

Determination of Ideal Broth Formulations Needed to Prepare Hydrous Hafnium Oxide Microspheres via the Internal Gelation Process

December 2008

**J. L. Collins
R. D. Hunt
S. G. Simmerman**



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Nuclear Science and Technology Division

**DETERMINATION OF IDEAL BROTH FORMULATIONS NEEDED TO
PREPARE HYDROUS HAFNIUM OXIDE MICROSPHERES
VIA THE INTERNAL GELATION PROCESS**

J. L. Collins
R. D. Hunt
S. G. Simmerman *

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OAK RIDGE NATIONAL LABORATORY
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*Formerly University of Tennessee co-op student assigned to the Nuclear Science and Technology Division at ORNL.

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ABSTRACT

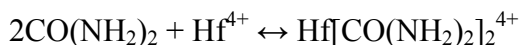
A simple test-tube methodology was used to determine optimum process parameters for preparing hydrous hafnium oxide microspheres by the internal gelation process.¹ Broth formulations of hafnium chloride [HfOCl_2], hexamethylenetetramine, and urea were found that can be used to prepare hydrous hafnium oxide gel spheres in the temperature range of 70–90°C. A few gel-forming runs were made in which microspheres were prepared with some of these formulations in order to equate the test-tube gelation times with actual gelation times. These preparations confirmed that the test-tube methodology is reliable for determining the ideal broths.

1. INTRODUCTION

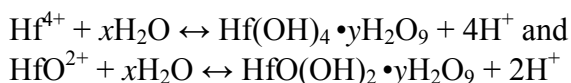
The internal gelation process is one of the sol-gel processes developed for the preparation of microspheres of hydrous metal oxides. In this process, chilled clear broth droplets containing the salt of the metal, hexamethylenetetramine (HMTA), and urea are heated, which causes homogenous gelation and solidification of the droplets.¹⁻¹⁵ After washing treatments, the gel spheres can be either air dried for use as engineered ion-exchange materials⁸⁻¹² or, depending upon the metal, dried, calcined, and sintered to ceramic microspheres for use as nuclear fuel,²⁻⁷ catalysts,⁸⁻¹² getters,⁸⁻¹¹ or dielectrics.¹³⁻¹⁵ A previously reported test-tube methodology,¹ which was employed to determine the optimum process parameters for preparing hydrous metal oxide microspheres, was also used in this study to determine the optimum process parameters for preparing hydrous hafnium oxide microspheres. The testing procedures are described in Appendixes A and B. The key to being able to prepare hydrous hafnium oxide gel spheres by internal gelation depends upon finding a hafnium salt which will precipitate or gel at a pH <7 in a nitrate solution. In solution, HMTA acts as a buffer that keeps the pH <7. Hafnium tetrachloride (HfCl₄), a Hf⁴⁺ salt, was tested and found to provide usable stable broths. The pH of precipitation of hafnium salts in a chloride solution was ~2. A broth is composed of the hafnium salt, HMTA, and urea chilled to 0–5°C. A stable broth is one that remains clear and does not gel or precipitate for reasonable periods (≥1 h) at that temperature.

The basic chemical reactions of the internal gelation process are as follows:⁵

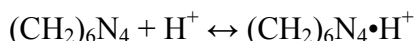
(1) *complexation/decomplexation*



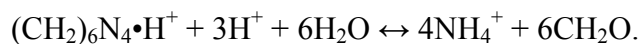
(2) *hydrolysis*



(3) *HMTA protonation*



(4) *HMTA decomposition*



Urea serves as a complexing agent for the metal (reaction 1). For broths of certain concentrations, the urea allows stable broths to be prepared at 0°C. As the temperature of the broth droplets rises after the droplets have been injected into the hot organic medium, decomplexation occurs (reaction 1), allowing hydrolysis of the hafnium to take place (reaction 2). HMTA, a weak organic base, drives the hydrolysis reaction to completion. At first the HMTA molecules are singularly protonated (reaction 3). Once most of the HMTA molecules ($\geq 95\%$) are protonated, they begin to decompose (reaction 4) into ammonia molecules, which makes the system even more basic. Each protonated HMTA molecule can effectively remove three additional hydrogen ions. The reaction products are formaldehyde and ammonium chloride. In addition to its role as a complexing agent, urea also functions as a catalytic agent, which accelerates the decomposition of the protonated HMTA molecules.⁵

2. PREPARATION OF STOCK SOLUTIONS USED FOR MAKING BROTHS

Generally, the rule of thumb in preparing stock solutions for use in the internal gelation process is to make them as concentrated as possible, without allowing them to become supersaturated under the test conditions. In this study, stock solutions of HMTA, urea, and hafnium chloride were prepared. As is the case for the other elements in the IVB family in the periodic table (titanium and zirconium), stock solutions of hafnium cannot be preneutralized; rather, they have to be acidified to make clear concentrated solutions. The key to preparing usable hydrous hafnium oxide gel spheres that maintain their sphericity is to determine the ideal minimum amount of acid needed to prepare good broth formulations which gel in ≤ 10 s. If the gel-forming time is longer than 10 s, there is a greater chance that the broth droplets will coalesce with other broth droplets, which can cause operating problems.

2.1 Preparation of Acidified Hafnium Stock Solutions

Powdered HfCl_4 with a molecular weight of 320.3 g/mole was used as the source of hafnium. When water is added to the HfCl_4 , an exothermic reaction occurs that results in the formation of hydrous hafnium oxide gel and hydrochloric acid (HCl). To prepare a stable stock solution of HfCl_4 , the water is acidified with HCl before being added to HfCl_4 to dilute the broth. When a sufficient amount of HCl is added, the hydrolysis reaction is suppressed and gel formation is prevented. Soluble hafnium oxo-chloro anion species $[\text{HfO}_2\text{Cl}_4]^{4-}$ and $[\text{HfOCl}_5]^{3-}$ are known to form in the acidic solutions. As will be shown in Sect. 3, the amount of HCl used in the broth is a critical process parameter in making hydrous hafnium oxide gel spheres or gels in other configurations. In this study, three acidified hafnium stock solutions were prepared by the procedure described in Appendix C. The concentrations of HfCl_4 and HCl used were as follows: (1) 0.98 *M* HfCl_4 and 1.21 *M* HCl, (2) 0.97 *M* HfCl_4 and 0.96 *M* HCl, and (3) 1.01 *M* HfCl_4 and 0.75 *M* HCl.

