<DL	.069	<DL	<DL	.005	<DL	<DL
8	<DL	<DL	.089	<DL	<DL	.011	<DL	.048

<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

Waste forms in samples 2,3 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 4,5,6 made with SRS ash show a decrease in chemical species leaching except for As. The waste forms in samples 7,8 made with both blowdown and SRS ash show a leaching decrease in all blowdown chemical species.

Discussion

SRS Acceptance Criteria for freshly prepared waste forms are shown in Table V.

Table V. Acceptance Criteria for Freshly Prepared Waste Forms

Property	Acceptance Criteria
Bleed water	0 volume after 24 hours
Set time	Less than 3 days (shorter time preferred)
Mixability	1 component addition and low viscosity

SRS Acceptance Criteria for cured waste forms are shown in Table VI.

Table VI. Acceptance Criteria for Cured Waste Forms

Property	Acceptance Criteria
Compressive Strength	> 500 psi
Permeability	$< 10^{-8}$ cm^2/s
TCLP	As-5, Hg-.025, Ba-7, Cr-0.86, Pb-0.37, Se-0.16, Ag-0.3, Cd-.69 (ppm) (40CFR 268.48 Universal Treatment Standards)

Conclusion

Phosphate Ceramic technology was used to stabilize and solidify radioactive ash and off gas scrubber waste (blowdown) that was generated from the incinerator at SRS. The solid waste forms generated exhibited high compressive strength and effectively stabilized hazardous contaminants in the wastes through chemical reaction and microencapsulation.

Viscosity of the phosphate ceramic is less than traditional Portland cement and should require less mixing torque. Bleed water was observed initially for the waste forms 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. Permeability of a blank made with only phosphate ceramic and no SRS ash or blowdown were in the range of $1x10^{-4}$ cm^2/s which does not meet the current SRS permeability of 10^{-8} cm^2/s.

The 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. The technology should be acceptable for similar waste not required to meet stringent permeability requirements.

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References

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