SOL-GEL TECHNOLOGY APPLIED TO GLASS AND CRYSTALLINE CERAMICS [a]

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ABSTRACT

Fixation of high level and transuranium radioactive waste in glass or alternative ceramic forms requires remotely operable processes and equipment, and sol-gel technology developed for reactor fuel refabrication appears to be applicable. Advantages of the sol-gel process are absence of dust, easy pneumatic transfer and sampling of either liquids or free-flowing solid microspheres, excellent sinterability, and equipment amenable to remote operation because of mechanical simplicity. Synroc microspheres and pellets containing up to 25% simulated defense waste have been prepared by the sol-gel process.

INTRODUCTION

Fixation of radioactive nuclides in glass or alternative ceramic waste forms and storage in salt formations or other geological repositories are thought to be adequate methods for the safe disposal of wastes. The purpose of this paper is to describe application of sol-gel technology to the fixation of nuclear waste in glass or other ceramics. Recent experimental results demonstrating process feasibility are described.

More than a dozen countries and many more organizations have reported sol-gel process descriptions and results. Sol-gel processes have found application in the nuclear fuel and spherical catalyst preparation industries. Recently, sol-gel processes have been applied to fabrication of structural ceramics because

of good sinterability and the resulting microstructure and also because of the ease with which additives can be uniformly dispersed. Remotely operable sol-gel processes and equipment for fabrication of recycled reactor fuel have been under development for almost 20 years, and much of this technology is ideally suited for fabrication of glass or alternative waste forms.

In particlular, the sol-gel process[1-5] developed for making ceramic fuel spheres appears useful for producing feed to a glass plant or for preparing spheres of alternative ceramic waste forms. In this process, which is shown schematically in Fig. 1, sols or solutions containing the waste are pumped through an orifice to break up the liquid stream in a controlled manner to yield individual droplets, which then gel into rigid spheres.
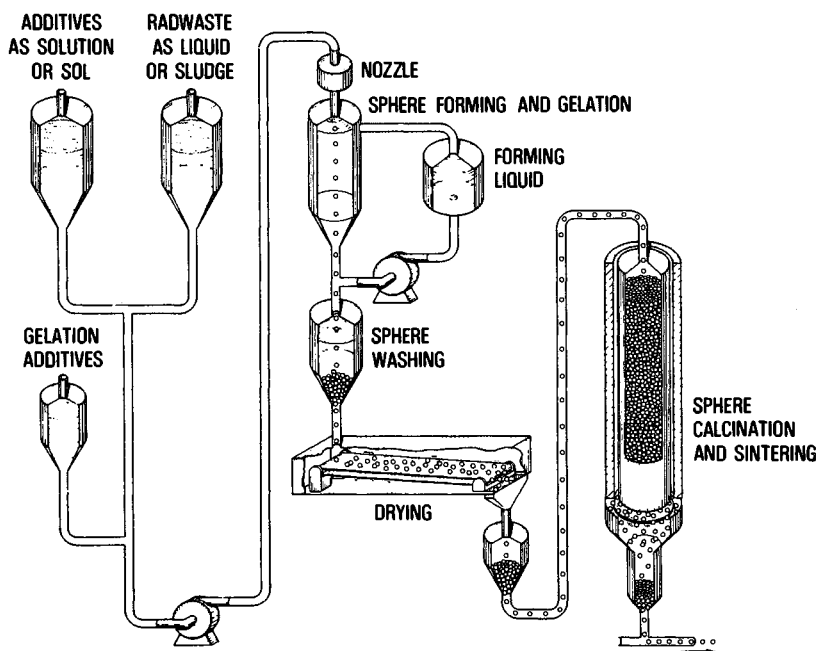

Fig. 1. Major Steps in the Sol-Gel Process

Subsequent washing, drying, calcining, and solid-state sintering
yield dense crystalline spheres. Such spheres, having a diameter
of about 1 mm, could be loaded into a canister and stored in a
repository without further treatment. If a greater degree of
inertness is desired, the spheres could be coated with carbon and
silicon carbide, again using technology[6-9] developed for remote
fuel fabrication. Additionally, the spheres (coated or uncoated)
could be incorporated into ceramic cylinders having a matrix of
Al_2O_3, $ZrSiO_4$, porcelain, SiC, or other material. A process
flowsheet illustrating the range of final products is given in
Fig. 2.

Sol-gel technology was developed for remote fuel fabrication
because the process and equipment are simple and reliable. These
are requirements for remote operation and maintenance. The
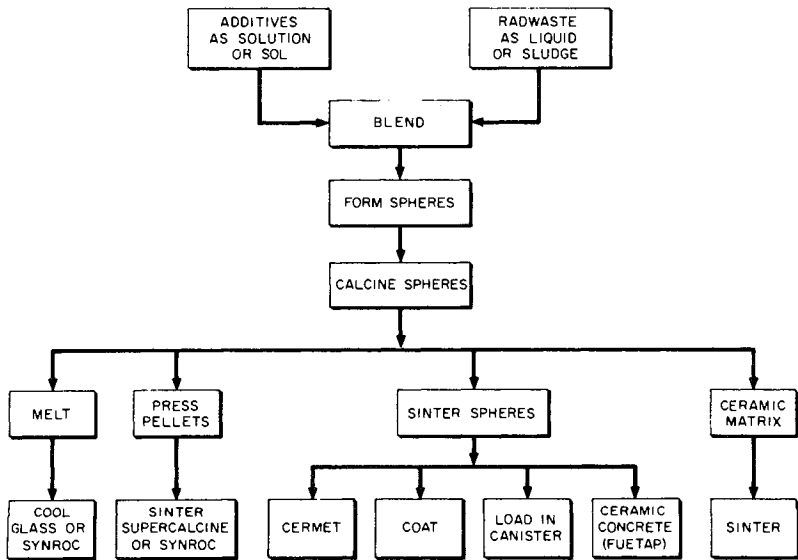process involves only liquids or solid spheres, so the materials

Fig. 2. Sol-Gel Technology Appears Applicable to Production
of Numerous Waste Forms

are easily conveyed in closed pipe systems. Further, processing and transport of the spheres do not produce dust, so equipment decontamination and maintenance are easier and result in less radiation exposure. Thus the sol-gel process could replace the calcination system (an inherently dusty process) used as the first step in the Supercalcine[10] and Synroc[11-13] processes and in one of the current vitrification[14,15] systems. Another advantage of the sol-gel process is that mixing of components as liquids or sols results in a very homogeneous material, which, because of minimum diffusion distances, enhances formation of stable crystal phases and solid solutions. Further, the desired phases containing dissolved fission products can form early in the sintering process and thus minimize loss of volatile fission products. Also, sol-gel processes have been applied to many compositions and are usually insensitive to moderate composition changes. Further, materials produced from sols typically sinter to strong, nearly theoretically dense spheres at temperatures several hundred degrees Celsius lower than those required for conventional powder processes.[16] Use of gel-derived feed also would reduce the temperature or time required for glass melting and perhaps yield a more homogeneous product.[17]

SOL-GEL PROCESSES

The purpose of this section is to characterize in a general way the various sol-gel processes[5] being considered for preparation of glass and crystalline waste forms. The characteristic operation of all sol-gel or gel-sphere processes is the dispersion of a fluid aqueous hydrosol or an aqueous solution as droplets into an immiscible phase. The aqueous droplets become spherical as a result of interfacial tension and are subsequently solidified into "gel" spheres by mechanisms described later. The gel spheres are then treated to remove water, solutes, and organic compounds. In waste applications, the waste would be mixed with hydrosols or aqueous solutions of the matrix elements to form the feed solution.

