

Cermet High Level Waste Forms

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CERMET HIGH LEVEL WASTE FORMS

A Progress Report

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ABSTRACT

The fixation of high level radioactive waste from both commercial and DOE defense sources as cermets is currently under study. This waste form consists of a continuous iron-nickel base metal matrix containing small particles of fission product oxides. Preliminary evaluations of cermets fabricated from a variety of simulated wastes indicate they possess properties providing advantages over other waste forms presently being considered, namely thermal conductivity, waste loading levels, and leach resistance. This report describes the progress of this effort, to date, since its initiation in 1977.

INTRODUCTION

Investigations have shown positive indications that cermets may provide a suitable and advantageous solid form for high level radioactive waste fixation. The cermet process involves the isolation of fission product waste as oxides in a corrosion resistant, thermally conductive metal matrix. The cermet produced by this process is defined as a continuous metal phase containing small particles ($\sim 1 \mu\text{m}$) of waste oxide. Wastes being considered for fixation as cermets are those of commercial facilities such as Nuclear Fuel Services; however, since these wastes are similar, as far as the cermet process is concerned, to

wastes stored at Savannah River and Hanford, the cermet process is also applicable to DOE defense wastes.

PROCESS PROCEDURES

A chemical coprecipitation of waste and additives from molten urea is the primary process step by which the unique characteristics of the cermet waste form are obtained.¹ Liquid waste and/or sludge together with desired additives (discussed below) are evaporated to form a concentrated solution (or slurry) to which is added urea (m. p. 132°C), and the temperature is increased gradually to 180°C. At this point all of the solids (waste and additives) have been taken into solution with the molten urea. After approximately one hour, a precipitate is obtained from the then molten urea solvent (see page 16 for an alternate process); the precipitate appears to be a water insoluble mixture of hydrated oxides and amides. It should be noted that zeolite 13X (appearing in some waste tanks) is also soluble in molten urea and would be homogenized with other waste components. As precipitation continues, gaseous reaction products, primarily ammonia and carbon dioxide, are evolved as shown in the process flowsheet in Figure 1. The precipitate of intimately mixed components is calcined in air at 800°C to remove residual urea and to convert the precipitate to its component oxides. Decomposition products are volatilized during the calcination process. Calcined oxides are, at this point, a loose aggregate of fine particles of up to 1-2 μm in size; particle size is dependent to some degree upon the amount of urea originally added in the precipitation step--larger initial amounts of urea result in smaller particle size precipitates. It is thought that this occurs because when urea is added in great excess to the amount required to decompose the nitrates, the precipitation reaction kinetics are slowed, allowing the nucleation of a large number of smaller particles. As the amount of added urea is decreased, the precipitation

