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DEVELOPMENT OF MULTIBARRIER NUCLEAR WASTE FORMS

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DEVELOPMENT OF MULTIBARRIER NUCLEAR WASTE FORMS*

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INTRODUCTION

The High Level Radioactive Waste Immobilization Program conducted by the Pacific Northwest Laboratory (PNL) for the Department of Energy (DOE) has as one of its objectives to develop processes for converting high level liquid waste (HLLW) from alternative fuel cycles to solid forms demonstrated to be physically, chemically, and radiolytically stable and inert. A major part of this program has been in-depth studies on low-melting (1000-1150°C) borosilicate glasses (1,2). To provide for waste streams not readily vitrifiable and to ensure that other options for encapsulation of fission product waste were considered, an effort was initiated to develop alternative waste forms based upon a multibarrier concept (Fig. 1). The multibarrier concept aims to separate the radionuclide-containing inner core material and the environment by the use of coatings and metal matrices. The resultant composite waste form exhibits enhanced inertness due to improved thermal stability and mechanical strength, and the added barriers greatly improve leach resistance.

Two options were developed for the inner core of the multibarrier concept: supercalcine pellets and glass marbles. Supercalcine is a crystalline assemblage of mutually compatible, refractory, and leach-resistant solid solution phases incorporating HLLW ions. Supercalcine powder is produced by spray calcining the liquid waste stream to which Al_2O_3, CaO, SiO_2, and SrO have been

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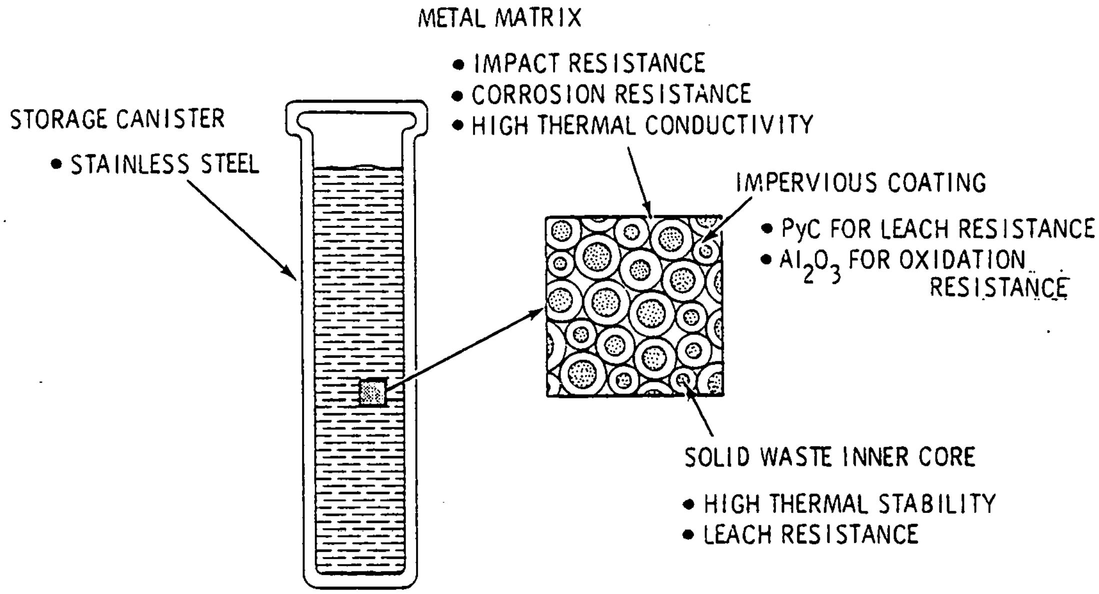

Fig. 1 Multibarrier Concept for Isolating High-Level Waste.

added. Supercalcine pellets are produced by disc pelletizing. The amorphous supercalcine crystallizes into solid solution phases after subsequent heat treatment.

Glass marbles provided an alternative to the cast glass waste form and do not require the development of a crystalline waste form (e.g., supercalcine). Technology exists to produce waste glass in a continuous ceramic melter (3). In this process, since the glass is directly drained into a canister, product quality verification is a potential problem. Marble production would provide a separate step between the melter and the canister to allow for quality assurance and ease of recycling to the melter if a below-standard product is produced.

The development of coatings for supercalcine was pursued to provide an additional protective layer between the radionuclides and the environment. The coatings include the application of a 40-µm pyrolytic carbon (PyC) layer as a barrier to enhance leach resistance and a 60-µm Al_2O_3 layer as a barrier to increase oxidation resistance. Glass coating of supercalcine by frit and glaze, which is a less complex coating process, was also investigated. Although coatings offer a high level of increased inertness, a high level of technological complexity is also required.