2.2 Preparation of Stock Solution of 3.2 *M* HMTA plus 3.2 *M* Urea

The solubility of HMTA in water at room temperature was found to be about 3.7 *M*, whereas the maximum solubility of HMTA in a solution containing 3.2 *M* urea

was only about 3.2 *M*. In this study, only 3.2 *M* HMTA plus 3.2 *M* urea solutions were used, which had a density of 1.14 g/mL. It was also discovered that a good technical grade of crystalline HMTA must be used. Free-flowing HMTA powder that is easy to pour contains additives that have a detrimental effect on the broth chemistry.⁴ A 2-L stock solution was prepared by adding 383.38 g urea (NH₂CONH₂) and 892.22 g HMTA (C₆H₁₂N₄) to a clean 3-L beaker and dissolving them with chilled (5 ± 5°C) deionized water. The volume was brought up to about 2 L by slowly adding the deionized water and mixing. Once the solids were completely dissolved, the liquid was transferred to a 2-L volumetric flask and brought to volume. The solution was then mixed well, and a sample was taken for analysis to determine the exact concentrations of the HMTA and urea. For this study, it was 3.2 *M* HMTA and 3.2 *M* urea.

3. EXPERIMENTAL RESULTS

Optimum broth formulations and gel-forming temperatures were determined for making structurally strong hydrous hafnium oxide microspheres by the internal gelation process. The stock solutions described in Sect. 2 were used to prepare the broths given in Table 1 for the test-tube gelation experiments. The broths used to prepare hydrous hafnium oxide microspheres in laboratory-scale apparatus are also indicated in Table 1. Broth stability tests were conducted on each of these broths as described in Appendix A. As noted earlier, a stable broth is one that remains clear and does not gel or precipitate for ≥1 h at 0°C. All broths in Table 1 were stable broths.

Figure 1 shows gelation time as a function of HMTA/HCl mole ratio for hafnium broths heated at 90°C in which the HCl concentration in the broth was varied from 0.38 to 0.68 *M*. The HMTA/Hf⁴⁺ mole ratio is also given at each data point. The goal of these experiments was to determine usable broth formulations with gelation times of ≤10 s, which in Fig. 1 are the ones located under the dashed line. All usable broth formulations in Fig. 1 had HMTA/Hf⁴⁺ mole ratios ≥1.85. Table 2 gives the characteristic of all usable broths found which gelled in ≤10 s at the gel-forming temperature of 90°C. Concentrations of the broth varied from 0.50–0.66 *M* for Hf⁴⁺ and 0.40–0.81 *M* for HCl. One broth had a HMTA/HCl mole ratio of 1.25. The pH of the aged gels formed from these usable broths ranged from 3.1 to 5.2. The rigidity

Table 1. Concentrations of HMTA, urea, Hf^{4+} , and H^+ used in experimental broths

HMTA/H^+ mole/ratio	HMTA/Hf^{4+} mole/ratio	HMTA (<i>M</i>)	Urea (<i>M</i>)	Hf^{4+} (<i>M</i>)	H^+ (<i>M</i>)	pH^a
1.00	1.24	0.68	0.68	0.55	0.68	
1.00	1.24	0.87	0.87	0.70	0.88	
1.25	1.55	0.85	0.85	0.55	0.68	0.9
1.25	1.54	1.02	1.02	0.66	0.81	
1.50	1.48	0.89	0.89	0.60	0.59	
1.50	1.85	1.11	1.11	0.55	0.68	1.2
1.50	1.84	1.14	1.14	0.62	0.76	
1.58 ^b	1.98	1.18	1.18	0.61	0.75	
1.75	2.16	1.19	1.19	0.55	0.68	1.6
1.75	2.17	1.26	1.26	0.58	0.72	
2.00	2.47	1.36	1.36	0.55	0.68	1.9
2.00	1.98	1.20	1.20	0.60	0.59	
2.07 ^b	2.07	1.23	1.23	0.60	0.60	
2.50	2.47	1.48	1.48	0.60	0.59	
2.50	1.85	1.13	1.13	0.61	0.45	0.5
2.49	1.86	1.17	1.17	0.63	0.47	0.6
3.02	2.16	1.33	1.33	0.61	0.45	
2.75	2.30	1.24	1.24	0.61	0.45	0.7
2.75	2.74	1.37	1.37	0.50	0.50	
2.23	2.23	1.12	1.12	0.50	0.50	1.0
2.25	2.23	1.27	1.27	0.57	0.57	
2.50	2.49	1.24	1.24	0.50	0.50	
2.50	2.45	1.35	1.35	0.55	0.54	
2.47	2.47	1.22	1.22	0.50	0.50	1.2
2.72	2.72	1.36	1.36	0.50	0.50	1.7
2.75	2.74	1.37	1.37	0.50	0.50	
2.75	2.75	1.43	1.43	0.52	0.50	
2.96	2.96	1.48	1.48	0.50	0.50	2.1
2.92 ^b	2.10	1.30	1.30	0.62	0.45	
3.02	2.23	1.36	1.36	0.61	0.45	
3.22	2.33	1.35	1.35	0.58	0.42	
3.21 ^b	2.30	1.37	1.37	0.60	0.43	
3.46	2.58	1.43	1.43	0.55	0.41	
3.77	2.26	1.35	1.35	0.60	0.36	
3.83	2.86	1.51	1.51	0.53	0.40	
4.16	2.50	1.43	1.43	0.57	0.34	
4.85	2.92	1.59	1.59	0.55	0.33	

^apH of chilled, clear gel-free broth.