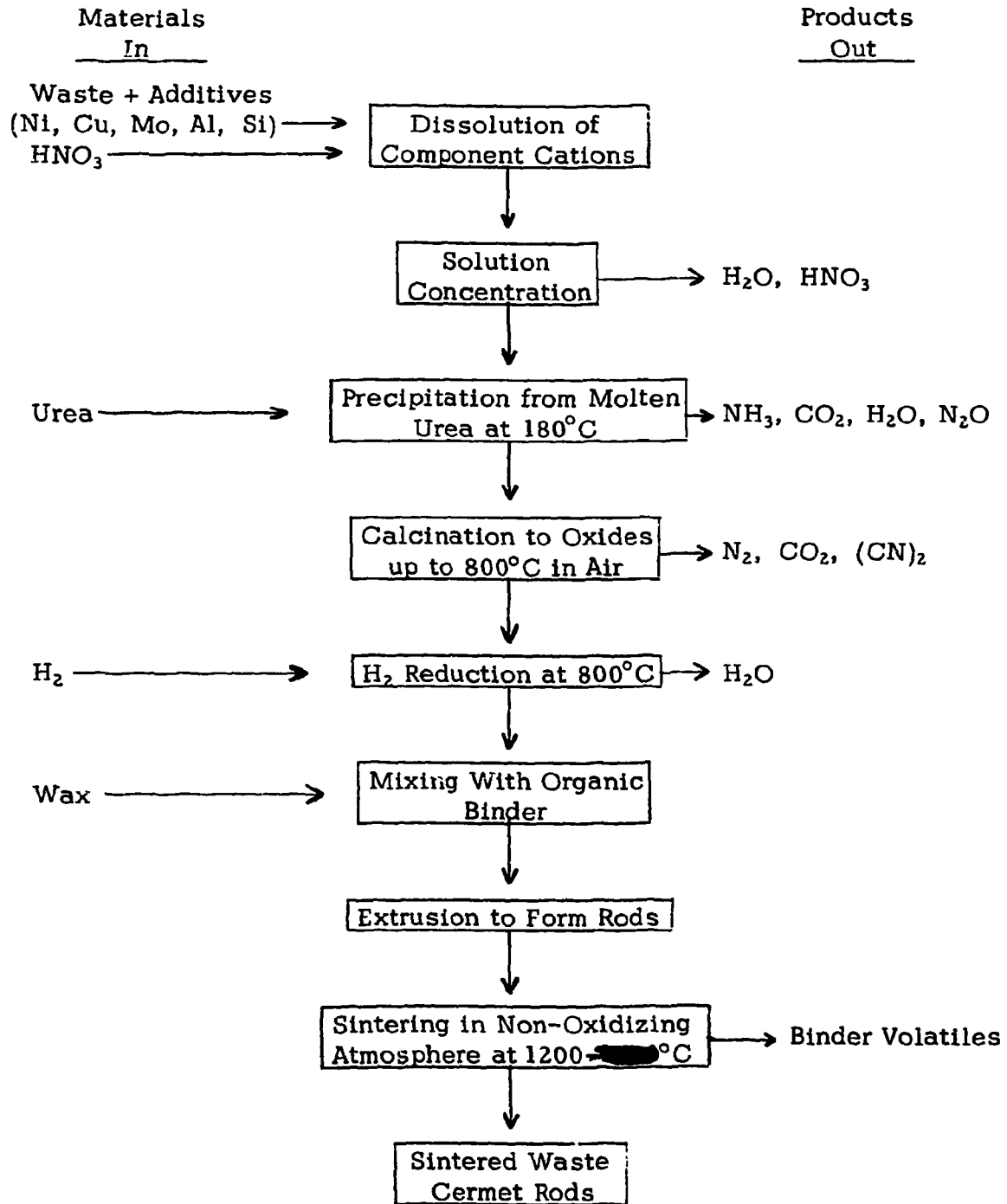


Figure 1. Flowsheet: Laboratory Scale Operations Used to Produce Cermet Storage Forms From High Level Waste

reaction proceeds more rapidly producing larger particle sizes. Since the entire original solution of waste and additives is precipitated and calcined yielding calcined solid and gaseous reaction products, the process is quantitative.

Calcined oxide powders at this point can be densified by standard techniques such as sintering or hot pressing to form monolithic ceramic forms. However, most existing wastes contain large amounts of metal species, primarily iron, which when heated in a reducing atmosphere, such as hydrogen, convert from an oxide to a metallic form. Densification of this reduced metal-oxide mixture appears to hold many advantages over the formation of ceramic compacts. Densification of reduced material by either hot pressing or extrusion with a binder followed by sintering yields a cermet with low porosity, purportedly low leachability, and high thermal conductivity, as compared with ceramic or vitreous waste forms. When high level wastes containing large quantities of reducible metal cations, together with some metal additives from DOE stockpiles of contaminated metals, such as nickel (1), are formed into cermets, little, if any additions of pure materials need be made.

CERMET COMPOSITIONS AND PROPERTIES

Evaluation of cermet properties as a function of the process by which it is formed, and chemical content is in progress. A variety of cermets has been made from synthetic fission product wastes simulating typical wastes at National Fuel Services, Savannah River, and Hanford. The final metal matrix composition of the cermet is tailored through additions of hydrogen-reducible metal ions and other cations to the waste at the

(1) For example, approximately 720 tons of contaminated nickel metal wastes from gaseous diffusion plants are currently in storage.

head-end of the process. These component additions together with the quantities of reducible metal ions already present in the waste are adjusted to yield alloys having predictable thermal conductivity and corrosion resistant properties. To date pure nickel, a 50 wt. % Fe - 50 wt. % Ni alloy, and a 70 wt. % Fe - 20 wt. % Ni - 5 wt. % Cu - 5 wt. % Mo metal matrices have been investigated. The last matrix is similar to a Hastelloy series alloy and provides the best corrosion resistance and thermal conductivity yet produced.