The final phase in the demonstration of the multibarrier concept is matrix encapsulation to improve the mechanical strength of the composite waste form to improve thermal conductivity, yielding lower internal temperatures. As the selection of the metal matrix is dependent upon temperature limitations of the inner core, several matrix materials were investigated and two encapsulation processes were developed: vacuum casting and gravity sintering. Other researchers have studied calcine particles (4) and glass beads (5) in metal matrices.

This paper describes the development of four multibarrier waste forms, which were demonstrated by the production of four 1-liter stainless steel canisters, each containing one of the waste forms (6). These 1-liter demonstrations are described in Table 1.

SUPERCALCINE-CERAMIC CORES

The "Supercalcine Concept"

The concept states that the mixture of elements contained in high-level nuclear waste can be modified with chemical additives and thereby tailor-made into an assemblage of high-integrity crystalline phases. Wherever applicable, high-survivability minerals are chosen as models for these phases (7-14).

Research on a high-integrity ceramic advanced waste form began in 1973 (10). The design specifications on this ceramic waste form included low leachability, low waste volatilization during processing and thermodynamic stability at temperatures as high as 800°C. Waste loading was to be as high as reasonably possible, and at least comparable to the cast glass HLW product. The first step in processing this ceramic was to be calcination using spray or fluidized-bed technologies. The precursor powder to this ceramic

Table 1. Materials and Parameters Used for the One-Liter Multibarrier Demonstrations

Inner Core	Coating	Matrix	Encapsulation
72-68 glass marble (∿10 mm dia)	none	Pb-10Sn	vacuum cast 400°C
supercalcine (∿7 mm dia)	none	Al-12Si	vacuum cast 650°C
supercalcine (∿7 mm dia)	glass glaze (<1 mm thick)	Al-12Si	vacuum cast 650°C
supercalcine (∿2 mm dia)	CVD PyC (40-μm thick) Al_2O_3 (60-μm thick)	Cu	gravity sintered 900°C, 8 hrs

would physically resemble ordinary calcine but would have superior properties when subsequently heat treated, hence the name "supercalcine." After this crystallization/sintering step, the product would become "consolidated supercalcine" or "supercalcine-ceramics."

Supercalcine-ceramics have been successfully developed to these specifications but have not yet been tailored for thermodynamic equilibrium with any of the candidate repository rock types, although many of its current minerals should be stable in basalts, shales, and granites. The hydrothermal stability of existing products is described elsewhere in this volume (15,20).

Once the precursor supercalcine powder has been formed, there are at least four alternative products that can be made from it.

- Crystallized, but unconsolidated calcine (14)
- Fusion-cast ceramics
- Hot-pressed ceramic (11,23)
- Cores of a multibarrier product (10).

Crystal Chemistry of Current Supercalcine-Ceramics

Two supercalcine synthetic mineral models have been developed for use as a core material of the multibarrier product. Crystal chemistry has been described previously (12,13) and will only be summarized here. The crystal chemical roles of waste ions are given in Table 2. The formulae in this table are only nominal. Each of the nominal compositions has been synthesized separately and its x-ray diffraction pattern matched to the corresponding reflections in the diffractogram of the crystallized supercalcine-ceramic.

The major roles given in Table 2 have been determined from more than 200 crystal chemical and compatibility studies (12), but minor solid solution and partitioning of ions among two or more phases is to be expected. For example, Ln is partitioned between the apatite and monazite phases and a small amount may also be substituting in the fluorite and tetragonal-zirconia phases. The submicrometer dimensions of most of the crystals disqualify routine electron microprobe elemental characterization, but scanning transmission electron microscopy (STEM) will be utilized for direct characterization of elemental distributions in supercalcine crystals in the near future.

From Table 2 it can be seen that only three additives are needed to tailor the liquid waste compositions: Ca, Al, and Si.