The first requirement for selecting a gel-sphere process is to specify the product composition and size. It is difficult or impossible to compare alternative processes unless the product characteristics are specified. Feed solution or sol preparation procedures and compositions as well as gel treatment procedures, must be tailored to the specific gelation technique once it has been selected.

Droplets of acidic feed solutions or sols prepared from nitrate or chloride salts are converted to gel spheres by one of three different mechanisms: (1) extraction of water by an organic liquid, such as an alcohol, (2) external gelation by transfer of ammonia into the droplet from a gas and/or liquid, or (3) internal chemical gelation by ammonia generated homogeneously within the droplet. Generic flowsheets of these processes are shown as Figs. 3, 4, and 5, respectively. The details of each proposed flowsheet depend on the desired product composition and size. New products require experimental testing and development of flowsheet details.

For gelation by extraction of water (Fig. 3) the mass transfer of the water in the organic liquid outside the droplet is slower than the mass transfer of water in the sol droplet and therefore rate controlling. Large sol droplets require relatively long residence times in a column of organic liquid and are more subject to distortion and cracking. From experience with ThO_2 sols, the largest sintered spheres that can be prepared by this technique have a diameter of about 600 μm. Gelation by extraction of water generally requires well-crystallized hydrosols, so feed preparation can be more involved than in other gelation techniques. A potential advantage of water extraction is that waste solutions or sludges can be added to the washed sol, eliminating a wash step after sphere forming. This may enable the gel sphere to retain soluble fission products. This of course would depend on the waste composition. The most frequently used organic liquids for water extraction are the monohydroxy alcohols such as 2-ethyl-1-hexanol and isoamyl alcohol. The alcohol may be recycled after water is distilled off above 100°C.

The most characteristic feature of external gelation with ammonia (Fig. 4) is that ammonia is transferred very rapidly to the surface of the aqueous droplet. Solution droplets must be formed in a gas or liquid phase free of ammonia and then exposed to the ammonia. A tough surface skin must be formed to allow the droplet to survive impact from free-fall through a gas-liquid or liquid-liquid interface. The droplet develops a surface skin, usually by reaction with ammonia gas. Then gelation is completed in the liquid phase containing NH_4OH. Splattering or distortion at the interface becomes important as the droplet size increases. Careful washing is usually required to remove soluble components from the gel spheres to avoid cracking during drying. Ammonium carbonate is added to the forming and washing liquids to inhibit leaching of Ca^{2+} and Ba^{2+}.
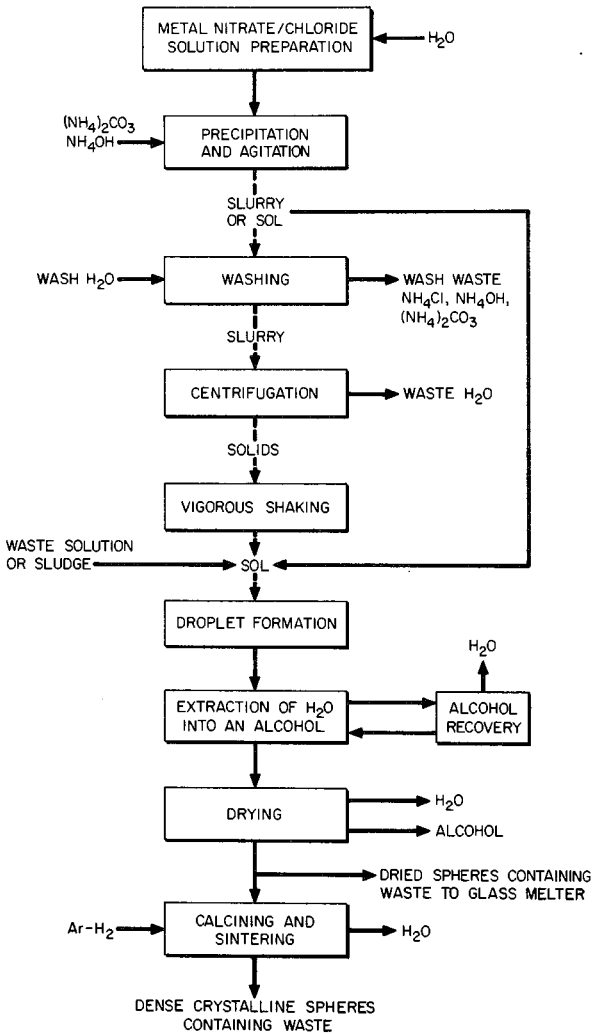
Fig. 3. Incorporation of Radioactive Waste into Crystalline or Glass Spheres by Water Extraction
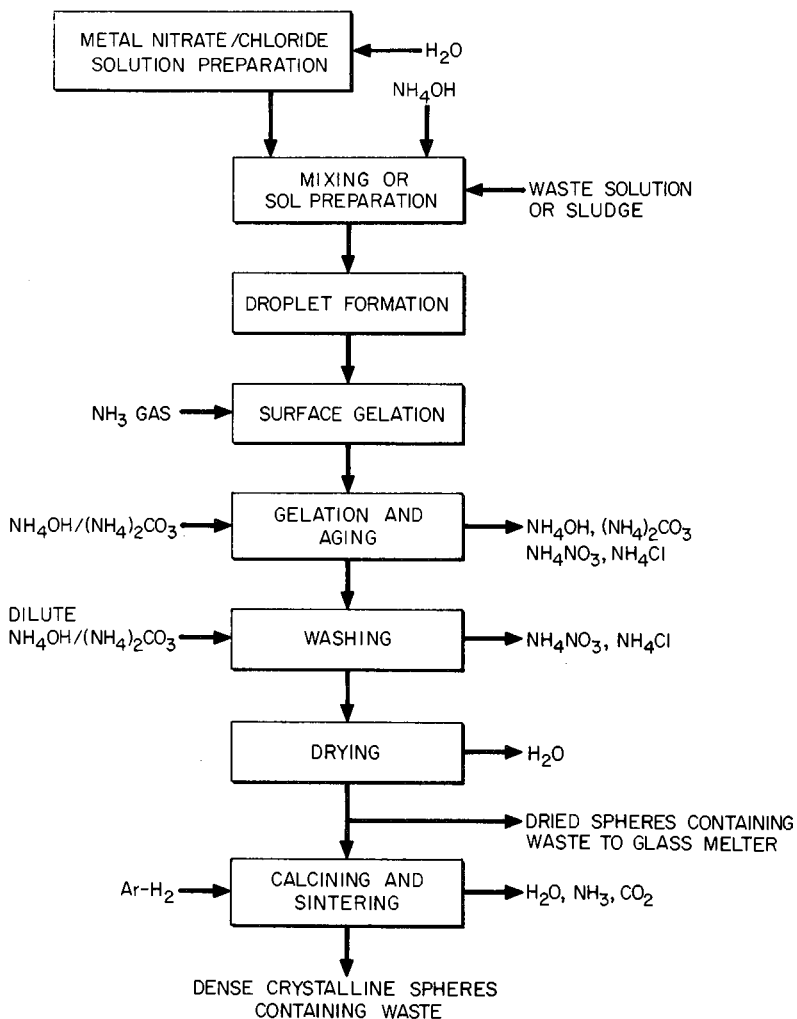
Fig. 4. Incorporation of Radioactive Waste into Crystalline or Glass Spheres by External Gelation
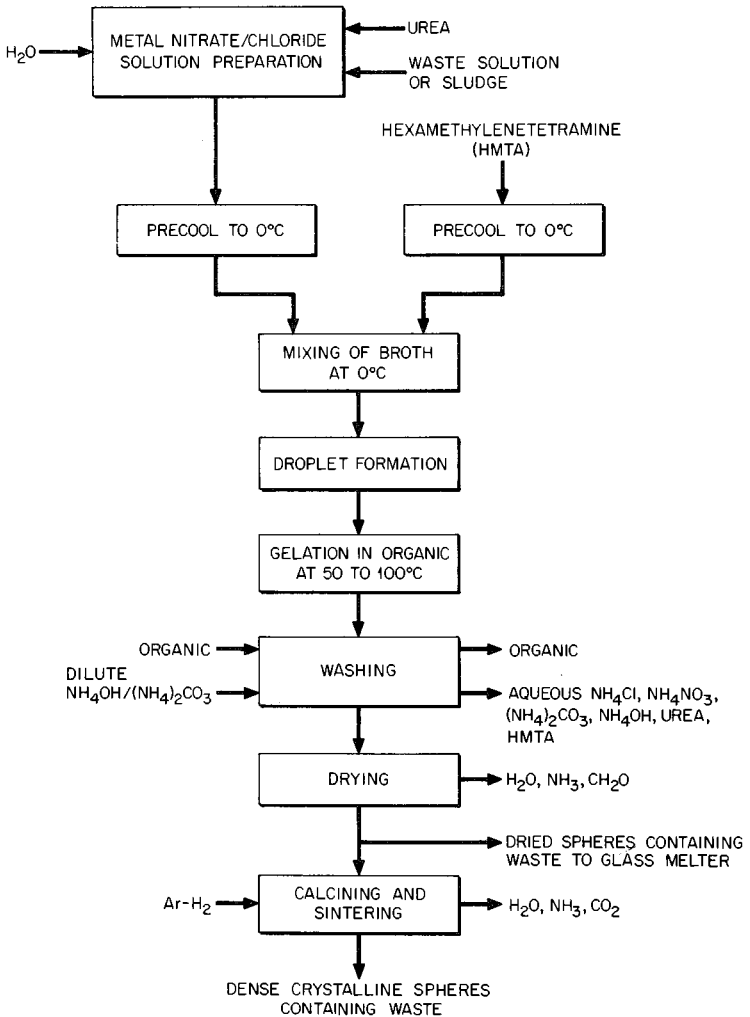
Fig. 5. Incorporation of Radioactive Waste into Crystalline or Glass Spheres by Internal Gelation