A range of loading ratios of compound oxides in the cermet metal matrix have also been investigated. Loadings were varied from 20 wt. % oxide: 80 wt. % metal to 40 wt. % oxide: 60 wt. % metal. It should be noted that actual waste loadings far exceed the waste oxide loading ranges of 20 wt. % to 40 wt. % because of the high content of reducible metal species in the waste, such as iron, which are incorporated in the metal matrix phase. Selection of the appropriate oxide loading level will ultimately depend on the desired cermet physical and leach rate properties as well as on the maximum decay heat concentrations allowed in the storage repository. As would be expected, with increasing weight percent of the oxide component in the cermet, thermal conductivity decreases. The degree of oxide loading has little or no effect upon the processing of wastes to form cermets since nearly any oxide-to-metal ratio can be produced by this process.

Processing various waste types into compactible cermets has been studied. Initially, experiments were done with a simulated waste solution, the composition of which is shown in Table 1. This composition simulates a waste resulting from a burnup to 30,000 MW days/ton with the waste at a concentration equivalent of 150 gal/ton U.

With additions of appropriate amounts of nickel and appropriate amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ and $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ (the latter additives to form pollucite from cesium), a series of cermets were formed with varying oxide-to-metal

Table 1. Simulated Waste Composition

<u>Element*</u>	<u>Molarity</u>	<u>Element*</u>	<u>Molarity</u>
La	0.104	U	0.041
Ce	0.0159	Fe	0.0315
Cs	0.0205	Ni	0.012
Sr	0.019	Cr	0.074
Ru	0.0203	Na	0.0038
Zr	0.0358		

*As nitrates.

ratio. Following precipitation, calcination, and hydrogen reduction, pellets of 2.5-cm diam were hot pressed at 4000 psi and 1100°C and the product measured for density and thermal conductivity; results are shown in Figure 2.

Simulated Savannah River waste was compounded; the distinguishing feature of this waste is its high iron content which can be used in the formation of alloys in the metal phase of the cermet. A typical composition of simulated SRP waste is shown in Table 2 (based on actual waste analyses).² Hot pressed cermets with two different metal matrix compositions were made from this waste formulation. A cermet having a 50 wt. % Fe - 50 wt. % Ni metal phase, and 20.8 wt. % oxide phase had a measured density of 7.35 g/cc after hot pressing at 1050-1100°C for one hour at 4000 psi. The cermet having a 70 wt. % Fe - 20 wt. % Ni - 5 wt. % Ni - 5 wt. % Cu - 5 wt. % Mo metal phase and 27.5 wt. % oxide phase had a measured density of 7.41 g/cc after hot pressing (under the same conditions). Experimentally determined thermal conductivity of this latter cermet is shown in Table 3; thermal conductivity for the "Hastelloy" matrix material is slightly higher than that of a corresponding oxide/metal cermet as indicated in Figure 2. It is interesting to note that the thermal conductivity of this cermet is very close to that of a Hastelloy series alloy

