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**MASTER**

SOL-GEL TECHNOLOGY APPLIED TO CRYSTALLINE CERAMIC  
NUCLEAR WASTE FORMS\*

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13	SECOND LINE OF TEXT*	13
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23	INTRODUCTION	
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26	The sol-gel process is being developed for the solidification	
27	and isolation of high-level nuclear fuel waste. Three gelation	
28	methods are being developed for producing alternative waste	
29	forms. <sup>1</sup> These include (1) internal gelation for producing spheres	
30	of up to 1 mm diam suitable for coating, (2) external gelation,	
31	and (3) water extraction methods for producing material suitable	
32	for alternate ceramic processing. This report addresses the	
33	internal gelation process and the characteristics of materials	
34	produced by that method. Gel derived materials of the Synroc <sup>2</sup>	
35	compositions containing up to 70 wt % simulated Savannah River	
36	Plant (SRP) <sup>3</sup> waste have been produced.	
37		
38	GELATION	
39		
40	A generic flowsheet for the preparation of gel spheres by the	
41	internal gelation method is shown in Fig. 1. Feed solutions con-	
42	taining cations of the desired waste form additives and the waste	
43	components are used to prepare a feed "broth" that contains all	
44	the necessary ingredients to form gel spheres when aqueous	
45	droplets of "broth" are dispersed into a heated immiscible organic	
46	liquid. Gelation occurs by the release of ammonia from hexamethy-	
47	lenetetramine (HMTA) in the feed broth (Eq. 1).	
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49	*Research sponsored by the Office of Waste Operations and	
50	Technology, U.S. Department of Energy, under contract	
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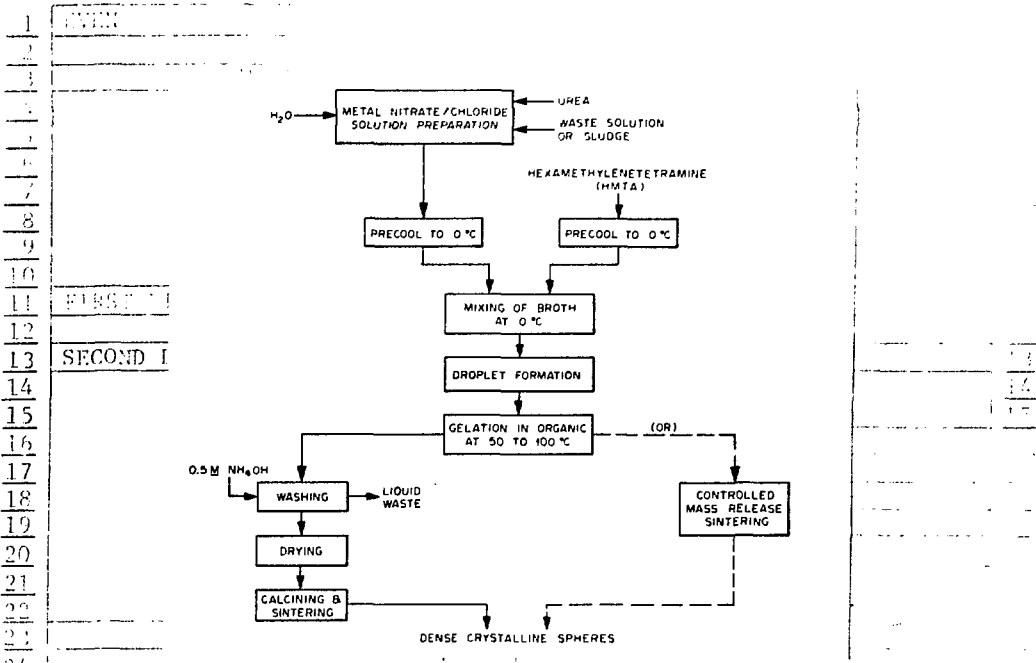
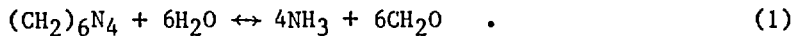


Fig. 1. Generic flowsheet for preparing spheres by the internal gelation process.