In internal gelation (Fig. 5), aqueous solution droplets containing the desired metal cations and waste components are suspended in an immiscible organic medium. They are gelled by the homogeneous release of NH_3 within the droplets without any mass transfer. For nuclear fuels, the release of NH_3 has been generally carried out at elevated temperatures to accelerate the decomposition of hexamethylenetetramine (HMTA) mixed into the solution. Before drop formation the "broth" is kept cold, usually around 0°C, to prevent gelation. Addition of urea to the feed broth is usually necessary to complex the metal cations and avoid premature gelation, even at 0°C, before droplet formation. The drops, after forming are heated by the hot organic liquid in which they are suspended. The NH_3 released by thermal decomposition of HMTA causes gelation in a few seconds. For this approach the composition of feed solutions and conditions of gel-sphere formation control the rate of gelation.

Internal gelation eliminates the mass transfer requirements for gelation and has been used to successfully produce larger gel spheres than either of the other two processes. However, it requires more washing than does external gelation with NH_4OH because more solutes are present from the additives urea and HMTA.

PREPARATION OF SYNROC GEL SPHERES

Sphere preparation and drying

We have had initial success with both external and internal gelation, although we have not yet explored a broad range of operating conditions for each of the gelation techniques. Dense oxide spheres as large as 1.2 mm in diameter have been prepared for compositions of Synroc-B,[13] Synroc-B + 1 wt % simulated commercial waste, and Synroc-B + 25 wt % simulated Savannah River Plant (SRP) [a] waste slurry. An internal gelation system[18] as shown in Fig. 6 was used to prepare this material.

Synroc feed solutions were prepared by dissolving the proper quantities of the corresponding metal salts [$TiCl_3$, $Al(NO_3)_3 \cdot 9H_2O$, $ZrOCl_2 \cdot 8H_2O$, $Ba(NO_3)_2$, and $Ca(NO_3)_2 \cdot 4H_2O$] in water. Urea was added to this solution in sufficient quantity to avoid gelation when mixed with HMTA and waste solutions at 0°C. Large broth

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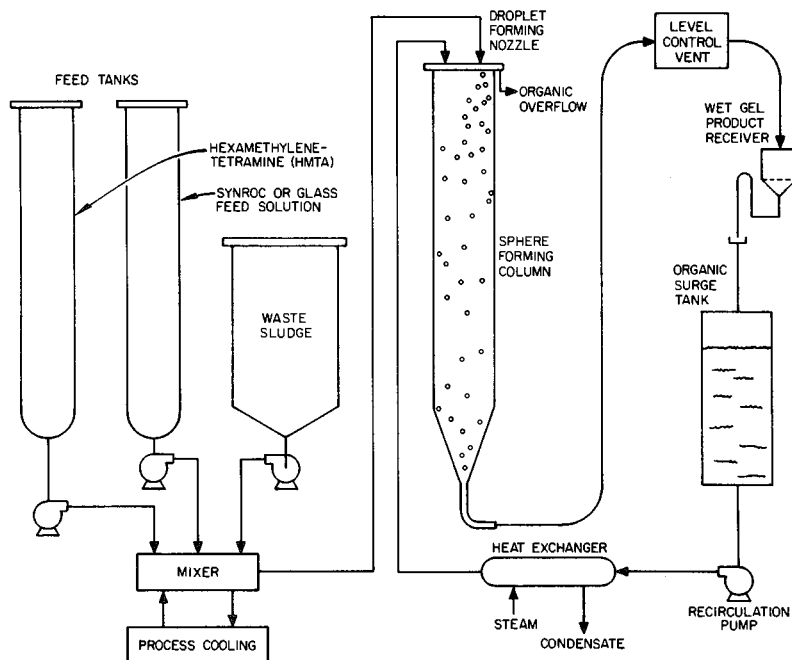[a] Purchased from Southwestern Analytical Chemicals, Austin, Texas.