^bBroth used in a laboratory-scale production run to determine actual gelation time and to prepare hydrous hafnium oxide microspheres.

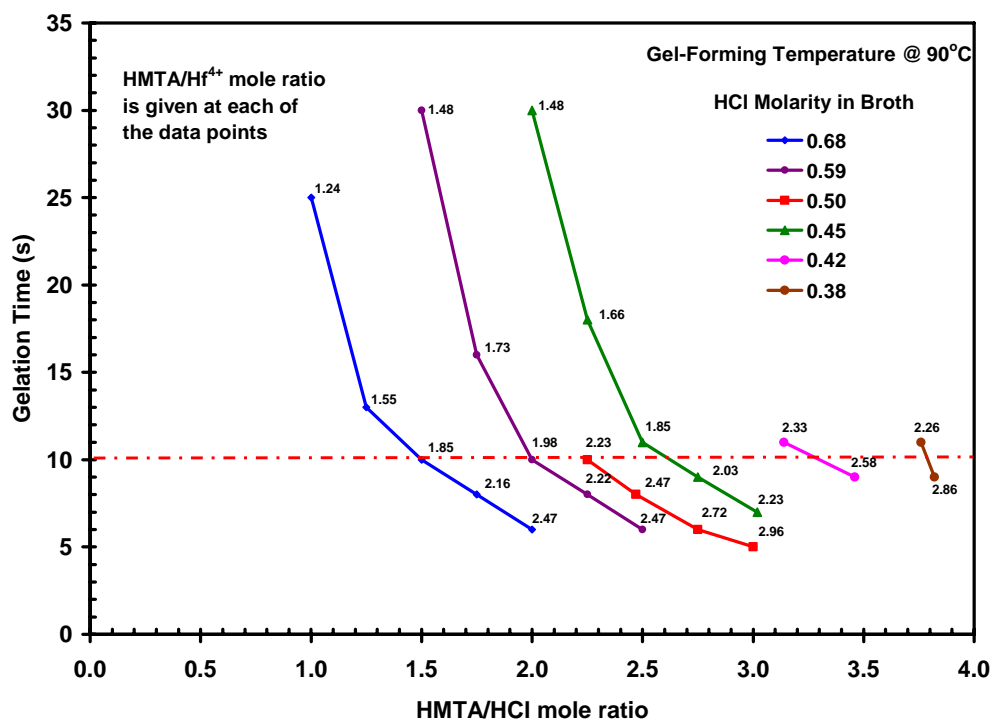


Fig. 1. Gelation time as a function of HMTA/HCl mole ratio for hafnium broths with HCl concentrations of 0.38–0.68 M at a gel-forming temperature of 90°C.

of the aged gels ranged from soft to very hard. For reason of economics, the most ideal broths are those that have the lowest concentrations of HCl and HMTA. The broth highlighted in Table 2 would be a very good choice.

The impact of lowering the gel-forming temperature on gelation time is shown in Figs. 2 and 3. The concentrations of Hf⁴⁺ and HCl in the broths tested in Fig. 2 were maintained 0.45 and 0.61 M, respectively, while the concentration of the HMTA was varied. Each of the broths was tested at 60, 70, 80, and 90°C. No usable broths were found at the gel-forming temperature of 60°C. At a gel-forming temperature of 90°C, it appears that a HMTA/HCl mole ratio of ≥ 2.6 was needed to have a gelation time of ≤ 10 s. At 80 and 70°C, estimated HMTA/HCl mole ratios of about 3 and 3.2, respectively, might be needed. In Fig. 3, broths with Hf⁴⁺ and HCl concentrations of 0.50 M were also tested at 60, 70, 80, and 90°C. At 90 and 80°C, HMTA/HCl mole ratios of ≥ 2.25 and ≥ 2.50 would be needed to have a gelation times of ≤ 10 s. As the HMTA/HCl mole ratios increased, the rigidities decreased. At a HMTA/HCl mole ratio

of 3, the gels are fairly soft and could be damaged during handling. Ones with rigidities of medium hardness would probably be more ideal (Appendix B). From the slope of the plot for the 70°C data in Fig. 3, a HMTA/HCl mole ratio of 3 would be needed to obtain a gelation time of 10 s; however, based upon the rigidity trend, this gel would be expected to be very soft. The data in Figs. 2 and 3 indicated that a gel-forming

Table 2. Characteristics of usable broths with gelation times of ≤ 10 s at 90°C

HMTA/H ⁺ mole ratio	HMTA/Hf ⁴⁺ mole ratio	HMTA ^a (M)	Hf ⁴⁺ (M)	H ⁺ (M)	G. T. ^b (s)	Rigidity	pH of aged gel
1.25	1.55	1.02	0.66	0.81	10	9	
1.50	1.85	1.11	0.55	0.68	10	4	4.0
1.50	1.84	1.14	0.62	0.76	9	7	3.5
1.58 ^c	1.98	1.18	0.61	0.75	10		
1.75	2.16	1.19	0.55	0.68	8	4	4.2
1.75	2.17	1.26	0.58	0.72	7	3	4.5
2.00	2.47	1.36	0.55	0.68	6	2	5.2
2.00	1.98	1.20	0.60	0.59	10	8	5.1
2.07 ^c	2.07	1.23	0.60	0.60	9	8	5.2
2.50	1.85	1.12	0.61	0.45	10–11	8	
2.50	2.47	1.48	0.60	0.59	6	8	
2.75	2.03	1.24	0.61	0.45	8	8	4.2
2.75	2.74	1.37	0.50	0.50	7	4	
2.23	2.23	1.12	0.50	0.50	10	7	3.1
2.25	2.23	1.27	0.57	0.57	8	8	
2.50	2.49	1.24	0.50	0.50	8	6	
2.50	2.45	1.35	0.55	0.54	7	5	3.6
2.47	2.47	1.22	0.50	0.50	8	6	4.0
2.72	2.72	1.36	0.50	0.50	6	3	4.8
2.75	2.74	1.37	0.50	0.50	6	3	
2.75	2.75	1.43	0.52	0.50	5	3	
2.96	2.96	1.48	0.50	0.50	5	3	5.1
2.92 ^c	2.10	1.30	0.62	0.45	10		
3.02	2.23	1.36	0.61	0.45	7	8	
3.21 ^c	2.30	1.37	0.60	0.43	10–11	8	
3.46	2.58	1.43	0.55	0.41	9		
3.63	2.74	1.45	0.53	0.40	10		
3.83	2.86	1.51	0.53	0.40	9		

^aUrea concentration is the same as the HMTA concentration.