Urea is also present in the feed broth and is necessary to complex the metal cations and avoid premature gelation of feed broth by HMTA at 0°C. The added urea also neutralizes excess acid in the metal salt solutions and reduces the acidity from pH values below 0 to about 2. Cations of the additives in the Synroc-B and Synroc-D compositions are usually derived by dissolving the appropriate amounts of the respective salts (Zr, Al, Ca, Ba). Titanium is added as TiCl<sub>3</sub> or TiO<sub>2</sub> sol and silicon as SiO<sub>2</sub> sol. The simulated waste has been introduced either as a solution or as a slurry.

Droplets of the feed broth are formed by metering it to a vibrating nozzle submerged beneath the immiscible organic liquid surface. Droplet size is governed by the feed flow rate and the imposed vibrational frequency. The droplets gel in 5 to 15 s of free fall in a heated column of organic liquid. Gelation depends on the composition of feed solutions and the temperature of heated organic medium. Kinetic studies<sup>4</sup> of NH<sub>3</sub> formation by Eq. (1) show that the reaction is rapidly accelerated by increasing temperature, and it proceeds with an activation energy of about 100 kJ/mol. The reaction is second order, depending on both the HMTA and hydrogen ion concentrations.

The immiscible organic liquid used throughout this work was a solution of 33 vol % trichloroethylene and 67 vol % 2-ethyl-1-hexanol. About 0.5 vol % of a surfactant was added to this solution to prevent the droplets from adhering to the forming column wall. We fabricated an internal gelation system capable of producing 100 g batches of alternative waste form microspheres. The heated 1.3-m column is maintained at 45 to 50°C, which is sufficient to affect gelation of the droplets. The spheres are collected and then washed with isopropyl alcohol to remove the adhering organic layer and finally with 0.5 M  $\text{NH}_4\text{OH}$  to remove  $\text{NH}_4\text{NO}_3$ , urea, and any unreacted HMTA and additive anions such as  $\text{NO}_3^{1-}$  and  $\text{Cl}^{1-}$ . It has been found part of the soluble  $\text{Ca}(\text{OH})_2$  and  $\text{Ba}(\text{OH})_2$  is leached from the gelled spheres upon washing. Materials have been produced with Cs, Sr, Nd, Mo, and Ru dopants to study the side waste streams and the effects of drying and sintering. Both washed and unwashed gel spheres have been successfully produced.

#### AND ADDITIVES

#### DRYING

Drying tests investigated batches of Synroc-B (1% simulated waste) material in either the washed or unwashed state. The Synroc-B (1% simulated waste) is referred to as Synroc-B for the remainder of this report. A brief summary of these results is as follows: (1) washed spheres dried without humidity at 100 and 300°C resulted in sintered densities of 89 and 95% of theoretical, respectively; particles dried with humidity resulted in sintered densities from 94 to 97%; (2) among the different batches, the sintered density varied only 2 to 5%, (3) unwashed spheres dried in air without humidity resulted in sintered densities of 45 to 54% and produced cracked spheres (the interest in unwashed spheres is due to cesium retention), and (4) drying at different humidity levels varied the sintered density of particles by 2 to 3%. These effects will be investigated further with a new, programmable dryer.

Synroc-B spheres have been formed with dopant amounts of Cs, Ru, Nd, Sr, and Mo. Initial measurements indicated that essentially all the cesium added (0.5%) was removed during sphere washing, while the other elements were retained. Thus, the drying of unwashed spheres was initiated in order to retain the cesium. Air drying of unwashed material resulted in cracked spheres. Vacuum drying produced essentially crack-free spheres [Fig. 2(a)]. Washed, air dried [Fig. 2(b)], and sintered spheres were crack-free. The cesium content of sintered spheres appears to depend upon the sintering conditions and perhaps to a lesser extent upon the drying conditions. Spheres unwashed, dried, and sintered at 1025°C had two small and very broad unidentified x-ray diffraction peaks. At 1225°C, there were broad  $\text{CaZrTi}_2\text{O}_7$  (zirconolite) peaks and another small and broad unidentified peak.