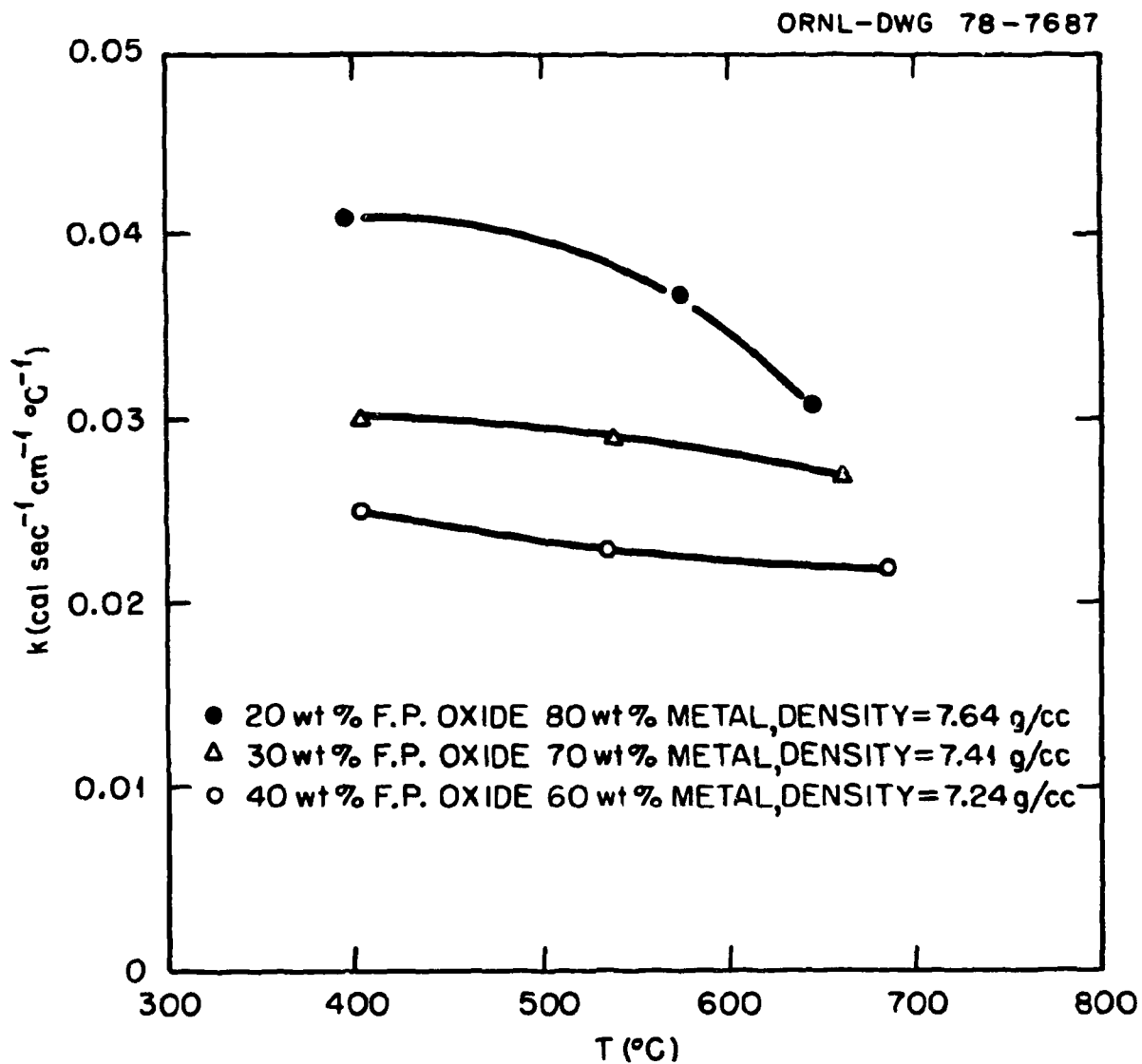


Figure 2. Thermal Conductivity for Various Cermet Oxide-Metal Ratios

Table 2. Waste Composition and Additives for Cermet Preparation Having a "Hastelloy" Matrix

	<u>Element</u>	<u>Molarity</u>
<u>Waste</u>	Fe	1.4
	Mn	0.4
	Al	0.02
	Ce	1.6×10^{-5}
	Zr	1.28×10^{-3}
	Sr	1.32×10^{-3}
	U	4.3×10^{-2}
	Ru (for Rh and Pd)	6.6×10^{-5}
	Cs	1.38×10^{-4}
	Sm (for actinides and all rare earths except Ce)	4.76×10^{-4}
	Na	2×10^{-4}
<u>Additives</u>	SiO ₂	0.02 (mol. equivalent of Al)
	Ni	Variable to achieve desired metal component alloy composition
	Cu	
	Mo	

Table 3. Thermal Conductivity of 70 wt. % Fe - 20 wt. % Ni - 5 wt. % Cu - 5 wt. % NiO - 27.5 Oxide Cermet

<u>T (°C)</u>	<u>k cal °C⁻¹ sec⁻¹ cm⁻¹</u>
232	0.046
320	0.037
502	0.034
654	0.033

containing no oxides; this alloy composition seems preferable to the 50 wt. % Fe - 50 wt. % Ni alloy because it requires less nickel additive (the alloy is iron rich, as is the waste from which it is formed). For the same reason, higher waste loading per unit weight of cermet can be achieved. Again, it should be remembered that actual waste loading, which includes the iron content, amounts to ~75 wt. % of the cermet solid. This represents a weight concentration of sludge into cermet of 100:1 or a volume reduction of 200:1. Only about 10 wt. % of the total cermet mass is noncontaminated added material. The remaining 15 wt. % is made up from DOE stockpiles of contaminated metals. Further work on the thermal conductivity of this material, its densification by extrusion, and sintering is underway.