^bG. T. = Gelation Time (time needed for gelation to begin).

^cBroth used in a laboratory-scale production run to determine actual gelation time and to prepare hydrous hafnium oxide microspheres.

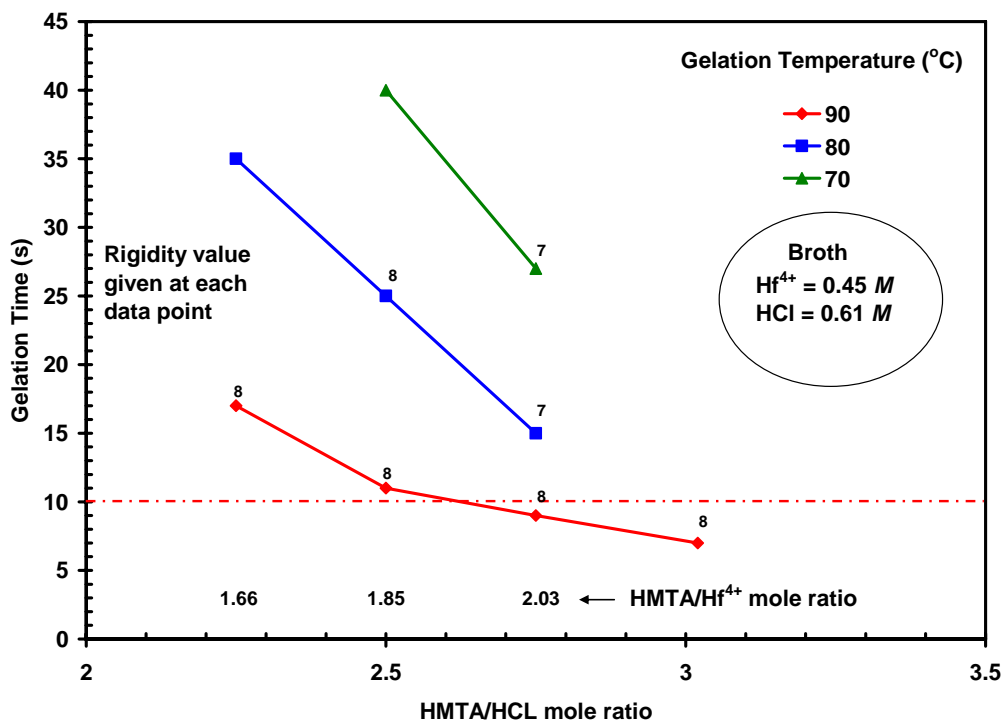


Fig. 2. Gelation time as a function of HMTA/HCL mole ratio for broths heated at 70, 80, and 90°C. The concentrations of Hf^{4+} and HCl in the broth were 0.45 and 0.61 M, respectively.

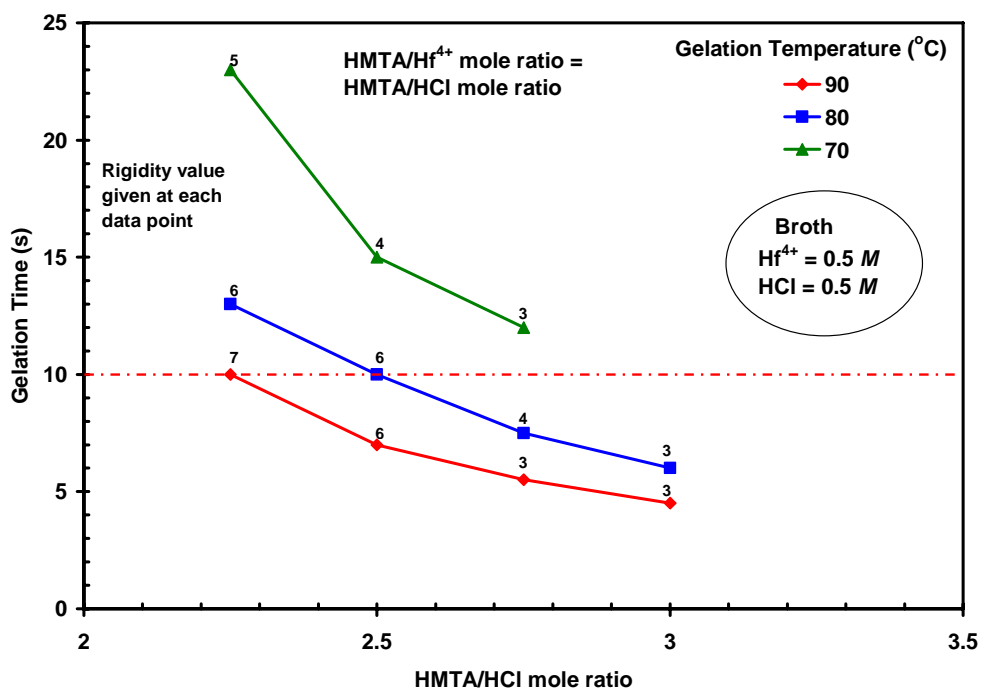


Fig. 3. Gelation time as a function of HMTA/HCL mole ratio for broths with Hf^{4+} and HCl concentrations of 0.5 M which were heated at 70, 80, and 90°C.

temperature of 80 or 90°C is needed to prepare good-quality hydrous hafnium oxide gel spheres.