<u>Fig. 6.</u> Internal Gelation System for Incorporation of
Radioactive Waste in Crystalline or Glass Spheres

droplets (4 to 6 mm in diameter) of about 0.5 M Synroc metal were
formed and gelled in organic liquid at 50 to 95°C in 2 to 10 s.
We have used silicone oils and mixtures of perchloroethylene and
2-ethyl-1-hexanol as gelation media. For gelation of large
droplets, organic liquids having densities slightly less than
that of the broth droplet are desirable to avoid production of
nonspherical shapes and to provide a longer free-fall time in the
organic liquid.

    The system shown in Fig. 6 provides for batch collection of
the wet gel spheres. Solutes (NH_4NO_3, NH_4Cl, HMTA, urea, etc.)
are removed from the spheres by passing 5 to 10 bed volumes of
dilute NH_4OH—$(NH_4)_2CO_3$ through the bed of spheres for 1 to 2 h.
Wash volumes and times depend strongly on gel sphere size and

composition. The drying temperature and atmosphere (air vs steam) in which the washed spheres are dried had a strong effect on the integrity and density of the sintered spheres. Spheres dried in large flows of air cracked excessively upon sintering, whereas those dried in steam sintered without cracking. A steam atmosphere is supplied conveniently by water evaporating from the spheres as they dry in partially covered containers in an oven at 200 to 250°C.

Conditions most recently used to prepare Synroc spheres by internal gelation are given in Table I. The concentrations of urea and HMTA will vary for Synroc feed solutions prepared from metal salts other than those currently used. In general they will depend on broth pH and type and concentration of anions (NO_3^-; Cl^-, etc.) present. The last sphere batch (IG-13) described in Table I is particularly noteworthy. The broth was prepared by adding the waste slurry to a chilled solution of the Synroc metal salts and urea, followed by addition of chilled 3.2 M HMTA solution. This broth was maintained at 0°C and stirred continuously during sphere forming to ensure uniform suspension and feeding of the waste solids. The droplets gelled from a deep translucent brown to a lighter opaque brown in about 4 s. To thoroughly remove the oil, the gel spheres were rinsed with trichloroethylene, then washed in 0.5 M NH_4OH 0.025 M $(NH_4)_2CO_3$ solution. A small quantity of spheres was left unwashed. Both the washed and unwashed spheres survived steam drying at 235°C without cracking; however, the unwashed spheres shrank less, indicating a higher dried gel porosity. This gelation test demonstrated (1) that silicone oil, which has a desirably low solubility (extractability), appears to be suitable as a gelation medium and (2) that a wash step may not be required before calcining and sintering, so a potential liquid waste stream would be eliminated.

Calcination and sintering

The calcination and sintering behavior of Synroc prepared by internal and external gelation have been examined by thermal analysis and dilatometry. Thermal analysis included differential scanning calorimetry to determine transition temperatures and chemical reactions, thermogravimetric analysis (TGA) to measure weight loss upon heating, and mass spectrometry to determine decomposition products in programmed heating experiments. The initial weight loss was about 6% in the TGA as the samples were

TABLE I. Sphere Preparation Conditions for Recent Synroc-B Internal Gelation Runs[a]

Batch	Metal Conc. (M)	Broth Composition				Organic Gelation Medium and Temperature	Drying Conditions	Dried Sphere Density (Mg/m³)	General Remarks
		Mole Ratios		Waste Type	Waste Conc. (wt %)				
		$\frac{Urea}{Metal}$	$\frac{HMTA}{Metal}$						
IG-8	0.50	9.9	2.68	Acid raffinate	0.9	2EH/PERC, 85—90°C	Covered container at 105°C	1.09	Translucent, amber. <10% cracked. About 25% clustered during drying.
IG-9	0.50	9.9	2.68	Acid raffinate	0.9	2EH/PERC, 85—93°C	Covered container at 78°C	1.25	Translucent, amber. <10% cracked. Less clustering than IG-8.
IG-10, -11, -12	0.41	9.9	2.73	SRP sludge	25.5	2EH/PERC, 90°C	Covered container at 90 and 240°C		Both washed and unwashed survived drying with minimal cracking. Dried unwashed spheres more porous.
IG-13	0.45	10.0	2.70	SRP sludge	20.0	Silicone oil, 93°C	Covered container at 235°C	0.95	Deep brown, <10% cracked. No clustering during drying.

[a]Batch feeding of broth at $\sim$0°C through single-fluid nozzles. Forming and collection of gel spheres in 10-cm-ID, 60-cm-long column. At least 30 min aging in cooling organic before wash. Wash procedure: Initial isopropanol or trichloroethylene rinse, then 0.5 M NH$_4$OH, 0.025 M (NH$_4$)$_2$CO$_3$.

heated from room temperature to 100°C. They lost 7% more when heated from 100 to 800°C. As each sample was heated from 800°C to the sintering temperature, a weight loss of about 0.5% occurred. The gases accounting for these weight losses were identified with a time-of-flight mass spectrometer. For the mass spectrometer studies, samples of Synroc spheres were heated to about 800°C in a vacuum, and the resulting off-gases were monitored. By far the largest gaseous by-product was water, which was produced predominately at temperatures of 130 and 295°C. The loss of water at 295°C is probably from the decomposition of metal hydroxides to oxides. Ammonia in smaller amounts was released at temperatures similar to those causing water evolution. The only other significant compound released was CO_2, with a peak concentration at 610°C, which may be from the decomposition of metal carbonates. Samples produced by either internal or external gelation produced similar decomposition products.

The sintering behavior of six batches of Synroc-B microspheres has been carefully examined by mercury porosimetry density measurements and metallography. Each batch was sintered by heating to 1225°C in flowing Ar—4%H_2 and held for 4 h. The data in Table II show that different batches sinter to very different densities. This was expected since the broth preparation, sphere forming, and drying conditions were deliberately varied. Two batches (PPT-48 and IG-6) sintered to high densities with only about 1% open porosity and 5% closed porosity. Macro and micrographs of these two batches are shown in Figs. 7 and 8. The other four batches were only about 75% dense and had from 10 to 25% open porosity.

The data in Table II indicate that drying conditions influence sintering behavior. Batches that were dried at 180 or 235°C produced dense spheres whereas batches dried between 25 and 105°C produced porous spheres. It is not clear at this time by what mechanism the drying conditions are influencing sintering behavior, but similar effects have been previously observed for fuels. Drying conditions are known to influence the crystallite size within fuel gel spheres.

Four batches of Synroc-B spheres containing 20 to 25% simulated SRP waste have been prepared by internal gelation. Dried spheres from one of these batches are shown in Fig. 9. Batches containing 25% waste have survived the drying, calcining, and sintering process without cracking; however, detailed characterization has not been completed.

