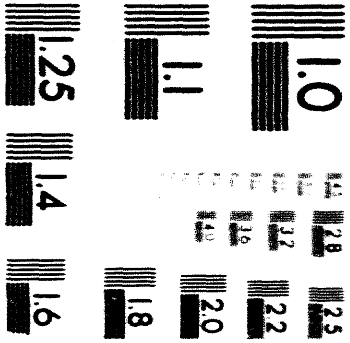
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IMMOBILIZATION IN CERAMIC WASTE FORMS OF THE RESIDUES FROM TREATMENT OF MIXED WASTES

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ABSTRACT

The Environmental Restoration and Waste Management Applied Technology Program at LLNL is developing a Mixed Waste Management Facility to demonstrate treatment technologies that provide an alternative to incineration. As part of that program, we are developing final waste forms using ceramic processing methods for the immobilization of the treatment process residues. The ceramic phase assemblages are based on using Synroc D as a starting point and varying the phase assemblage to accommodate the differences in chemistry between the treatment process residues and the defense waste for which Synroc D was developed. Two basic formulations are used, one for low ash residues resulting from treatment of organic materials contaminated with RCRA metals, and one for high ash residues generated from the treatment of plastics and paper products. Treatment process residues are mixed with ceramic precursor materials, dried, calcined, formed into pellets at room temperature, and sintered at 1150 to 1200°C to produce the final waste form. This paper discusses the chemical composition of the waste streams and waste forms, the phase assemblages that serve as hosts for inorganic waste elements, and the changes in waste form characteristics as a function of variation in process parameters.

INTRODUCTION

In the early 1980's LLNL developed a ceramic waste form based on titanate and zirconate minerals for the immobilization of the reprocessing residues held at Savannah River [1]. That waste form, Synroc-D, is presently being used as the basis for design and demonstration of a ceramic waste form for the immobilization of the residues resulting from the treatment of DOE hazardous and mixed wastes.

The Environmental Restoration and Waste Management Applied Technology Program at LLNL is developing a Mixed Waste Management Facility (MWMF) to demonstrate a variety of technologies that can be used as alternatives to incineration in the treatment of mixed wastes. The waste streams that will form the core of the demonstration project are DOE waste codes 2110 (7.8% Trimsol in water), 2120 (Aqueous/non-halogenated organic), 2210 (Trichloroethane), 5300 (Combustible), 5440 (Predominantly combustible), and 6100 (Lab packs- Scintillation cocktails). The residues from treatment of the Combustible waste streams (5300 and 5440) result in about 10 percent of the original weight of waste being recovered as ash. The ash composition for the LLNL combustible stream is dominated by SiO_2, Al_2O_3, MgO, ZnO, CaO, and Fe_2O_3, which collectively account for almost 90% of the ash. In contrast, the other waste streams result in a concentrated residue with very little of the major mineral-forming oxides found in the combustible ash; the low ash residues are dominated by Sb, Zn, and Ba, with lesser amounts of Be, Mo, Pb, and U. Other metals (Co, Cd, Ni, Cu, Mn, Ag, V, Tl, and Cr) will be present in trace amounts. These elements, recovered as nitrate salts or as oxides after the destruction of the organic liquid waste streams, are also found in small amounts in the ash residues from processing of the two combustible waste streams.

DESIGNING THE WASTE FORM

Our philosophy in designing a ceramic waste form for the waste treatment residues was to use the ash components from the combustible waste streams as the model for our base ceramic compositions, adding to that ash small amounts of additive chemicals to produce a final phase assemblage that had proven durability and known processing parameters. Addition of NaOH, ZrO_2, and TiO_2 to the combustible ash provides a phase assemblage similar to that found in Synroc D.

The major phases in Synroc-D are nepheline, perovskite, spinel, and zirconolite. For Savannah River wastes, which are high in iron, there were 2 spinels - Fe_2TiO_4 and $FeAl_2O_4$; however, the common natural spinel has the composition $MgAl_2O_4$ and is capable of extensive solid solution. For immobilization of residues from treatment of hazardous and mixed wastes we are using the phase assemblage of nepheline, perovskite, zirconolite, and MgAl-spinel as the major phases. The toxic metals and radioactive elements in the treatment residues will be incorporated into the waste form as solid solutions in the major phases. In some cases, elements such as Hg and Ag (as AgCl) will be volatile under the conditions used to make the ceramic waste form. These elements will be condensed from the off-gas line and converted into a suitable secondary waste form.