In Fig. 4, the concentration of HCl in broth is plotted as a function of HMTA/HCl mole ratio for broth formulations which gelled in about 10 s at 90°C. This data, in conjunction with the data in Fig. 1–3 and Tables 1 and 2, makes it possible to easily choose a broth formulation for gel-forming temperature to make quality microspheres. Once chosen, hydrous hafnium oxide gel spheres can be prepared on any scale to make microspherical sorbents or to make composite sorbents by the methods described in Refs. 8–11. The hydrous hafnium oxide gel spheres can also be converted to acid-insoluble hafnium monohydrogen phosphate while maintaining the sphericity (Appendix F). Hafnium monohydrogen phosphate is also a good sorbent for a number of cations. Gel spheres can be similarly prepared in which fine catalytic powder is

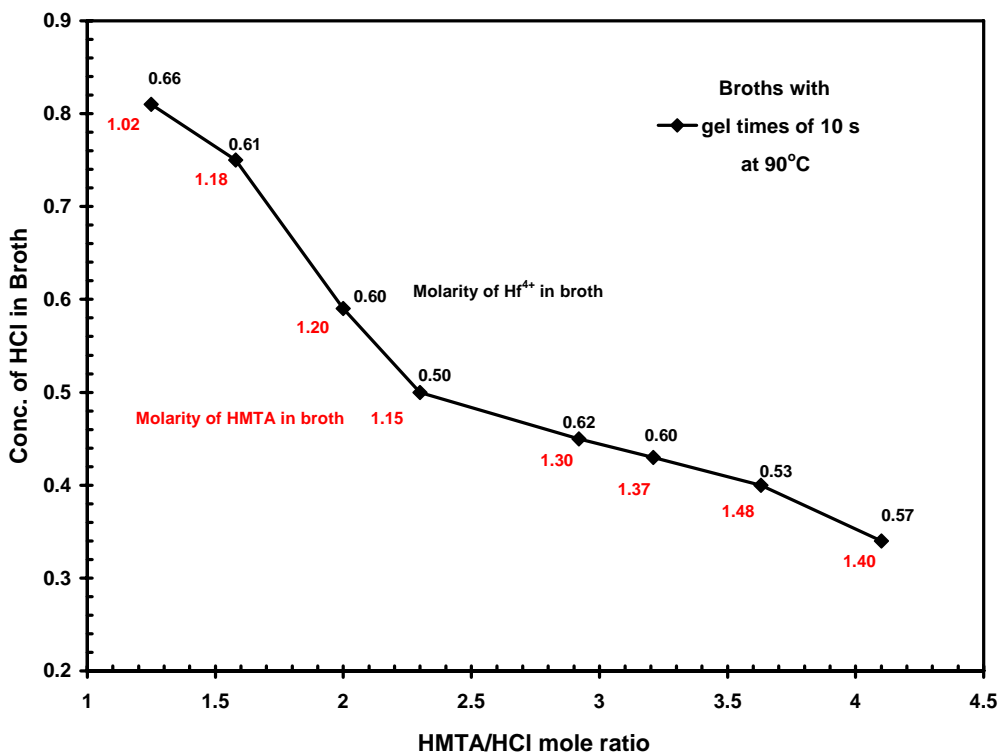


Fig. 4. Concentration of HCl in broth as a function of HMTA/HCl mole ratio for broth formulations which gelled in about 10 s at 90°C.

added and suspended in the broth droplets, which when heated form gel spheres with these particles homogenously set within the matrix. Treatment techniques have also been developed that can be used to further enhance the porosity of the microspheres, making them more effective as engineered catalytic forms for use in liquid or gas streams.

4. THREE EXAMPLES OF LAB-SCALE OF HYDROUS HAFNIUM OXIDE MICROSPHERES PREPARATION

4.1 Example 1

In this preparation, 129.0 mL of broth was prepared by slowly mixing 49.0 mL of chilled 3.11 *M* HMTA plus 3.11 *M* urea solution (0 to 5°C) with 80.0 mL of chilled 0.98 *M* HfCl₄ stock solution with HMTA/Hf⁴⁺ and HMTA/HCl mole ratios of 1.95 and 1.58, respectively. The concentrations of Hf⁴⁺, HCl, HMTA, and urea for the broth were 0.61, 0.75, 1.18, and 1.18 *M*, respectively. A two-fluid nozzle system using a 21 gauge flat-tipped needle was used to provide the broth droplets.¹⁰ From the tip of the needle, the broth droplets were introduced into a flowing stream of heated immiscible organic medium (~90°C). Silicone oil (Dow Corning 200 silicone fluid) was used in this preparation. The droplets were then transported into the gel-forming apparatus. The size of the droplets was controlled using a two-fluid nozzle concept and varying the gauge of the needle and the flow rates of the hot silicone oil and the chilled broth. The droplets began to gel in 10–11 s and were subsequently collected in a stainless steel mesh basket downstream. It took ~30 s for the gelled microspheres to reach the basket. Next, the microspheres were aged for 20 min in silicone oil at ~90°C to complete the gelation process, washed four times with trichloroethylene (TCE) to remove the silicone oil, and then washed six times with 0.5 *M* NH₄OH to remove the reaction impurities. The washed microspheres were then air dried and weighed. About 27.3 g of air-dried microspheres with a tap density of 1.6 g/mL were obtained.