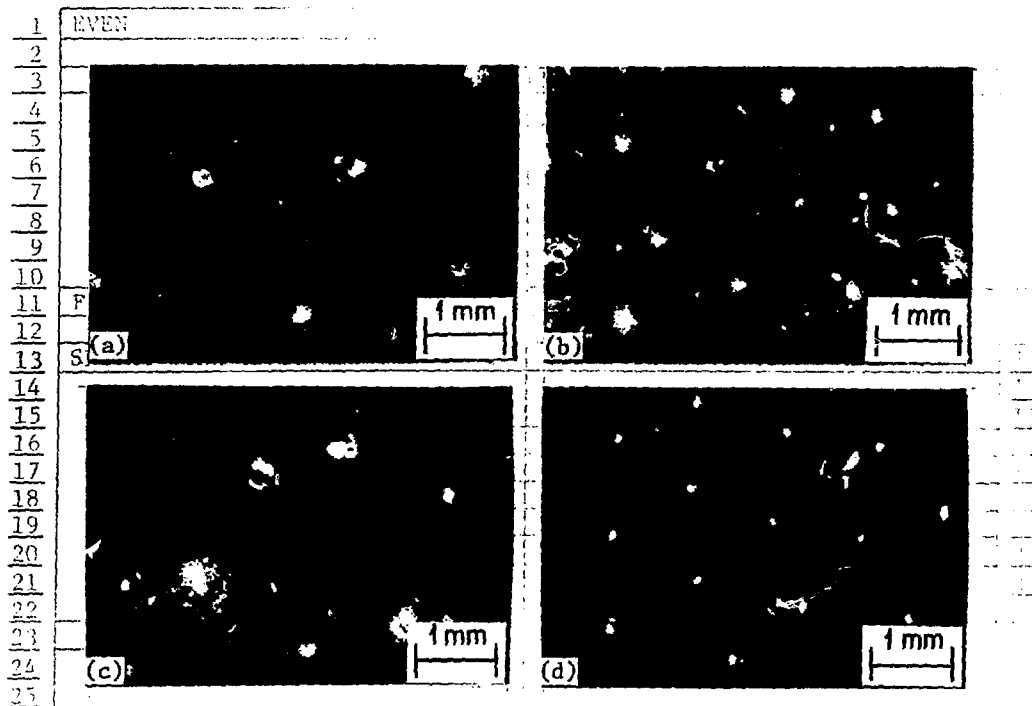


Fig. 2. As-dried surface macrograph of internal gelation derived waste forms. (a) Synroc-B (1% simulated waste) unwashed gel, vacuum dried; (b) Synroc-B (1% simulated waste) washed gel, air dried; (c) Synroc-D (70% simulated SRP waste) unwashed gel, nitrogen dried; (d) Synroc-D (70% simulated SRP waste) washed gel, air dried.

The phase identification of washed spheres is presented in the sintering section of this paper.

Drying tests were also performed on gel derived waste forms of (1) Synroc-B with about 10% simulated SRP waste and (2) Synroc-D (70% simulated SRP waste, 30% additives). The unwashed spheres of Synroc-B with 10% SRP waste showed only a small amount of cracking when dried under vacuum, and again washed spheres showed very little cracking but will probably have a low cesium content. Unwashed spheres of Synroc-D dried in nitrogen [Fig. 2(c)] and washed spheres dried in air [Fig. 2(d)] produced essentially crack-free spheres. Sintering, phase identification, and coating of gel-derived Synroc-D remain to be performed.

#### THERMAL ANALYSIS

Thermal analysis studies have been made on internal gelation Synroc-B microspheres. Washed and unwashed gel microspheres dried

and not dried have been examined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), differential thermal analysis (DTA), and evolved gas analysis (EGA) using mass spectrometry (MS). Water was a major component evolved - even from dried (200°C) microspheres. Thermograms from TGA and EGA-MS showed evidence for the release of different kinds of water - outer sphere or surface water, inner sphere or coordination water, and water formed from organic combustion and from hydroxide dehydration. Unwashed wet gel microspheres evolved several gases near 300°C from decomposition of urea and HMTA. Ammonia was released at two peak temperatures (160 and 220°C) - the first from HMTA hydrolysis and the second from urea decomposition. The thermal analysis of washed wet gel microspheres showed mainly the release of water at 100°C. A small water peak at about 350°C was probably due to hydrocarbon combustion. A CO<sub>2</sub> release at 600°C was due to calcium carbonate decomposition. Dried washed gel samples also released significant amounts of water. Water and other masses were released at higher temperatures than from the respective undried material. Activation energies were 36 kJ/mol for surface water, 179 kJ/mol for CO from urea, and 293 kJ/mol for CO<sub>2</sub> from organics combustion.