The most recent waste studied for isolation as a cermet is the NFS acid thorium waste.³ Simulated waste and additives required to yield a cermet with a 30 wt. % oxide phase and a 70 wt. % metal phase of the 70 wt. % Fe - 20 wt. % Ni - 5 wt. % Cu - 5 wt. % Mo alloy was prepared. The oxide phase of the simulated cermet is almost entirely ThO₂ since only small amounts of other species exist in the waste relative to thorium. This waste, along with additives, has been precipitated from molten urea, calcined, hydrogen reduced, and densified by hot pressing to yield a pellet suitable for thermal conductivity determinations. Preliminary data from thermal conductivity tests show that this type of cermet has a conductivity comparable to other cermets containing a 30 wt. % oxide loading.

CESIUM AND RUTHENIUM VOLATILITY

A study to determine how cesium is fixed in the cermet is in progress. Pollucite, a cesium-bearing aluminosilicate, is expected to form, with the proper additives, from the cesium contained in the waste. A urea precipitation of a solution containing only cesium ion and specific pollucite-forming

additives (soluble aluminum and silica salts) was performed followed by calcination of the precipitate at 500°C and 800°C. The presence of cesium as cesium cyanate in the material calcined at 500°C was observed by x-ray diffraction. The same material calcined at 800°C yielded an x-ray diffraction pattern typical of an amorphous state. It is postulated that the particle size of the 800°C calcine is too small for its structure to be detected using x-ray diffraction. Crystallite growth to a detectable and identifiable level probably would not occur for this material below approximately 1200°C. It appears that between 500°C and 800°C the cesium cyanate decomposes and a stable cesium-containing phase (probably pollucite) forms since the retention of cesium in the material calcined at 800°C has been proven by x-ray fluorescence. Recently completed x-ray diffraction studies on the hot pressed ceramic at 1200°C confirmed the formation of pollucite; however, further investigation of the mechanism by which cesium is rendered insoluble and in a low vapor pressure state is required. An associated volatility problem also exists with any elevated temperature processing of ruthenium. However, as discussed in more detail later, it is felt that characteristics of the cermet process eliminate the ruthenium volatility problem.

STUDY OF DENSIFICATION METHODS

Densification by extrusion with a binder and subsequent sintering was performed successfully using 50 wt. % Ni - 50 wt. % Fe alloy material. After the precipitated material had been hydrogen reduced, 15 g of the product was mixed with 4.5 g of cerecin wax as a binder and extruded through a 6.25-mm diam orifice. Extrusion pressure required at room temperature was ~3000 psi. Initial extrusions yielded "green" rods with some surface cracks which have since been eliminated by a change in the design of the extrusion orifice. Sintering of this 6.25-mm extruded rod at

1200°C for six hours yielded a cermet rod with a density of 6.21 g/cc as compared to 7.35 g/cc for the same material after hot pressing. Sintering resulted in a 25% dimensional shrinkage of the rod.

Preliminary studies show that reduction of the binder content used for extrusion results in the formation of sintered cermets having densities approaching that of hot pressed pellets without a significant increase in the pressure required for extrusion. Not only is less material added to the waste, but also less binder has to be volatilized and a faster rate of sintering results. A unique extrusion die has been designed (Figure 3) which will inject wax binder simultaneously with the waste material. A thin surface layer of binder will result as compared with binder dispersed throughout the total volume of the extruded rod. Although much smaller in quantity than currently being used, this co-extruded binder should still facilitate extrusion and hold the "green" compact together until it is sintered. This procedure should also yield comparatively higher "green" densities and ultimately higher final sintered densities, better thermal conductivity, and lower porosity.