4.2 Example 2

A 364.7-mL broth was prepared by slowly mixing 179.03 g (156.49 mL) of chilled 3.2 *M* HMTA plus 3.2 *M* urea solution (0 to 5°C) with 271.15 g (208.18 mL) of chilled 1.05 *M* HfCl₄ stock solution which had HMTA/Hf⁴⁺ and HMTA/HCl mole ratios

of 2.30 and 3.21, respectively. The density of the HfCl_4 stock solution was 1.302 g/mL. The concentrations of Hf^{4+} , HCl, HMTA, and urea for the broth were 0.60, 0.43, 1.37, and 1.37 M, respectively. A two-fluid nozzle system using a 18 gauge flat-tipped needle was used to provide the broth droplets.⁷ The droplets began to gel in 10–11 s in the forming column in silicone oil at 90°C and were subsequently collected downstream in a stainless steel mesh basket. The run lasted about 54 min. The microspheres were then aged for 20 min in silicone oil at ~90°C to complete the gelation process, washed four times with TCE to remove the silicone oil, and subsequently washed six more times with 0.5 M NH_4OH to remove the reaction impurities. The estimated gel-sphere volume was about 300 mL. Next, the gel spheres were air dried and weighed. The air-dried microspheres weighed 63.86 g and had a tap density of 1.65 g/mL and an average crush strength of >1200 g. The procedures for these two measurements are described in Ref. 7. Subsequently, an 11.3653-g sample of the air-dried microspheres was put in an alumina boat, placed in a tube furnace, and heated according to the schedule given in Appendix D. The sintered mass of the microspheres was 5.5931 g, so the weight loss was 50.8%. The average crush strength of the sintered microspheres was only 128 g, and the tap density was 4.74 g/mL. Figure 5 shows a 4× microscopic image of a small sample of the hafnium oxide microspheres prepared in this experiment. The microspheres were measured to be in the 500- to 600-μm-diam range. The low crush strength of the microspheres appears to be attributed to the fact that many of the microspheres had fine cracks in them. All usable broth formulations produce amorphous hydrous hafnium oxide gel spheres, which are very difficult to wash the organic reaction impurities from. The reaction impurities decompose at high temperatures and cause gassing and pressure buildup in the microspheres, which probably cause the microspheres to crack. To understand this phenomenon better, a study using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was conducted. The results are shown in Fig. 6. In this analysis, a 0.324-g sample of the air-dried microspheres was heated at a rate of 60°C/h in 100% oxygen, as shown in Fig. 7. In Fig. 6, the DTA profile shows an exothermic reaction beginning at ~200°C at the same time the TGA shows a sharp loss of mass. Separate TGA analyses were conducted with small samples of HMTA, urea, and NH_4NO_3 which were also heated in 100% O_2 at a rate of 60°C/h. Figure 8 gives the

percentage weight loss of each compound as a function of temperature. The hydrous hafnium oxide microspheres should contain trace amounts of each of these compounds; however, the TGA and DTA profiles in Fig. 6 appear to only match the behavior for the decomposition of NH_4NO_3 seen in Fig. 8. The TGA/DTA data provided the information needed to understand the decomposition behavior of impurities, which was needed to develop the calcining and sintering heating schedule given in Appendix D that was used in this study.

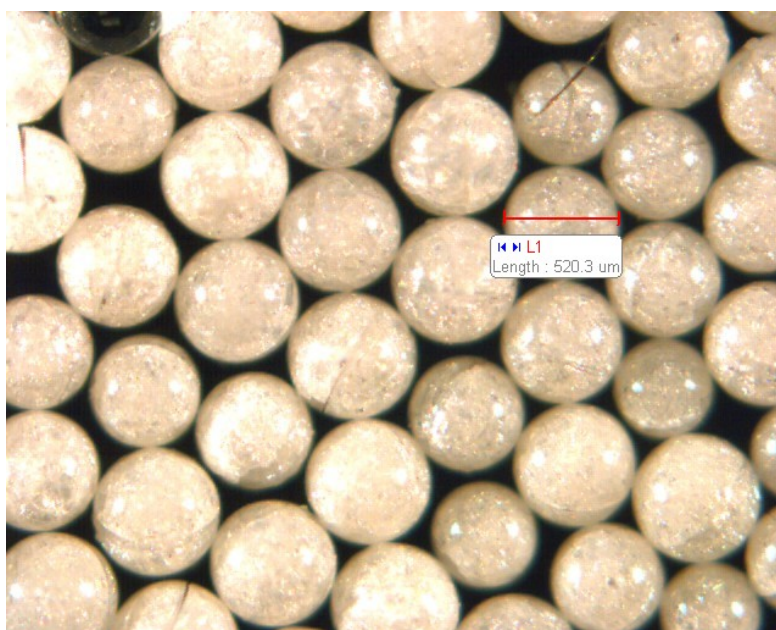


Fig. 5. A 4× microscopic image of a sample of hafnium oxide microspheres which were air dried at ambient temperature and then calcined at 600°C for 4 h.

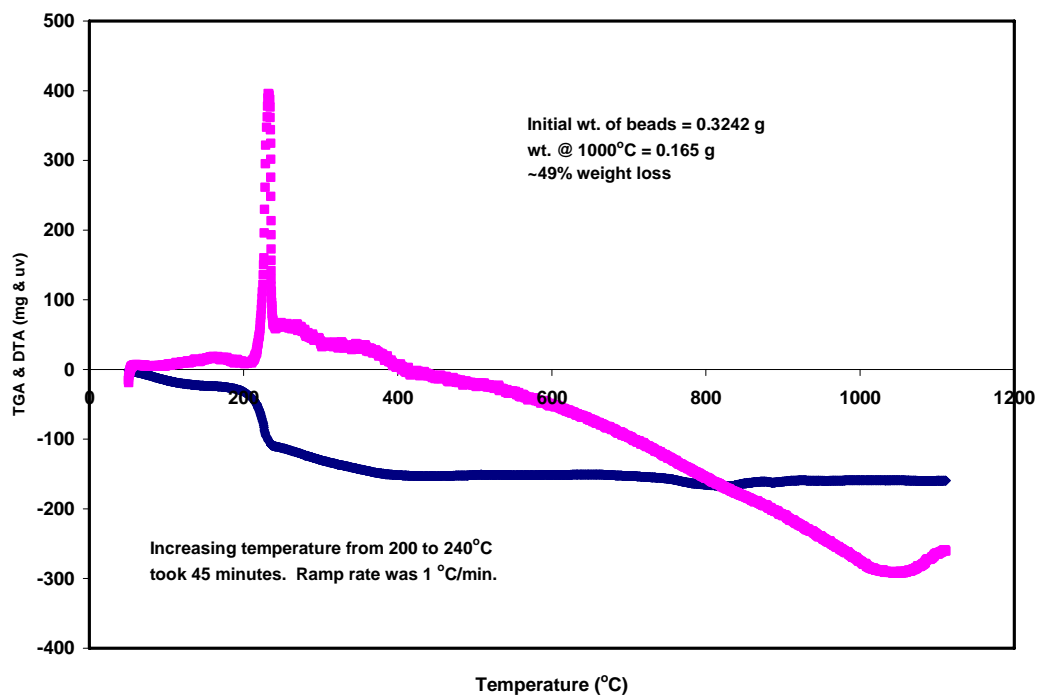


Fig. 6. TGA and DTA analytical profiles of hydrous hafnium oxide microspheres heated in oxygen.