#### SINTERING

The sintering behavior of washed and dried Synroc-B gel-derived microspheres has been investigated. Results in this section considers only this type of material. Dilatometry results showed that sintering of the Synroc microspheres occurred primarily between 550 and 800°C. Shrinkage of the microspheres continued from 800 to 1000°C but at a much slower rate. The density obtained when sintering in Ar-4% H<sub>2</sub> or in air at 825°C was about 3.94 Mg/m<sup>3</sup> (94% T.D.). The maximum density (95% T.D.) was obtained near 1000°C. At higher temperatures, the microspheres did not sinter to such high densities. For example, microspheres sintered at 1125°C had densities of about 3.88 Mg/m<sup>3</sup> (92% T.D.), and microspheres sintered at 1225°C had densities of about 3.75 Mg/m<sup>3</sup> (89% T.D.). The rate used to heat the microspheres from room temperature to the sintering temperature (50 to 200°C/h) did not influence the final sintered density. The densification at all temperatures was complete in less than 4 h.

The formation of phases in internal-gelation-derived Synroc-B has been observed after sintering at various temperatures. Phase identification of batches heated to 825 and 875°C in Ar-4% H<sub>2</sub> showed very broad peaks of TiO<sub>2</sub> and CaZrTi<sub>2</sub>O<sub>7</sub>. Formation of the phases hollandite and perovskite had not begun at these temperatures. The broad x-ray diffraction peaks indicate an extremely fine grain size. Metallography of samples fired at these temperatures showed no visible grains. Sintering at 925 and

1 EVEN

2  
3 975°C in Ar-4% H<sub>2</sub> revealed that TiO<sub>2</sub> and CaZrTi<sub>2</sub>O<sub>7</sub> were becoming  
4 more crystalline and BaAl<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub> (hollandite) was beginning to  
5 form at 975°C. Metallography showed very fine grains. By 1025°C,  
6 distinct peaks of CaZrTi<sub>2</sub>O<sub>7</sub> and BaAl<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub> were present and  
7 TiO<sub>2</sub> had disappeared. Also present at this temperature were about  
8 10 small peaks that could not be identified with confidence  
9 because the major peaks for the unidentified compounds were  
10 apparently obscured by coincident lines from other phases. Phase  
11 identification of microspheres sintered in Ar-4% H<sub>2</sub> at higher  
12 temperatures revealed the same phases. A trace of CaTiO<sub>3</sub>  
13 (perovskite) had formed by 1225°C. The shortage of CaTiO<sub>3</sub> from  
14 this batch is not understood because it has been observed by x-ray  
15 diffraction in other sol-gel batches.

16 AUTHOR'S NOTES

17 Slightly different results were obtained when batches of  
18 Synroc-B were sintered in air. The same phases, TiO<sub>2</sub> and  
19 CaZrTi<sub>2</sub>O<sub>7</sub>, were present at temperatures up to 975°C. Again a  
20 trace of hollandite formed at 975°C. At 1025 and 1075°C TiO<sub>2</sub>  
21 remained the major phase along with CaZrTi<sub>2</sub>O<sub>7</sub>. There were also  
22 minor amounts of alumina and hollandite. A careful examination of  
23 the hollandite phase revealed that the composition was actually  
24 BaAl<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub> instead of BaAl<sub>2</sub>Ti<sub>6</sub>O<sub>16</sub>. The x-ray diffraction  
25 patterns of these phases are very similar. When batches of  
26 Synroc-B microspheres were sintered in Ar-4% H<sub>2</sub> at 1025 and  
27 1075°C, the formation of the Synroc phases was complete and no  
28 TiO<sub>2</sub> remained.

29 LEACHING

30 Leach testing of sol-gel derived crystalline waste forms has  
31 only recently begun. Primary emphasis has been on developing the  
32 sol-gel processing techniques for producing crystalline ceramics  
33 that are known or are expected to have excellent leach resistance.  
34 Leach apparatuses are being assembled to perform tests specified  
35 by the Material Characterization Center.<sup>5</sup> Test results will be  
36 used in conjunction with verification of phase formation to  
37 characterize the sol-gel-derived waste form.