LEACH RATE STUDIES

Samples of both SRP simulated waste, hot-pressed cermet pellets and extruded-sintered rod were boiled in saturated NaCl solutions for 168 hours at atmospheric pressure. Mass spectrographic analyses of the leachant showed no detectable increase in ion content of the leachant, except for silicon and boron which apparently leached from the Pyrex test vessels. No etching or corrosive attack was observed on the extruded rod sample after testing. Spotty surface discolorations were observed on the hot-pressed pellet samples; however, this was caused by carbides that had formed on the surface during hot pressing in the graphite die. No discoloration of the extruded rod was observed. No other indication of

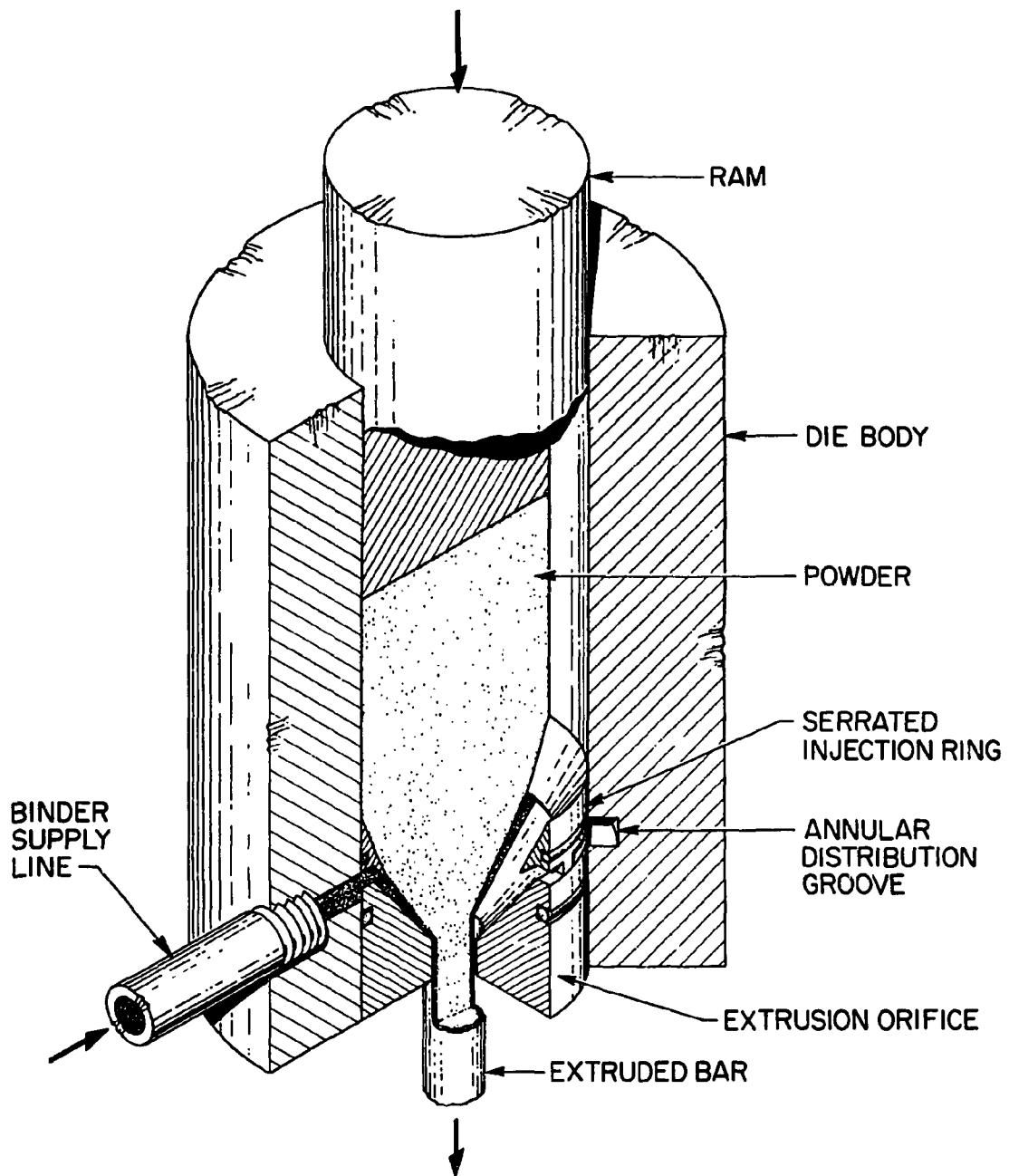


Figure 3. Conceptual Design of Binder Injection Extrusion Die Assembly

attack by the leachant was observed. Although this type of leach test is not definitive (radiotracer studies are being initiated), it does provide a preliminary indication that the cermet form will have satisfactory leach resistance. Future leach tests will include brine compositions and elevated temperature and pressure conditions which are being adopted for leach testing of waste forms that may be sent to the Waste Isolation Pilot Plant (WIPP) in the future.⁴

RADIOTRACER STUDIES

Ancillary studies on the cermet process are for the most part in their early stages. Design work and preparation for products analysis of the entire cermet process is underway. The off-gas species generated in the process need to be experimentally identified for a process material balance to be used in the total system design (use of scrubbers, for example). Use of radiotracers to analyze the cermet formation process and the resulting cermet itself is required. Such studies are presently beginning.

Ruthenium, cesium, and strontium are the species present in fission waste that are considered most troublesome from the standpoint of volatility during processing and/or are probably most easily leached from the final solid waste composite, be it cermet or vitreous mass or some other agglomerate. Tracer experiments with each of these nuclides will be performed and off-gases and leach solutions will be analyzed for these species. Because of the basic, reducing chemical system in which the cermet powder is produced (precipitation from molten urea), ruthenium would be expected to be in the elemental or dioxide state (non-volatile). Using selective additives to the waste, cesium is to be compounded as the insoluble mineral pollucite (cesium aluminosilicate) while strontium has an unknown (at present) chemical form. In any case, the "micro-encapsulation" occurring as the result of metal coating of the oxides or

other compound crystallites in the cermet should result in very low leach rates. A variety of leach solutions will be employed so that comparison with other waste forms can be made. Finally, placement of cermet tracer-containing samples in actual salt repository material under expected temperature, pressure, and humidity conditions will be performed to simulate the actual storage environment.

PROCESS IMPROVEMENT CONSIDERATIONS