Table 2. Crystal Chemical Roles of Waste Ions[a]

Ions	Nominal Composition Of Synthetic Mineral	Structure Type
Sr,Ln[b]	$(\underline{Ca},Sr)_2Ln_8(\underline{Si}O_4)_6O_2$[c]	Apatite $[A_{ss}]$
Ln, $[PO_4]$	$LnPO_4$	Monazite $[M_{ss}]$
Cs,Rb,Na	$(Cs,Rb,Na)\underline{AlSi_2}O_6$	Pollucite [P]
Sr,Ba	$(\underline{Ca},Sr,Ba)MoO_4$	Scheelite $[S_{ss}]$
U,Ce,Zr	$(U,Ce,Zr...)O_{2+x}$	Fluorite $[F_{ss}]$
Zr,Ce,U	$(Zr,Ce,U...)O_{2+x}$	Tetragonal-Fluorite $[T_{ss}]$
Fe,Ni,Cr	$(Ni,Fe)(Fe,Cr)_2O_4$ and	Spinel $[Sp_{ss}]$
	$(Fe,Cr)_2O_3$	Corundum $[Fe_2O_3]_{ss}$
Ru	RuO_2	Rutile

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[a] Te,Pd,Rh,Tc,Pm,Np,Pu,Am,Cm were not included in the simulated waste.

[b] Ln=La,Pr,Nd,Sm,Eu,Gd,Y.

[c] Additive ions are underlined.

Nitrates of Ca and Al and colloidal silica are the liquid sources of these elements. Typically, twice the stoichiometrically required level of additives are specified, because the day-to-day compositions are expected to vary considerably. The extra Ca would fix transient excesses of Mo and the (Al+Si) serves the same purpose for the alkali elements. If the excess additives are not needed, they form an inert, but generally x-ray amorphous, calcium aluminosilicate matrix for the supercalcine-ceramic phases.

SPRAY CALCINATION

Process simplicity, an advanced stage of process development, demonstrated operating capability, and highly desirable calcine powder characteristics make the spray calciner ideally suited to the production of a chemically altered calcine, "supercalcine." The developmental spray calciner constructed as part of the Waste Fixation Program (16) was used to prepare 50-kg quantities of two supercalcine compositions (SPC-2 and SPC-4). Both supercalcines simulated the PW-7 waste composition (17) with individual constituents added in a nitrate form (6). Chemical substitutions were made as indicated to eliminate radioactive material (uranium), reduce the amount of costly materials (ruthenium), and to simulate the lanthanides and actinides (rare earth mixture) present in the waste.

Spray-calcined material consists of metal oxides, a trace of moisture and some level of residual nitrates or carbonates, depending on feedstock composition. The powder is very fine and typically displays surface areas of 10 to 20 m^2/g.

DISC PELLETIZING

Disc pelletizing is an agglomeration technique that forms spherical pellets from powders (18). The purpose of pelletizing the spray-calcined supercalcine powders was to produce consolidated high-density spheres (pellets) of about 1 to 7 mm diameter that would be sintered and crystallized by subsequent heat treatment. Disc pelletizing is an optimum method of compacting nuclear waste compositions when followed by sintering; this is because the spray-calcined powder is highly reactive.

The operating capacity of this process is exceptionally high. The smallest unit commercially available, a 16-in dia lab-scale pelletizer, has a maximum powder feed rate of 35 to 55 kg/hr. The next size, a 3-ft dia unit, will pelletize at a rate of 135 to 225 kg/hr. With 150 g of oxides per liter of waste the large spray calciner operated by PNL has a projected maximum feed rate of 350 ℓ/hr and a maximum calcine production of 52.5 kg/hr. This output could be handled by the lab-scale unit alone. The 3-ft unit could handle the maximum solids output of four large spray calciners.

SUPERCALCINE SINTERING BEHAVIOR

The sintering behavior of supercalcine was studied to identify parameters to be used in the densification and crystallization of supercalcine pellets preparatory to the coating process and to identify differences in sintering behavior between various preparation techniques and/or supercalcine formulations. Two methods were used, one incorporating a bulk-vibrated sample with a density typical of disc pelletizing and the other a pressed sample representative of standard sintering tests.

For the bulk test, alumina crucibles were filled and vibrated to produce powder samples with green densities comparable to that of pelletized supercalcine (0.90 to 1.15 g/cm^3). The second series of sintered samples were produced by pressing as-prepared supercalcine powder at 3400 psi in a 0.75-in steel punch and die. Table 3 summarizes the sintering information for pressed, vibrated, and disc pelletized supercalcine.

Table 3. Sintered Density of Supercalcine

Material	Sintering Temperature	Bulk Sintering Density, g/cm^3
SPC-2 pressed	1100°C	3.22
SPC-4 pressed	1200°C	4.21
SPC-2 vibrated	1200°C	4.06
SPC-2 pelletized	1175°C	3.84
SPC-4 pelletized	1230°C	3.60

GLASS MARBLE PRODUCTION

The technique used to produce simulated waste glass marbles for multibarrier development is a laboratory-scale version of a process developed by Corning Glass Works (19). The process incorporates the direct casting of a glass stream into vibrating molds. The cavities in the molds are cylindrical with a hemispherical bottom.