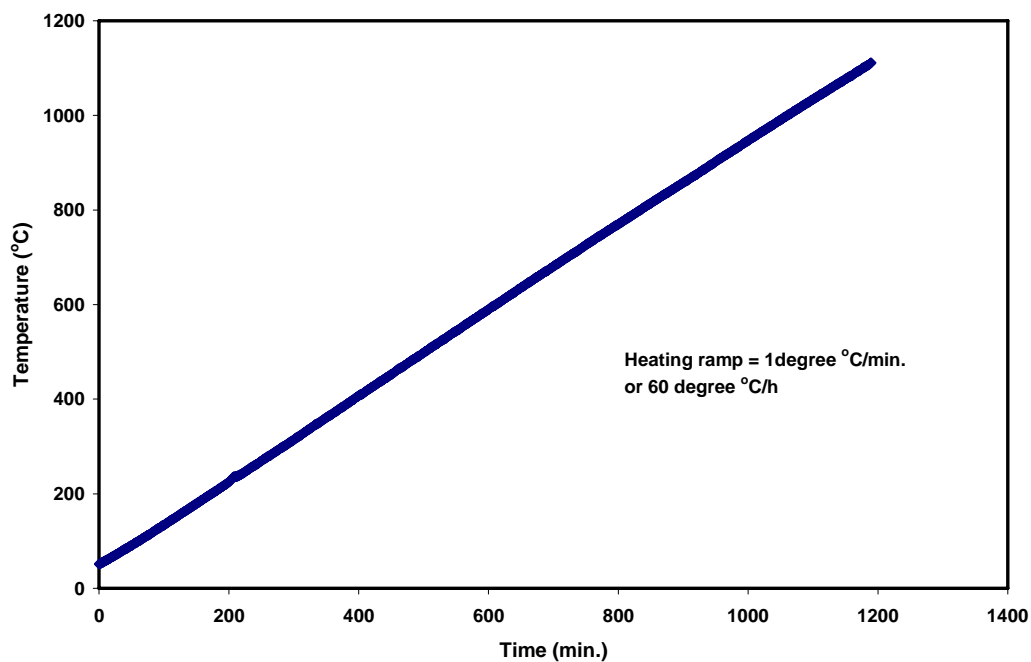


Fig. 7. Temperature-vs-time profile for the TGA/DTA analysis of hydrous hafnium oxide microspheres given in Fig. 6.

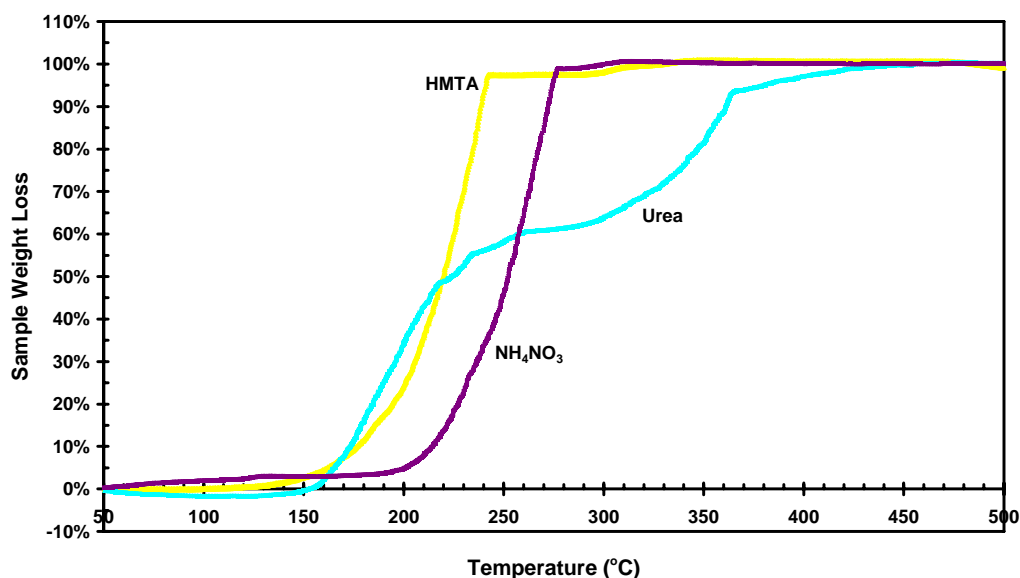


Fig. 8. Separate TGA analyses of HMTA, urea, and NH₄NO₃ for small samples of these compounds which were heated in 100% O₂ at a rate of 60°C/h.