TABLE II. Characterization of Sintered Synroc-B (1% Waste) Microspheres Using Mercury Porosimetry Density Measurements

| Batch	Gelation Method	Method of Drying	Density (Mg/m³)	Density (%)	Porosity, % Open	Porosity, % Closed
PPT-48[a]	External	Flowing 60°C air then 180°C	3.99	95.0	1.4	3.6
IG-5B	Internal	Flowing 60°C air	3.37	80.3	9.8	9.8
IG-6	Internal	Covered container at 235°C	3.88	92.5	1.3	6.2
IG-7	Internal	Flowing room-temperature air	3.07	73.1	23.2	3.7
IG-8	Internal	Covered container at 105°C	3.27	77.9	10.6	11.5
IG-9	Internal	Covered container at 78°C	3.08	73.2	23.0	3.8

[a]This batch does not contain waste.
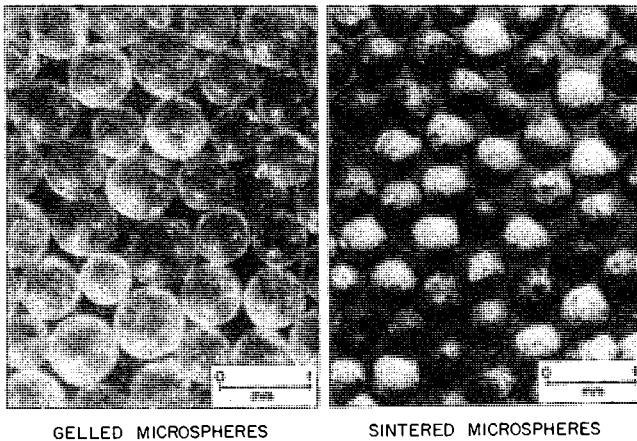
GELLED MICROSPHERES   SINTERED MICROSPHERES

Fig. 7. Microspheres of the Synroc-B (1% Waste) Composition Made by Internal Gelation. Batch IG-6
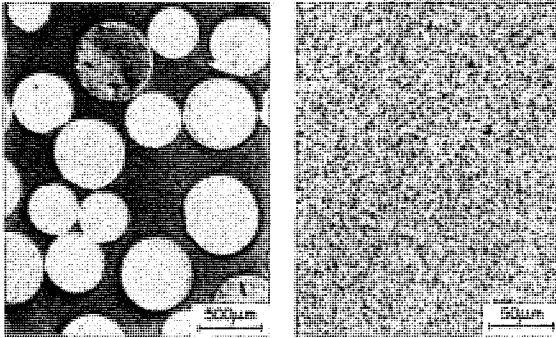
INTERNAL GELATION BATCH IG-6
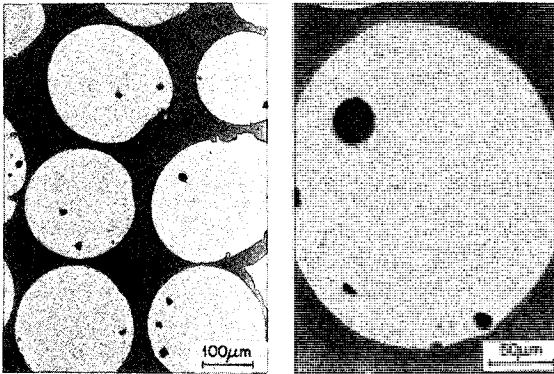
EXTERNAL GELATION BATCH PPT-48

Fig. 8. High-Density Microspheres of Synroc-B Prepared by
Internal and External Gelation

The sintering behavior of sol-gel Synroc-B spheres was
studied by dilatometry. With this technique the diameter of an
individual microsphere is monitored continuously during sin-
tering. Typical results for Synroc-B (1% waste) spheres prepared
by internal gelation are shown in Fig. 10. Note that before sin-
tering the spheres are only about 25% of theoretical density. A
large amount of densification occurs below 800°C. This indicates
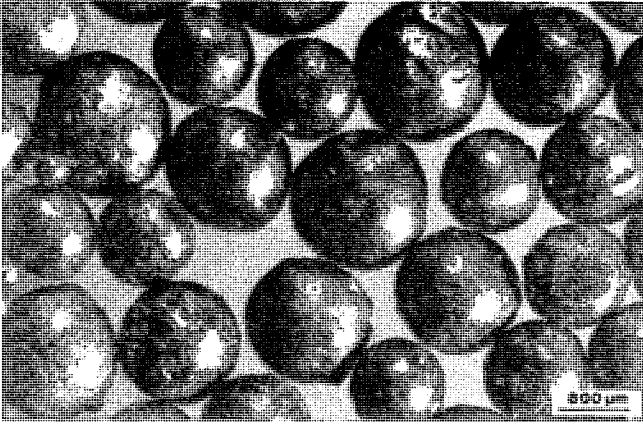that a low-temperature sintering process might be achievable.

Fig. 9. Dried Synroc-B Spheres Containing 25% Simulated Savannah River Plant Waste
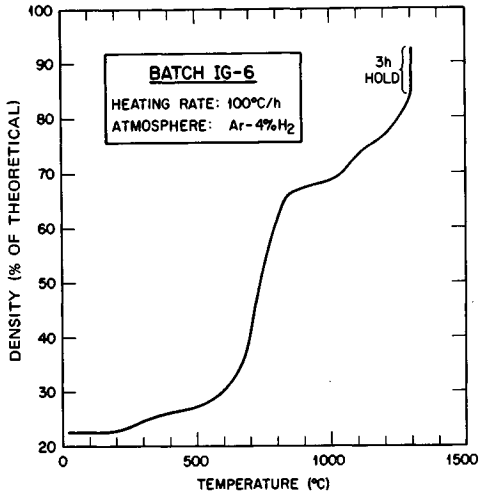

Fig. 10. Dilatometry Reveals Extensive Low-Temperature Sintering of Synroc-B Microsphere

Sol-gel-derived Synroc-B spheres have been used as feed for cold-pressing and sintering of pellets, as shown in Fig. 11. Crack-free sintered pellets have been produced from feed prepared by water extraction and internal and external gelation. Pellet densities have not yet exceeded about 80% of theoretical. Pellet density as a function of temperature is shown in Fig. 12. From previous fuels work, we expect that much higher densities will result when the sphere properties are optimized for pellet pressing. [19]

To obtain good leach resistance, the desired phases for Synroc-B are zirconolite, hollandite, and perovskite. Many sintered batches of Synroc-B spheres prepared by internal and external gelation have been examined by x-ray diffraction to determine which phases are present. Since the volatility of certain fission products depends on oxygen potential, we have used sintering atmospheres of Ar–4% H_2, Ar–4% H_2 saturated with water at 20°C, and air. We chose Ar–4% H_2 saturated with water for these tests since its oxygen potential at the sintering temperature is very near that of the Ni-NiO equilibrium suggested by Ringwood. [13] We have consistently found that the three desired phases and traces of extra phases are produced in undoped Synroc-B when sintering is performed only in Ar–4% H_2. When either of the other two atmospheres are used, hollandite is not formed. Instead, another barium aluminum titanate phase containing less titania than hollandite and free titania is present. Thus, the preferred atmosphere is Ar–4% H_2. Fortunately, this same highly reducing atmosphere will likely minimize the volatilization of fission products such as ruthenium.
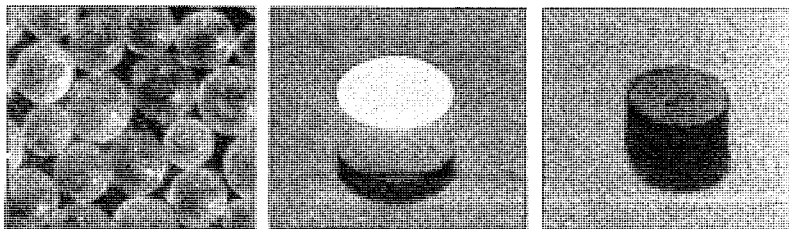
GEL MICROSPHERES   **AS-PRESSED PELLET**   **SINTERED PELLET**