The production of acceptable-quality simulated waste glass marbles was successfully demonstrated on a laboratory scale by the production of three kilograms of marbles. The laboratory-scale vibratory technique is similar to that successfully used by Corning Glass Works; thus, scale-up to engineering-scale production of waste glass marbles should not be too complex. A major requirement for engineering-scale production is the delivery of the glass from the furnace to the marble machine.

PyC AND METAL OXIDE COATINGS BY CVD

Several approaches were explored at BCL in an effort to overcoat PyC-coated supercalcine particles with a metal oxide. The PyC coating was deposited in a fluidized bed from C_3H_8 or C_2H_2. The primary function of the PyC layer is to provide leach resistance to ground water. The metal oxide coating protects the PyC layer from oxidation at elevated temperatures and also provides additional leach resistance.

In preliminary work, SPC-2 supercalcine material was overcoated with PyC and Al_2O_3 in a fluidized bed with ZrO_2 diluent as an expedient way of supplying materials for testing. This method yielded good-quality Al_2O_3 and PyC coatings on 20-g beds of particles, but the Al_2O_3 coatings were only successful when the substrate size was less than 2 mm. The modifications necessary to extend this process to beds of more economical size containing larger particles (<2 mm) were not justified in comparison to simpler approaches. Consequently, the application of Al_2O_3 coatings in a drum coater were explored.

Drum coater coatings of Al_2O_3 were applied directly to supercalcine cores and did not crack in thermal tests. The major problem with this method of creating PyC/Al_2O_3 duplex coatings was the oxidation loss of PyC during the Al_2O_3 overcoating. Silica (SiO_2) was then considered as an alternative to Al_2O_3 because it could be applied to PyC-coated supercalcine cores under essentially nonoxidizing conditions, thus preserving the PyC coating. PyC was not oxidized during SiO_2 overcoating, but the SiO_2 coating was porous and allowed PyC oxidation during subsequent testing. Good-quality protective coatings were obtained by first overcoating the PyC with SiO_2, which then protected the PyC layer during application of an impervious layer of Al_2O_3. The negative feature of this approach was that two chemically different oxide layers were required. Because of this complication in the drum coating system, a vibrating bed system was examined.

Alumina overcoating in a vibrating bed of PyC-coated supercalcine cores (2-3 mm) was successfully applied to beds of $\sim$100 cm^3. This was the method used to overcoat $\sim$1100 cm^3 of PyC-coated supercalcine cores for matrix encapsulation tests. The PyC coatings had been applied previously by the fluidized-bed method.

GLASS COATING DEVELOPMENT

One alternative to CVD coatings is the application of glass coatings. Two techniques to produce such a coating were examined on a laboratory scale. In both cases a coating material, glass frit or glaze slip, was applied to sintered supercalcine spheres at room temperature and heated to form a continuous glass coating over the sphere surface. The object was to produce an acceptable product for characterization. Process development and material evaluation was conducted as required to meet this end.

Glass Frit Coating

A ground frit coating up to 1 mm in thickness was applied to sintered supercalcine spheres 5 mm to 10 mm in diameter using the disc pelletizer. The technique was similar to that used in the pharmaceutical industry to coat pills. The sintered pellets were placed in the rotating pelletizer, and a quantity of frit and a fine water spray were simultaneously added. The frit coating built up in a snowballing fashion until the coated pellets were removed. Green strength was sufficient to withstand handling without destroying the coating. Corning code 7740, 7059, and 1723 frits all produced an acceptable pellet coating in spite of their differences in grain size and composition. The ground frit coating was converted to glass by heating the coated pellets on tabular alumina on a stainless steel tray.

Glaze Slip Coating

Spraying and dipping techniques were used to apply the glaze slip to sintered spheres. While spraying has considerable process advantages and was quite promising, it required tight control of slip properties. Dipping is a more complex process, but it was not as sensitive to the fluctuating slip properties that were encountered.

Since the control of slip consistency is a complex situation faced by commercial ceramic glazing operations, an attempt to obtain better control over slip properties was made by use of a commercial glaze composition, Ferro-CM-857*. The glaze slip was prepared by the addition of water to the dry glaze powder. One liter of coated SPC-4 pellets was produced by dipping in the prepared Ferro glaze. The coatings were vitrified at 1000°C for 10 minutes and rapidly cooled by air quench.