The process we are using for producing the final ceramic product differs substantially from the original flow sheet for Synroc-D processing. We are planning to use a rotary calciner operating at 600 to 750°C to calcine and denitrate the ceramic waste form feed stream and induce formation of the primary bonds in the ceramic. This is the process used for Synroc-C processing at the Australian Nuclear Science and Technology Organisation, rather than the fluidized bed calciner ultimately employed at LLNL for work on Synroc D [2]. Following calcination, the powder will be pressed at room temperature into 1-cm-diameter pellets using a high capacity, commercially available, pellet press. The pressed pellets will be sintered in air or in a controlled atmosphere at approximately 1200°C to densify the pellets and produce the desired phase assemblages.

WASTE FORM COMPOSITION AND CHARACTERISTICS

We have chosen two basic compositions for the waste forms we are using to develop process parameters and waste form characteristics for the treatment process residues. The first waste form represents the pure end-member composition for low ash residues and is illustrated in Table 1. Rather than use the expected concentrations of waste elements, which are high in Sb, Zn, and Ba, we have chosen to use equal amounts of 10 elements at approximately 0.5% each so that we have enough present in

Table 1: Compositions of ceramic mixtures using oxide starting materials used to simulate residues from treatment of low-ash streams and to investigate volatility of waste elements. Waste oxides are equal weight percents of oxides of Co, Cu, Sb, Cr, Zn, Mo, Ag, Cd, Ba, and Pb.

Component	Weight %	Mineral in which component is found
CaO	16.1	Perovskite, Zirconolite
TiO_2	29.9	Perovskite, Zirconolite, Rutile
ZrO_2	10.8	Zirconolite
MgO	6.8	Spinel
Al_2O_3	22.0	Spinel, Nepheline
SiO_2	5.7	Nepheline
Na_2O	3.0	Nepheline
Waste Oxides	5.7	Various

Mineral Phase	Weight %	Composition of end member phase
Perovskite	29.5	$CaTiO_3$
Zirconolite	31.2	$CaZrTi_2O_7$
Spinel	25.1	$MgAl_2O_4$
Nepheline	14.2	$NaAlSiO_4$
Rutile	0	TiO_2

the waste form to easily characterize the product. We have prepared samples of this synthetic waste form using oxide materials (gibbsite and kaolin for Al and Si oxides) as well as alkoxide preparations. For the alkoxide and one batch of oxide material we have also used 1.6% NaCl in the mixture to investigate the effects of the presence of chloride ions on the behavior of the waste elements and to determine whether sodalite could be formed as part of the phase assemblage.

For each mixture we have prepared samples by mixing the oxides or alkoxide precursors with the waste element oxides using water to facilitate mixing. The mixture is then dried in air at 90°C to remove the bulk of the water, calcined at 600°C for periods between 1 and 8 hours, and cooled to room temperature. The powder is then mixed with Carbowax to act as a binder and pressed into pellets at 25,000 psi in tool steel dies. The pressed pellets are sintered for 1 hour at temperatures between 1050 and 1250°C. The green density of pellets prepared using oxide starting materials and the binder material is generally about 52 to 57% of the theoretical maximum density of the sintered product.

Figure 1 shows the density of samples as a function of sintering temperature. The five data sets marked Oxide + NaCl, Oxide, no NaCl, and Alkoxide + NaCl all had approximately the composition shown in Table 1. For pellets made using oxide starting materials, sintering at 1050°C drives off the Carbowax, but does not appreciably densify the pellet; thus, the sintered density is a little less than the green density. Sintering at temperatures between 1100 and 1200°C produces an increase in density that is approximately linear with temperature. Samples sintered at 1200°C achieve about 90% of theoretical density. Differential thermal analysis of our samples has shown that the solidus is at about 1180°C, so these samples experience some melting. Scanning electron microscopy and transmission electron microscopy do not reveal any significant evidence of melting, so it must have been confined to grain boundaries. Sintering an oxide mixture at 1250°C produced a sample with 97% of theoretical density and obvious signs of melting.

