

LETTERS TO THE EDITOR



CRYSTALLINE CERAMICS FROM DEFENSE HIGH-LEVEL WASTES

The "supercalcine concept" states that the mixture of elements contained in high-level nuclear waste can be modified with chemical additives and thereby be tailored into an assemblage of high-integrity crystalline phases. Wherever applicable, high-survivability minerals are chosen as models for these phases.¹⁻⁴ This concept has been reduced to practice in the tailoring of ceramics for Purex-process commercial high-level wastes.^{5,6} In this Letter, I describe how the concept can be applied also to defense high-level wastes and use as an example the Savannah River Plant (SRP) sludges.

Table I lists the oxide compositions of the calcines one would obtain if two typical SRP sludges were heat-treated for several hours at 600 to 800°C. During calcination, nitrate, nitrite, mercury, and carbon (coal) would have volatilized. The important aspect of these compositions is that they are made up largely of the refractory and low-solubility oxides of iron, aluminum, manganese, uranium, calcium, nickel, and silicon. These oxides could be crystallized and consolidated into a ceramic at 1100 to 1300°C. During the calcining or this consolidation heat treatment, most of the sulfate would decompose and volatilize,^a leaving Na₂O as the only volatile oxide. Application of high-sodium supercalcine-phase formation models^{5,8} would specify adding sufficient extra aluminum and silicon to crystallize all sodium as the refractory compound NaAlSiO₄ (nepheline). Based on experience with the phase formation in fired calcines² and supercalcines,^{3,5} I would expect the following major phases to form during the high-temperature firing of the compositionally modified sludge:

(Ni,Fe,Mn)(Fe,Mn,Al) ₂ O ₄	Spinel
(Al,Fe) ₂ O ₃	Corundum
NaAlSiO ₄	Nepheline
UO _{2+x}	Uraninite
Ca ₂ (Fe,Al) ₂ O ₅	Brownmillerite.

The small amount of phosphate would form whitlockite [Ca₃(PO₄)₂] or another metal phosphate.

Thus, by modification of the composition of the SRP sludges with but a few percent of selected additives, a high-level waste product having only one-third to one-fifth the volume of a corresponding vitreous product could be made.

Of course, criteria for comparing alternative waste forms also include feasibility of processing and effectiveness of radionuclide fixation under transportation and geologic-repository conditions. Standard ceramic technology such as

pelletization or hot pressing would have to be adapted for remote operation. The Swedish hot isostatic pressing (HIP) technology⁹ looks especially promising in that it requires only a few processing steps, permits virtually no waste volatilization, and yields an almost theoretically dense product.

There are two mechanisms for radionuclide fixation in these ceramics: atomic-scale incorporation into individual crystals ("primary containment") and microencapsulation of radionuclide-containing phases in the ceramic matrix of mineral-like phases ("secondary containment"). The matrix phases would be characterized by routine methods (XRD, SEM, EDS, etc.). However, because the radionuclides are present in such small concentrations (fractions of a percent), one may need to employ tools such as electron diffraction (for crystal structure), electron microprobe (for microchemistry), and scanning transmission electron microscopy (for structure and chemistry on the 100-Å scale) for characterization of the primary containment phases.

Potential primary containment phases are suggested by the oxide crystal chemistry of these elements in complex nuclear waste ceramics^{3,5}:

TABLE I
Typical Compositions of SRP Sludges*
After Calcining (wt%)

Component	F-Area Composite	H-Area Composite
Fe ₂ O ₃	32.8	26.0
Al ₂ O ₃	6.8	49.2
Mn ₂ O ₃	6.5	8.7
U ₃ O ₈	9.7	4.0
Na ₂ O	6.5	3.6
CaO	2.3	2.9
NiO	6.2	0.8
SiO ₂	7.6	0.7
[SO ₄] ²⁻ ^a	21.4	2.3
[PO ₄] ²⁻	0.2	1.8
Principal radionuclides (in mCi/g): ⁹⁰ Sr (30 to 50), ¹⁴⁴ Ce (~2), ¹⁰⁶ Ru (~1), ¹³⁷ Cs (~0.5), ¹⁵⁴ Eu (~0.3), ¹²⁵ Sb (~0.4), ⁶⁰ Co (~0.2), and gross α (~0.3)		

*Modified from data provided in Ref. 7.

^aMuch of the sulfate could be volatilized by calcining near 800°C.

^aIron, aluminum, and manganese sulfates decompose below 800°C; some refractory CaSO₄ could remain.

Strontium	in $\text{Ca}_2(\text{Fe,Al})_2\text{O}_5$ as $\text{SrAl}_2\text{Si}_2\text{O}_8$	[Brownmillerite] [Sr-feldspar]
Cerium, Europium	in UO_{2+x} as $\text{Ca}_2(\text{Ce, Eu, Ln})_8$ (SiO_4) $_6\text{O}_2^b$	[Uraninite] [Apatite]
Cesium	as $(\text{Ce, Eu, Ln})\text{PO}_4$ in NaAlSiO_4 as $(\text{Cs, Na})\text{AlSi}_2\text{O}_6$	[Monazite] [Nepheline] [Pollucite]
Ruthenium	as RuO_2	
Cobalt	in (Ni, Fe, Mn, Co) $(\text{Mn, Fe, Al})_2\text{O}_4$	[Spinel]

Formation of the radionuclide-containing phases is controlled by the bulk composition of the modified sludge. If one or more of these phases were found to be unsuitable, then further tailoring could be affected through additional modification of the bulk composition. For example, if it were found more desirable to have strontium crystallize as SrTiO_3 , TiO_2 additions would also be made to the sludge. Here again, only a very few percent of additives would be required.

The stability of a dense ceramic consisting of the mineral-like phases described above should be excellent in any of the routine "leaching" tests and in a geologic repository in which the host rock is a silicate (granite, basalt, shale, tuff, etc.) because many of the phases would be at or near equilibrium with such rocks.¹⁰

In summary, I have described how a crystalline mineral-like ceramic can be made from typical defense high-level waste sludges by application of the supercalcine concept. Tailoring of the ceramic would require only a few percent of additives resulting in a product with but a fraction of the volume of a comparable vitreous product. The development of phase formation models would appear to be straightforward in the light of our present knowledge. For processing, a substantial effort at adapting well-established ceramic technology to remote operation would be required.

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^bLn = lanthanides: La, Ce, Pr, Nd, Pm, Sm, Gd, Tb, and Dy.

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