A scanning electron microscope fitted with an x-ray energy dispersive analyzer has recently been obtained which will permit detailed structure studies of the cermet waste forms as a function of preparative method. Effects of process parameters such as the volume of urea from which the precipitate is formed, types and quantities of additives, and sintering times and temperatures can be evaluated with this analytical equipment in relation to final cermet properties. This work will be complemented by standard metallography, x-ray diffraction for compound identification, and possibly determination of radiation effects on the cermets. Electron microprobe studies for the distribution of cermet constituents are also planned. Thermal conductivity determinations will be made on cermets throughout the course of developmental study.

Consideration is also being given to pilot level and production level translation of the above-described laboratory experimental methods. Methods are evaluated, whenever feasible, in our current effort to accelerate full development of large scale processing. Efforts to minimize the quantity of additives to the process without compromising structural or physical property characteristics are being made. Additives include urea at the head end of the process, metal alloying additives, and the wax binder required for extrusion. It is believed possible and advantageous to combine the urea precipitation and calcination steps by injection

of the molten urea with its dissolved components into a rotary or spray calciner wherein "precipitation" and calcination will occur almost simultaneously. It is quite likely that this would also permit significant reduction in quantity of urea required in the process.

The feasibility of combining two or more process steps into a single step is also being evaluated, see Figure 4 (compare with Figure 1). Although not shown in Figure 4, tests are currently underway which may ultimately eliminate the cation dissolution and solution concentration steps from this "improved" flowsheet. Sludge (precipitated from simulated SRO feed stock with ammonium hydroxide) has been successfully dissolved in molten urea. Molten urea is an extremely effective solvent so the initial cermet formulation can possibly be made without the use of the nitric acid step at the head end and subsequent removal of nitric acid in the solution concentration step. Simultaneous reduction and sintering of calcined material has been successfully performed and may improve cermet properties as a bonus.

SUMMARY

A variety of simulated radioactive wastes have been successfully processed into cermet waste forms. Fission product waste, as oxides or metals, are isolated in a corrosion resistant thermally conductive alloy metal matrix to form the cermet where the metal is the continuous phase. Structure and property determinations to date indicate that the cermet may provide an improved radioactive waste form as compared with vitreous or ceramic forms. Quantification and more intensive investigation of the cermet and the process by which it is formed are in progress including studies from which continuous processing methods may be derived.