Samples produced from alkoxide precursors with the compositions given in Table 1 also had green densities of 52 to 55%, but showed considerable densification upon sintering at 1050°C, indicating that the alkoxide materials are more reactive than the oxide equivalents. Somewhat surprisingly, these samples did not reach more than 80% of theoretical density when sintered at higher temperatures. It has been suggested [3] that this may be due to the high surface area of the alkoxide powders and the adsorption of gases on the powders after calcination. These gases may then be trapped in the pellets after pressing and cause porosity in the sintered pellet. Alternatively, the nitrates added with waste elements may not have completely decomposed during calcination.

Table 2 shows the composition of a simulated waste form designed to represent the high ash residues obtained by processing a mixture of combustible solids such as plastics, rubber, and paper products. We used the average of a one-year inventory of such wastes at LLNL to generate the composition of the waste stream. In the waste form composition given, all of the Si and Mg come from the waste stream residues, as well as 1/4 of the Al and most of the Ca. The waste loading in the simulated waste form is about 50% and the waste stream is low in components such as Sb and Ba that are high in the low ash residues. The simulated waste form for the composition in Table 2 has a different proportion of phases than the low ash host, notably being high in both nepheline and spinel, and with little perovskite. (The apatite is assumed to be present because of the phosphate content; it has not yet been positively identified and the phosphate may be in another phase). Despite the gross difference in phase proportions and in bulk composition of the two phase assemblages, the processing characteristics for both are similar and the SEM images and energy dispersive x-ray characterization of both indicate that they are similar. Because of these similarities, we anticipate that it will be possible to combine the residues from the low ash stream with the high ash residues from treatment of combustible solids and produce a single waste form for both streams.

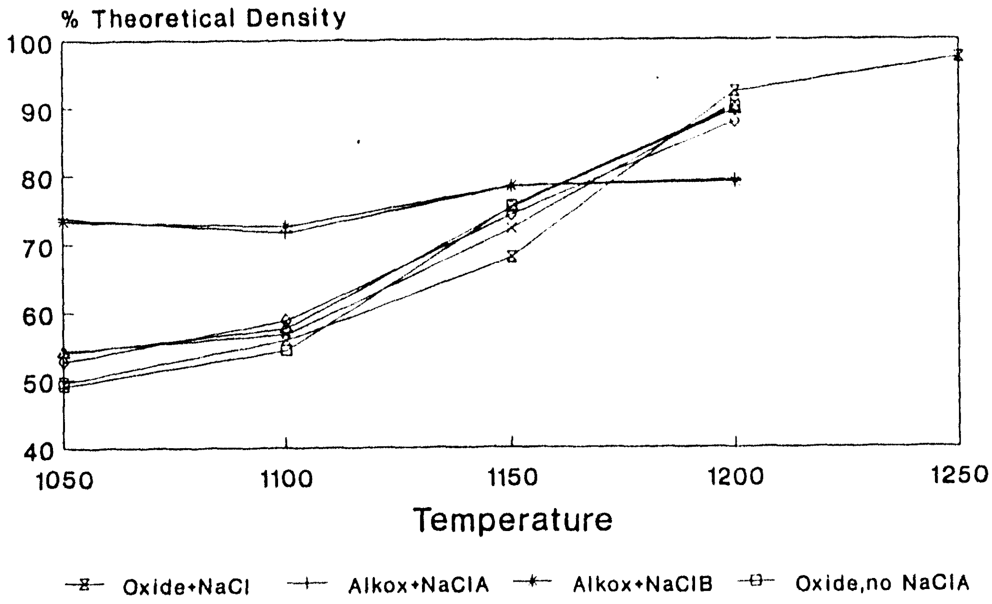

Fig. 1 Density of waste form pellets as a function of sintering temperature. Samples marked A and B are duplicate pellets separately processed.

Table 2: Compositions of ceramic mixtures using oxide starting materials to simulate residues from processing of combustible materials through the Molten Salt process (MSD ox 50% in Fig. 1). Waste oxides are 0.1% of oxides of Cu, Sr, Cr, Ce, Mo, Mn, Ni, and V, 0.05% PbO, 0.15% BaO, 0.2% each of oxides of B and Sb, and 0.6% sodium sulfate.