38 COATING OF GEL-DERIVED WASTE FORMS

39 Pyrocarbon coatings with densities less than 1 Mg/m<sup>3</sup> were  
40 deposited at temperatures as low as 1000°C from acetylene. The  
41 purpose of these deliberately low-density buffer coatings was to  
42 prevent cracking of the dense pyrocarbon outer layer. Cracking  
43 could otherwise result because of a thermal expansion mismatch  
44 between the Synroc kernel and the dense pyrocarbon layer. Many  
45 pyrocarbon coatings with densities of about 2.0 Mg/m<sup>3</sup> were applied  
46 at temperatures as low as 1100°C with acetylene and 1200°C with  
47 propylene [Fig. 3(a)]. Preliminary results indicate that very

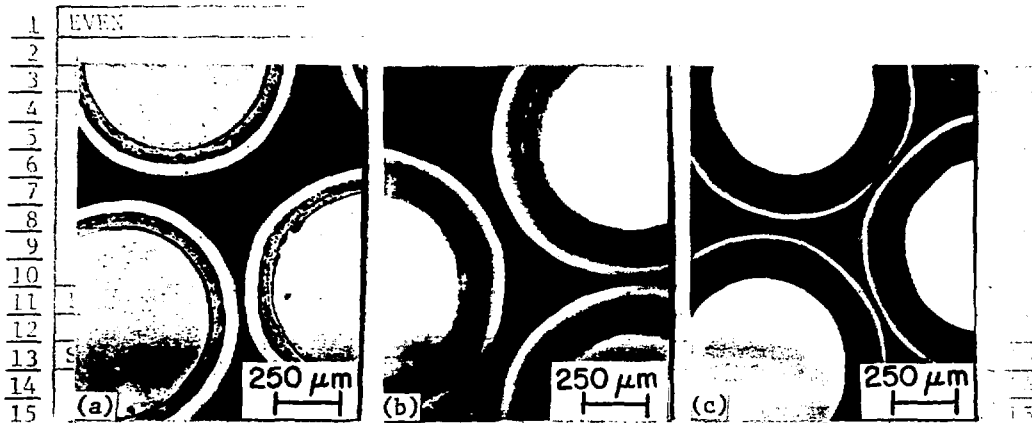


Fig. 3. Pyrolytic-carbon-coated and silicon-carbide-coated gel-derived Synroc spheres. (a) micrograph of two-layer pyrolytic carbon coating; (b) radiograph showing SiC outermost-layer deposited at 1400°C; (c) radiograph, SiC outermost layer deposited at 900°C.

high-density pyrocarbon<sup>6</sup> was deposited at the temperatures mentioned. The results of chlorine leach at 1000°C indicated that less than one particle in 10<sup>4</sup> was cracked or defective. From previous experience, we expect that defective fractions of less than one particle in 10<sup>6</sup> can be obtained. Temperatures of 1100 to 1200°C could still be too high for some applications. Efforts are in progress to deposit coatings at lower temperatures.

Many pyrocarbon coatings have also been deposited in an attempt to contain molten Synroc during the 1400 to 1500°C SiC coating process. This has proven to be quite difficult because most pyrocarbon coatings crack when heated to 1400°C because of the large volume increase that occurs when the kernels melt. Initially 75% of the coatings cracked when the particles were heated to 1400°C. Modifications in the buffer coating procedure to produce thicker and less dense coatings have reduced the cracking to 3 to 5% of the batch. We expect to be able to eliminate all cracking in the near future.

Silicon carbide coatings have been applied to several pyrocarbon coated batches. These coatings were applied at 1400 [Fig. 3(b)] and 1500°C. It was encouraging to note that even though the kernels melted and penetrated the buffer they did not reach or react with the SiC coatings. These SiC coatings were very dense (98% T.D.) and are expected to be very leach resistant. Silicon carbide has also been applied at 700 to 1000°C [Fig. 3(c)] on pyrocarbon-coated particles. The objective of the experiment was to obtain a high-density SiC layer at the lowest possible temperature. The coatings are currently being evaluated.



1 OPEN

2  
3 SUMMARY

4 Internal gelation has been used to produce ceramic spheres of  
5 various alternative nuclear waste compositions. A gelation system  
6 capable of producing 100-g batches has been assembled and used for  
7 development. Waste forms containing up to 70 wt % simulated  
8 Savannah River Plant waste have been produced. Dopants such as  
9 Cs, Sr, Nd, Ru, and Mo were used in some experiments to observe  
10 side waste streams and sintering effects. Synroc microspheres  
11 were coated with both low-density carbon, high-density impermeable  
12 carbon, high-temperature dense SiC, and SiC deposited at  
13 temperatures near 900°C. Other gelation methods and other  
14 alternative waste forms are being developed.  
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16  
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27 REFERENCES

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