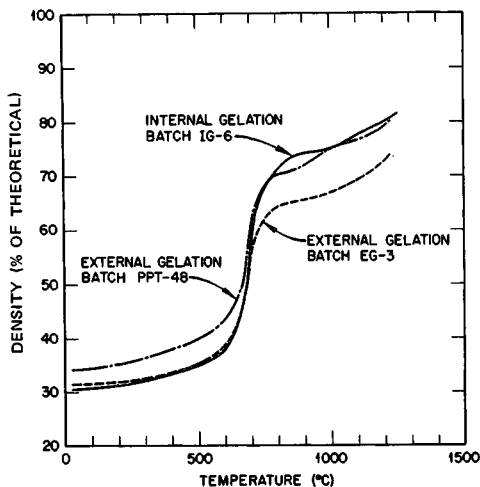Fig. 11. Synroc-B Pellets Produced by the Sol-Gel Process

Fig. 12. Densification During Sintering of Synroc-B Pellets Pressed From Sol-Gel Microspheres

Hot-pressing

Since other laboratories are considering hot-pressing as a process for the production of Synroc, a batch of sol-gel-produced microspheres was used as feed material for hot-pressing. A batch of gel-derived Synroc-B (1 wt % waste) was hot-pressed at 1275°C and 35 MPa (5 ksi) to produce a pellet with a density 95% of theoretical. Hot-pressing at 1325°C increased the pellet density to 97%. The microstructures of these pellets are shown in Fig. 13. Some remnants of the initial microsphere structure are still evident. The success of these first two trials indicates that sol-gel-derived Synroc spheres are amenable to hot-pressing.

LEACHING OF SYNROC

Leaching studies were begun on four samples of Synroc-B. This material was not prepared by sol-gel techniques but was prepared by melting and solidification under an Ar—4% H_2 atmosphere. The samples had been spiked with uranium and varying amounts of one or more of the following isotopes: ^{239}Pu, ^{241}Am, and ^{244}Cm. The samples were placed in small baskets made of polypropylene

97% T.D.   35MPa   1325°C   95% T.D.   35MPa   1275°C
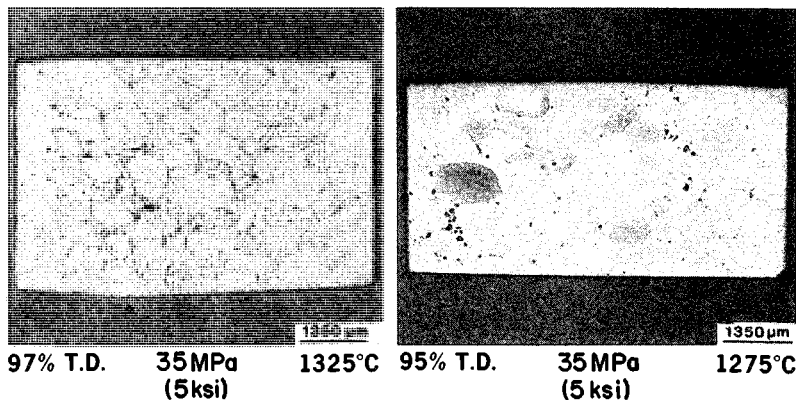**(5ksi)   (5ksi)**

Fig. 13.   Polished Cross Sections of Pellets Hot-Pressed from Sol-Gel-Derived Synroc-B Spheres (1% Waste)

netting and suspended in 10-ml portions of deionized water in polypropylene containers. Sample weights and other pertinent data are given in Table III.

Each sample in Table III was analyzed by x-ray diffraction to determine the phases present. The phases hollandite, zirconolite, and perovskite were identified.

TABLE III.   Doped Synroc Characteristics

Sample	Leach Sample Mass (g)	M/S^a (g/cm^2)	V_L/S^b (cm)	Isotopes in Samples, wt Fraction			
				U	^{239}Pu	^{241}Am	^{244}Cm
1B	0.024	0.1569	63	0.02	0.002	0.004	0.001
3B	0.1351	0.2762	20	0.02		0.004	
4B	0.0521	0.2010	38	0.02			0.001
SYN-2B	0.4645	0.4169	9	0.02	0.0024		

^aM = mass of leach sample; S = surface area based on spherical sample.

^bV_L = volume of leaching medium.

Leach data for each sample are shown in Table IV. The leach rate is determined for each respective isotope as

$$R = A_0 M / I_0 S t_i$$

where

A_0 = weight of isotope leached during leach period of t_i (d), μg;

I_0 = weight of isotope originally in the sample, μg;

M = total mass of leach sample, g;

S = equivalent spherical surface area of sample, cm[2].

The leach rates of Synroc-B based on the isotopes [239]Pu, [241]Am, and [244]Cm are nearly 1.5 orders of magnitude lower than data reported for glass.[20] Data are presented in Fig. 14 for sample 1B, which contained U, [239]Pu, [241]Am, and [244]Cm. This sample possessed the highest alpha dose and also the highest uranium leach rate. The results for the leach rate based on uranium show a dependence on alpha radiation levels within the specimens.

An additional sample of 0.806 g gel-derived Synroc-B microspheres of about 800 μm in diameter, was leached for 2 d, and the leachate was analyzed by the inductive coupled plasma technique. The results for the five major elements in Synroc-B are presented as follows:

Ti, not detected at 2 E–09 g/cm^{2} d;
Zr, Al, not detected at 5 E–09 g/cm^{2} d;
Ca, 5 E–07 g/cm^{2} d;
Ba, not detected at 9 E–09 g/cm^{2} d.

These data reflect extremely low leach rates. The values for Ti, Zr, Al, and Ba are at least 3 orders of magnitude lower than the leach rate of glass based on silicon.[20] The leach rate of Synroc-B based on calcium was 1 order of magnitude less than that of glass. Leach testing of melted Synroc as well as sol-gel-derived spheres and pellets is continuing.

SOL-GEL PREPARATION OF GLASS

Gel techniques for preparing homogeneous feed for glass melting are not new.[17,21-23] At ORNL scoping tests have shown that spheres of the Frit-21 [a] composition can be formed by an internal gelation technique. Feed solutions were prepared by

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[a] Frit-21 is the reference frit to be added to Savannah River Plant sludge for glass production.