Component	Weight %	Mineral containing component
CaO	4.4	Perovskite, Zirconolite, Apatite
TiO_2	8.9	Perovskite, Zirconolite, Rutile
ZrO_2	3.9	Zirconolite
MgO	7.4	Spinel
Al_2O_3	40.2	Spinel, Nepheline
SiO_2	16.8	Nepheline
Na_2O	7.9	Nepheline
K_2O (waste only)	1.0	Nepheline
Fe_2O_3 (waste only	1.6	Spinel
ZnO (waste only)	3.7	Spinel
P_2O_5 (waste only)	2.2	Apatite (with Ca, Ce, Sr, Ba?)
Waste Oxides	2.0	Various

Mineral Phase	Weight %	Model Composition
Perovskite, Rutile, Apatite,	9	$CaTiO_3$, TiO_2, $Ca_5(PO_4)_3(OH,Cl,F)$
Zirconolite	11	$CaZrTi_2O_7$
Spinel	40	$MgAl_2O_4$
Nepheline	40	$NaAlSiO_4$

CHARACTERIZATION OF SINTERED WASTE FORMS

Each sintered sample is weighed and measured to determine density; x-ray diffraction and fluorescence are also done. Selected samples are then examined by scanning electron microscope. Samples sintered at 1200°C, with 90% of theoretical density, show porosity distributions that indicate the formation of gas bubbles inside the sample during sintering. Thus, the porosity is largely not interconnected and should not greatly affect the leaching characteristics of the waste form pellets. The SEM micrographs show that the grain size of the sintered pellets remains small - less than 1 micrometer on average - even at the highest sintering temperatures. Increasing the sintering time from 1 hour to 10 hours did not produce noticeable additional grain growth. The very fine grain size makes identification of the mineral phases and characterization using SEM energy dispersive x-ray analysis (EDX) very difficult. Despite the fine grain size, we have been able to obtain a number of EDX spectra that show nearly pure phase compositions for each of the major mineral phases.

The sample sintered at 1250°C was examined by SEM and EDX to determine the distribution of waste elements within the major mineral phases. For elements where clear identification was possible, the host phases are listed in Table 3.

Because the waste streams that will be treated in the MWMF will not be uniform in chemical composition, and because other mixed waste streams may eventually be treated in the MWMF, we are interested in identifying which chemical elements may affect the processing characteristics and final quality of the waste form. Chloride is the first element that we have examined, because it will be present in the residues from treatment of chlorinated hydrocarbon wastes and is readily soluble as NaCl. Addition of NaCl to the oxide and alkoxide mixtures with compositions given in Table 1 did not adversly affect the densification of the waste form at a given sintering temperature. Examination by x-ray fluorescence analysis using pellets formed from uncalcined powders as control samples showed that pellets formed from calcined powders were indistinguishable in composition from the control samples. Sintering at 1050°C caused most of the Ag in the samples to be lost, presumably because of the volatility of AgCl (vapor pressure of 6.6 mm Hg at 1050°C using the data given in [4]). For samples sintered at 1200°C in the presence of Cl, all Ag was gone. Ion microprobe analysis of these samples gave some indications that Pb and Sb might also be partially lost in the presence of Cl at the highest sintering temperatures.

Mixtures having the composition given in Table 1, but without NaCl intentionally added also showed loss of Ag at 1050°C; however, no further loss occurred at higher sintering temperatures. Silver oxide decomposes at

Table 3: Distribution of waste elements in major phases for the mixture given in Table 1. Sample sintered at 1250°C. Partial melting occurred.

Waste Element	Host phases
Molybdenum	AlSiCa phase (unidentified)
Antimony	Zirconolite and perovskite
Cadmium	Zirconolite and perovskite
Copper	Spinel, (nepheline/glass ?)
Zinc	Spinel, (nepheline/glass ?)
Cobalt	Spinel
Chromium	Spinel

temperatures above about 160°C [5]. Since the vapor pressure of Ag metal at 1050°C is very low [4], we presume that trace Cl impurities in the materials used to make the simulated waste forms have combined with the Ag released on Ag_2O decomposition and later volatilized. Chloride could not be excluded in any practical waste treatment operation, so provisions for collection of Ag from off-gases will need to be included in the waste form fabrication area for any processes operating at temperatures above about 900 to 1000°C.

CONCLUSIONS

We have designed a ceramic waste form based on the phases nepheline, zirconolite, perovskite, and spinel to use for immobilization of the residues from treatment of organic mixed waste. The waste form is similar in composition and processing parameters to SYNROC D, so would also be suitable for immobilization of sludges. Chloride has been shown to cause Ag to be lost during processing at temperatures of 1050°C, and may also enhance volatility of Pb and Sb.

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