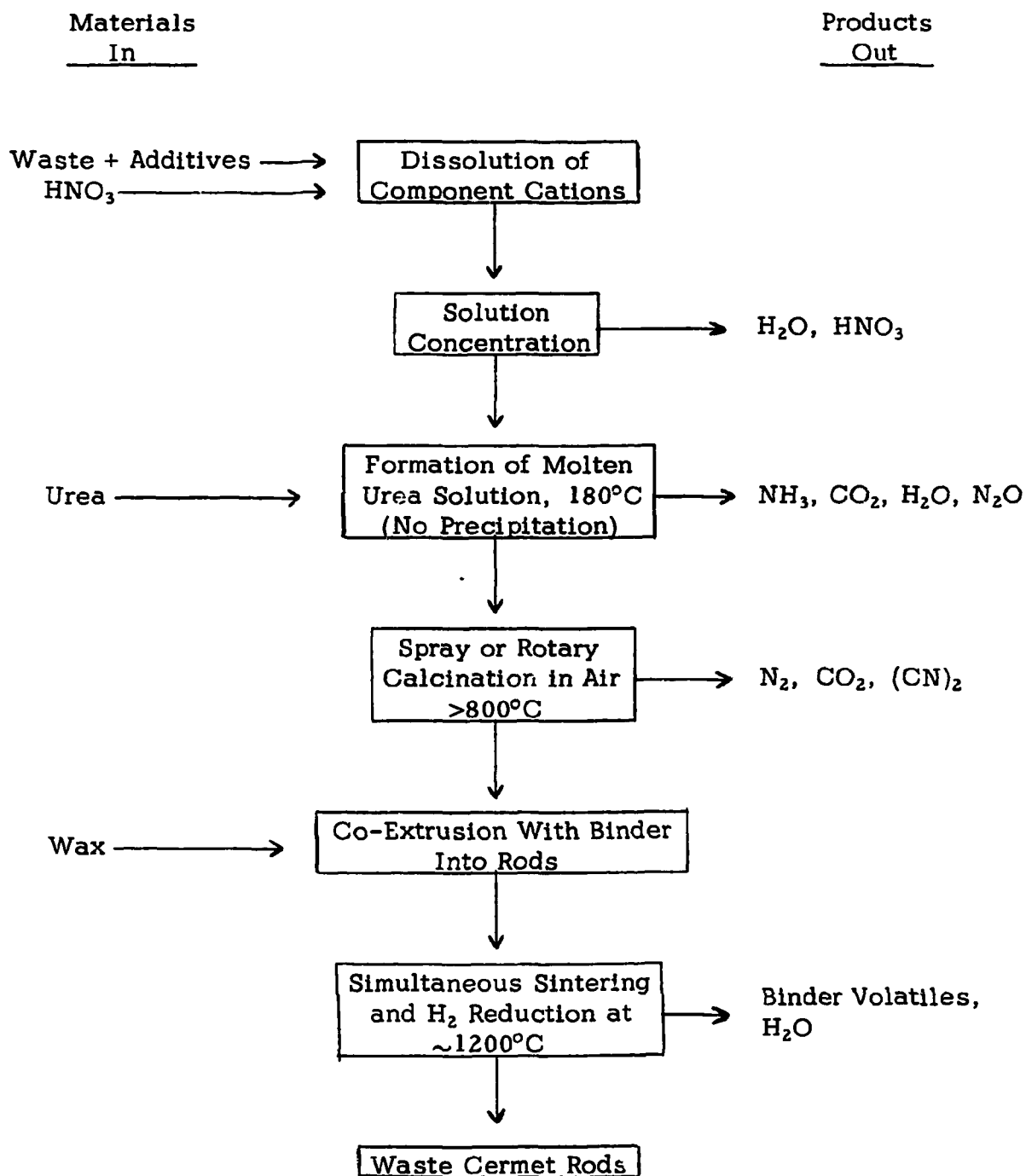


Figure 4. Conceptual Production Oriented Flowsheet: Combination Processes for Cermet Storage Forms From High Level Wastes

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