TABLE IV. Leach Data for Doped Synroc-B Samples

R, Leach Rate, g/cm^2-d

Leach Time[a] (d)	Sample 1B				Sample 3B		Sample 4B		Sample SYN-2B	
	U	^{239}Pu	^{241}Am	^{244}Cm	U	^{241}Am	U	^{244}Cm	U	^{239}Pu
0.5	2.75 E-05	1.23 E-07	1.60 E-08	1.87 E-08	2.3 E-06	5.27 E-08	5.40 E-06	6.95 E-08	8.90 E-07	1.47 E-07
1.5	2.75 E-05	6.01 E-09	4.53 E-09	6.96 E-09	2.4 E-06	9.26 E-09	4.82 E-06	7.60 E-09	9.90 E-07	1.13 E-07
2.5	2.28 E-05	3.07 E-08	5.03 E-09	7.60 E-09	2.66 E-06	6.19 E-09	4.44 E-06	2.59 E-09	8.53 E-07	2.27 E-08
3.5	3.16 E-05	3.89 E-08	4.90 E-09	6.01 E-09	2.66 E-06	1.54 E-09	4.63 E-06	4.78 E-09	9.87 E-07	5.83 E-09
5.5	7.4 E-06	1.78 E-08	4.79 E-09	4.79 E-09	1.02 E-0?	6.65 E-10	1.29 E-06	8.49 E-10	2.54 E-07	1.05 E-09
8.5	7.5 E-06	4.76 E-08	2.55 E-09	2.62 E-09	9.20 E-07	5.30 E-10	1.48 E-06	7.60 E-09	2.99 E-07	3.09 E-09
12.0	5.9 E-06	7.60 E-09	1.66 E-09	2.09 E-09	6.13 E-07	7.55 E-09	1.11 E-06	1.24 E-08	1.79 E-07	1.42 E-09
17.5	3.30 E-06	8.32 E-09	1.30 E-09	1.94 E-09	4.99 E-07	4.02 E-09	6.89 E-07	1.21 E-10	1.28 E-07	<1.0 E-09
24.5	3.90 E-06	4.25 E-09	9.18 E-10	2.03 E-09	3.07 E-07	9.43 E-08	5.79 E-07	1.16 E-07	1.15 E-07	4.06 E-09
31.5	3.75 E-06	1.25 E-08	1.57 E-09	2.15 E-09	2.92 E-07	7.67 E-08	4.69 E-07	1.05 E-07	1.22 E-07	2.56 E-09
38.5	3.12 E-06	3.23 E-08	5.27 E-09	9.22 E-09	3.52 E-07	6.15 E-08	6.89 E-07	8.16 E-08	1.28 E-07	2.46 E-09
56.0	9.90 E-07	<1.0 E-09	9.38 E-10	1.75 E-09	6.57 E-08	4.84 E-08	1.24 E-07	7.73 E-08	3.21 E-08	1.43 E-09

[a]Time at midpoint of leach period $\{\Sigma t_i - t_n/2\}$.
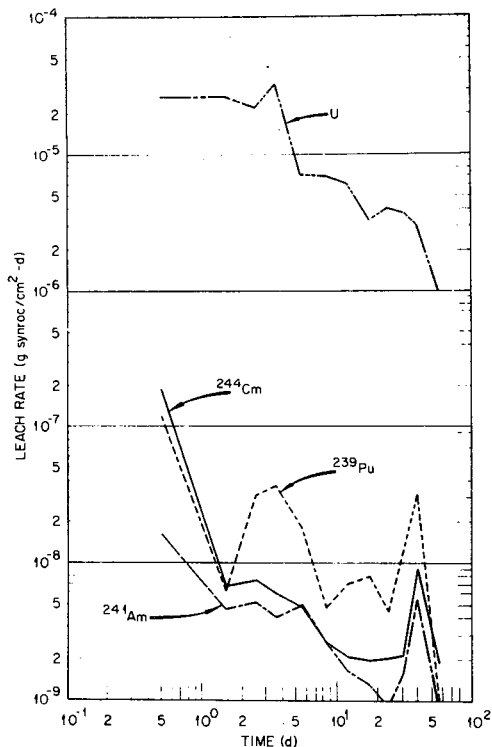
Fig. 14. Leach rate of Synroc-B Based on U, ^{239}Pu, ^{241}Am, and ^{244}Cm in Distilled Water (22°C)

dissolving the metal salts [NaNO$_3$, TiCl$_3$, LiNO$_3$, Ca(NO$_3$)$_2$·4H$_2$O, and H$_3$BO$_3$] in water and adding the metal salt solutions to a commercially available silica hydrosol. The source of silica for these tests was LUDOX, a Dupont colloidal silica. Spheres 1.0 to 1.5 mm in diameter in the dried state were prepared (see Fig. 15) by the same forming, washing, and drying procedures described for Synroc sphere preparation via internal gelation. Present studies involve the application of other gelation techniques and other sources of silica, such as sodium silicates.
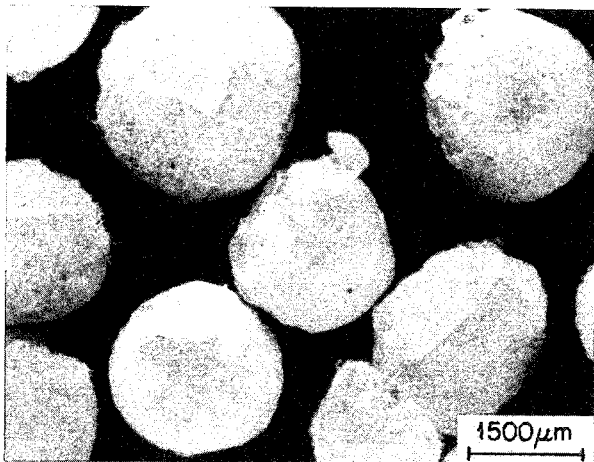
Fig. 15. Dried Spheres of the Frit 21 Composition Prepared by Internal Gelation

COATING OF WASTE FORMS

Sol-gel spheres are an attractive substrate if one wishes to produce coated waste forms. Extensive remote coating technology has been developed for High-Temperature Gas-Cooled Reactor (HTGR) fuels.[6,9,24] For both waste and fuels impervious coatings are desired. In particular, much experience exists in the pyrolytic deposition of carbon[25,26] and silicon carbide[7] onto sol-gel spheres. Silicon carbide is a hard, strong, unusually inert material having extremely good corrosion and abrasion resistance. Its use for coating waste would undoubtedly result in a high-quality product. Silicon carbide may not be required if a single coating layer of dense carbon provides adequate leach resistance. Recently sol-gel-derived Synroc-B (1% waste) spheres were coated with pyrolytic carbon as shown in Fig. 16. There is no indication of kernel-coating reaction, and the coating appears to be of high quality. Detailed characterization including leach testing is currently under way.
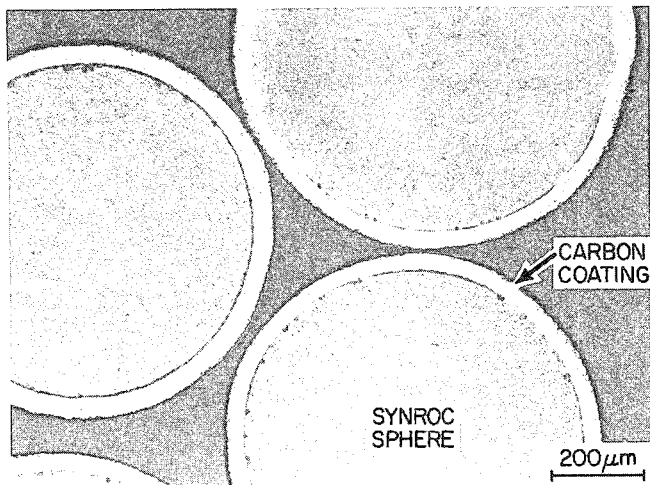
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Fig. 16. Pyrolytic Carbon Coating on Sol-Gel-Derived Synroc Spheres.