SELECTION OF MATRIX MATERIALS

Two types of processes were considered for the encapsulation of solidified HLW: gravity-sintered metal powders and vacuum-cast alloys. Selection of these processes is based on the compatibility of different metals with the advanced waste particle forms, the ease of the encapsulation process, and the optimization of high thermal conductivity, impact strength, and corrosion resistance.

Gravity-Sintered Metal Powder

Gravity-sintered metal powders are considered prime candidates for use as metal matrices with supercalcine pellets, the waste form with the greatest volumetric heat generation and the highest allowable fabrication and storage temperatures. The primary reason for considering gravity-sintered matrices is that metals with high melting points can be employed (e.g., copper, bronze, stainless steels, etc.). Gravity sintering also lends itself well to remotely operated fabrication facilities because the process is fairly simple.

Since gravity-sintered matrices are formed from near-spherical metal particles, final matrix densities range from ∿40% to ∿65% of theoretical density. Compared to the cast, 100%-dense metal matrices, gravity-sintered matrices may not offer the optimum leach protection and thermal conductivity because of the interconnecting porosity of the sintered matrix.

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*Ferro-Tech Incorporated, Pittsburgh, PA 15218.

Vacuum-cast Alloys

Vacuum-cast alloys are considered prime candidates for matrix encapsulation of waste-glass marbles and glass-coated or uncoated supercalcine. Fabrication temperatures for the glass marble and glass-coated supercalcine waste forms are limited by the softening points of the glasses, which are ∿600°C. Uncoated supercalcine has a fabrication temperature limit of 1200°C, which is above the casting temperature of the candidate metal matrix materials. Vacuum-cast matrices have many advantages over the gravity-sintered matrices since the matrix will be cast at 100% density.

Lead, lead alloys, aluminum, and aluminum alloys are the best candidates for vacuum-cast matrices because of fabrication temperature restrictions and their relatively low melting temperatures. Aluminum and its alloys have higher thermal conductivity values, higher melting points, and higher strengths than the lead alloys. Although a greater density of lead provides increased radiation shielding, the increased weight adds difficulty in handling and transporting the canisters.

Preparation of One-liter Demonstration Encapsulations

The simulated waste pellets were poured into type 316 stainless steel canisters measuring 65 mm ID by 305 mm long with a wall thickness of ∿5 mm. The canisters were continuously vibrated during filling to facilitate packing of the particles. Encapsulation of CVD-coated supercalcine was accomplished by vibrating -100 mesh spherical copper powder into the voids between the supercalcine particles, sealing the canister, and sintering at 900°C for 8 hours under a dynamic vacuum. The canisters used for vacuum casting had a tube at the bottom connected to a vacuum pump and a sealed tube at the top extending into the canister through the cover. The canisters were preheated under a dynamic vacuum prior to casting; uncoated and glass-coated supercalcine were heated to ∿600°C and simulated waste-glass marbles were heated to ∿350°C. The preheated canisters were immersed in approximately seven liters of molten metal; the sealed tube was then severed, and the metal was drawn into the voids within the canister. Casting temperatures for Pb-10Sn and Al-12Si were 400°C and 650°C, respectively. After casting, the canisters were removed from the crucible and allowed to air cool.

CONCLUSIONS

Several alternatives for the immobilization of nuclear wastes are being considered. This paper describes the process development and one-liter lab-scale demonstration of four multibarrier concepts. Characterization of the multibarrier products are described elsewhere (21). In general, proposed waste form processes have properties falling within a narrow range (22). Thus process complexity and feasibility become important parameters.

Based on the multibarrier processes described in this paper, several conclusions can be made:

- Gravity sintering and vacuum casting are both applicable methods for metal matrix encapsulation.
- The multibarrier concept of glass marbles encapsulated in a vacuum-cast lead alloy provides enhanced inertness at a minimum increase in technological complexity.
- If it were desirable to develop a crystalline multibarrier waste form, uncoated sintered supercalcine pellets would offer enhanced inertness at a much lower level of technological complexity than glaze- or CVD-coated supercalcine.
- The 16-inch diameter pelletizer unit has enough capacity to handle the output of a large PNL spray calciner (52.5 kg of calcine/hr) and it can form spray-calcined material into pellets with diameters of 2 mm to 20 mm having strength enough to withstand handling without significant breakage.
- Chemical vapor deposition coating of supercalcine should be pursued only if a very high level of inertness is required.

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