CONCLUSIONS

Sol-gel technology appears useful for preparing a variety of waste forms including glass, alternative crystalline ceramics, and coated spheres. By using simpler equipment, the sol-gel process offers the promise of more reliable, safer remote operations for fixation of radioactive waste. Initial efforts at preparing sol-gel-derived microspheres of Synroc-B containing up to 25 wt % simulated Savannah River Plant waste have been successful. Pellets of Synroc have been prepared from sol-gel-derived microspheres by both cold-pressing and sintering and hot-pressing. Work is under way to coat Synroc microspheres with pyrolytic carbon and silicon carbide.

ACKNOWLEDGMENTS

REFERENCES

1. S. D. Clinton, P. A. Haas, and L. J. Hirth, "Process for Preparing Oxide Gel Microspheres from Sols," U.S. Patent 3,190,122 (July 1964).

2. P. A. Haas, "Preparation of Sol-Gel Spheres Smaller than 200 Microns Without Fluidization," *Nucl. Technol.* 10: 283–92 (1970).

3. M. H. Lloyd, O. K. Tallent, W. T. McDuffee, L. E. Morse, and R. G. Haire, *Symposium on Sol-Gel Processes and Reactor Fuel Cycles* (Gatlinburg, Tennessee, May 4–7, 1970), CONF-700502, p. 100.

4. A. L. Lotts, comp., *Fast Breeder Reactor Oxide Fuels Development — Final Report*, ORNL-4901 (November 1973).

5. W. J. Lackey and J. E. Selle, comps., *Assessment of Gel-Sphere-Pac Fuel for Fast Breeder Reactors*, ORNL-5468 (October 1978).

6. W. J. Lackey, D. P. Stinton, and J. D. Sease, "Improved Gas Distributor for Coating High-Temperature Gas-Cooled Reactor Fuel Particles," *Nucl. Technol.* 35: 227–37 (September 1977).

7. D. P. Stinton and W. J. Lackey, "Effect of Deposition Conditions on the Properties of Pyrolytic SiC Coatings for HTGR Fuel Particles," *Ceram. Bull.* 57(6): 568–73 (June 1978).

8. R. R. Suchomel, R. J. Braatz, B. J. Bolfing, and J. L. Heck, *Design Study for a 24-cm HTGR Microsphere Coating Furnace*, ORNL/TM-6321 (May 1978).

9. J. E. Mack, R. R. Suchomel, and P. Angelini, *Development of Nuclear Fuel Microsphere Handling Techniques and Equipment*, ORNL/TM-7143 (January 1980).

10. G. J. McCarthy, "High Level Waste Ceramics: Materials Considerations, Process Simulation and Product Characterization," *Nucl. Technol.* 32: 92–105 (1977).

416

11. A. E. Ringwood, *Safe Disposal of High Level Nuclear Reactor Wastes: A New Strategy,* Australian National University Press, Canberra, 1978.

12. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. Hibberson, and A. Major, "Immobilisation of High Level Nuclear Reactor Wastes in SYNROC," *Nature,* 278: 219—23 (March 1979).

13. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. O. Hibberson, and A. Major, "The Synroc Process. A Geochemcial Approach to Nuclear Waste Immobilization," *Geochem. J.* 13(4): 141—65 (August 1979).

14. A. M. Platt and J. L. McElroy, *Management of High-Level Nuclear Wastes,* PNL-SA-7072 (December 1978).

15. M. J. Plodinec, "Development of Glass Compositions for Immobilization of Savannah River Plant Waste," p. 31 in *Scientific Basis for Nuclear Waste Management,* Vol. 1 (Proc. Symp. "Science Underlying Radioactive Waste Management," Materials Research Society Annual Meeting, Boston, November 28—December 1, 1978), G. J. McCarthy, ed., Plenum Press, New York, 1978.

16. W. J. Lackey and R. A. Bradley, "Microstructure of Sol-Gel-Derived (U,Pu)O$_2$ Microspheres and Pellets," *Nucl. Technol.* 14: 257—68 (June 1972).

17. R. Roy, "Gel Route to Homogeneous Glass Preparation," *J. Am. Ceram. Soc.* 52(6): 344 (June 1969).

18. P. A. Haas, J. M. Begovich, A. D. Ryon, and J. S. Vavruska, *Chemical Flowsheet Conditions for Preparing Urania Spheres by Internal Gelation,* ORNL/TM-6850 (July 1979).

19. S. M. Tiegs, P. A. Haas, and R. D. Spence, *The Sphere-Cal Process: Fabrication of Fuel Pellets from Gel Microspheres,* ORNL/TM-6906 (September 1979).

20. D. J. Bradley, C. O. Harvey, and R. P. Turcotte, *Leaching of Actinides and Technetium from Simulated High-Level Waste Glass,* PNL-3152 (August 1979).

21. W. Luth and C. Ingamells, "Gel Preparation of Starting Materials for Hydrothermal Experimentation," *Am. Mineral.* 50: 255 (January—February 1965).

22. L. Allen and E. Matijevic, "Stability of Colloidal Silica: I. Effect of Simple Electrolytes," *J. Colloid Interface Sci.* 31(3): 287 (November 1969).

23. H. Dislich, "New Routes to Multicomponent Oxide Glasses," *Angew. Chem. Int. Edit. Engl.* 10(6): 363 (June 1971).

24. R. R. Suchomel, D. P. Stinton, M. K. Preston, J. L. Heck, B. J. Bolfing, and W. J. Lackey, *Design and Operation of Equipment Used to Develop Remote Coating Capability for HTGR Fuel Particles,* ORNL/TM-6581 (December 1978).

25. D. P. Stinton and W. J. Lackey, *Influence of Process Variables on Permeability and Anisotropy of Biso-Coated HTGR Fuel Particles,* ORNL/TM-6087 (November 1977).

26. B. A. Thiele, D. P. Stinton, and W. J. Lackey, "Properties of Pyrocarbon Coatings Influence Gas Permeability of High-Temperature Gas-Cooled Reactor Fuel Particles," (Summary) *Trans. Am. Nucl. Soc.* 28: 180—82 (June 1978).