4.3 Example 3

To be able to prepare strong, structurally stable calcined and sintered hafnium oxide microspheres, enough yttrium needs to be added to the broth so the sintered hafnium oxide microspheres will contain 5–10 mole % yttrium in the form of Y₂O₃ (Ce₂O₃ could also be used). In this example, a broth was prepared that was designed to yield sintered hafnium oxide microspheres with 8 mole % yttrium or 4.4 wt. % in Y₂O₃. To prepare the 445.16 mL broth, 222.7 g (194.7 mL) of chilled 3.2 M HMTA plus a 3.2 M urea solution which was cooled to 0–5°C were slowly added with mixing to 250.46 mL of a hafnium plus yttrium chloride solution which was also chilled. The hafnium plus yttrium chloride solution was prepared by dissolving 2 g of fine yttrium metal powder in 324.27 g (248.96 mL) of 1.047 M HfCl₄ stock solution which was 0.75 M in HCl. The density of the hafnium chloride stock solution without yttrium was 1.302 g/mL. The HMTA/(Hf⁴⁺ + Y³⁺) and HMTA/HCl mole ratios of the broth were 2.20 and 3.34, respectively. The concentrations of Hf⁴⁺, Y³⁺, HCl, HMTA, and urea for

the broth were 0.586, 0.51, 0.42, 1.4, and 1.4 *M*, respectively. A two-fluid nozzle system using an 18 gauge flat-tipped needle was used to provide the broth droplets. The droplets began to gel in 10–11 s in the forming column in silicone oil at 91°C and were subsequently collected downstream in a stainless steel mesh basket. The run lasted about 55 min. Next, the microspheres were aged for 20 min in silicone oil at ~90°C to complete the gelation process, then washed four times with TCE, washed six more times with 0.5 *M* NH₄OH, and then four more times with deionized water. The bead volume after the washing steps was about 330 mL. These gel spheres from this run were given to F. C. Montgomery of the Materials Science and Technology Division, who developed a washing procedure using Dowanol PM glycol ether that yielded sintered-yttrium-stabilized hafnium oxide microspheres (see Appendix E) with a high crush strength. A microscopic image of a sample of these microspheres is shown in Fig. 9. Note that a few of the larger ones were not completely spherical. To produce very high-density microspheres, they should be sintered under air at 1500°C. They could be used as abrasion-resistant microspheres for grinding other materials.

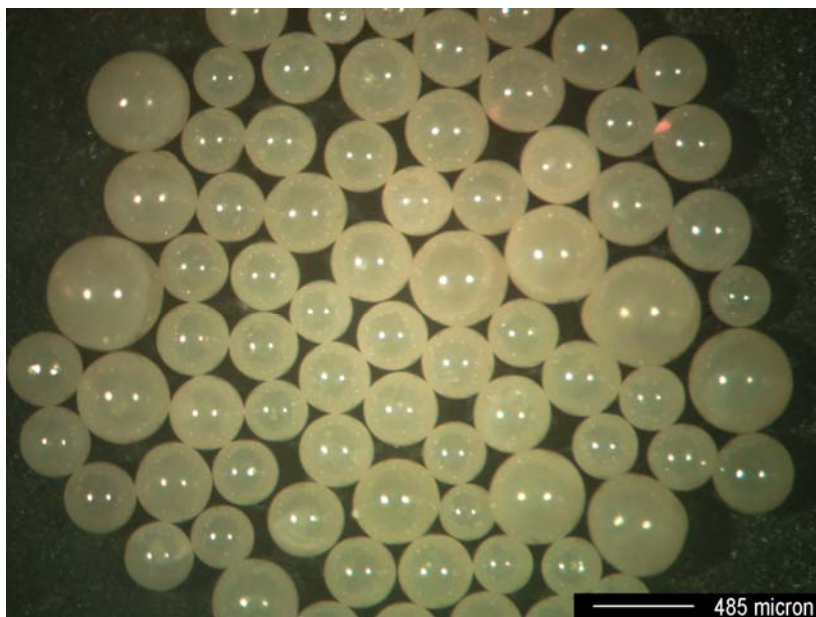


Fig. 9. Microscopic image of sintered HfO₂-Y₂O₃ microspheres.

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. J. L. Collins, *Experimental Methodology for Determining Optimum Process Parameters for Production of Hydrous Metal Oxides by Internal Gelation*, ORNL/TM-2005/102, June 2005.
2. F. W. van der Bruggens, A. J. Noothout, M. E. A. Hermans, J. B. W. Kanij, and O. Votocek, "A U(VI)-Process for Microsphere Production," in *Proc. Symp. Sol-Gel Processes and Reactor Fuel Cycles, Gatlinburg, Tennessee, May 4-7, 1970*, CONF-700502, U.S. Atomic Energy Commission, 1970.
3. P. A. Haas, J. M. Begovich, A. D. Ryon, and S. J. Vavruska, *Chemical Flowsheet for Preparing Urania Spheres by Internal Gelation*, ORNL/TM-6850, July 1979.
4. M. H. Lloyd, J. L. Collins, R. L. Fellows, S. E. Shell, D. H. Newman, and W. B. Stines, *A Gel Sphere Process for FBR Fuel Fabrication from Coprocessed Feed*, ORNL/TM-8399, February 1983.
5. J. L. Collins, M. F. Lloyd, and R. L. Fellows, "The Basic Chemistry Involved in the Internal-Gelation Method of Precipitating Uranium as Determined by pH Measurements," *Radiochim. Acta* **42**, 121-34 (1987).
6. M. H. Lloyd, J. L. Collins, and S. E. Shell, "Method of Controlling Crystallite Size in Nuclear-Reactor Fuels," U.S. Patent No. 4,502,987, March 5, 1985.
7. J. L. Collins, R. D. Hunt, G. D. Del Cul, and D. F. Williams, "Production of Depleted UO₂ Kernels for the Advanced Gas-Cooled Reactor Program for use in TRISO Coating Development," ORNL/TM-2004/123, Dec. 2004.
8. J. L. Collins, "Method of Preparing Hydrous Zirconium Oxide Gels and Spherules," U.S. Patent No. 6,602,919 B1, Aug. 5, 2003.
9. J. L. Collins, "Method of Preparing Hydrous Titanium Oxide Gels and Spherules," U.S. Patent No. 5,821,186, Oct. 13, 1998.
10. J. L. Collins, R. J. Lauf, and K. K. Anderson, "Method of Preparing Hydrous Iron Oxide Gels and Spherules," U.S. Patent No. 6,599,493 B2, July 29, 2003.

11. J. L. Collins and K. K. Anderson, *Development of Spheroidal Inorganic Sorbents for Treatment of Acidic Salt-bearing Liquid Waste*, ORNL/TM-2000/367, September 2001.
12. J. L. Collins and J. S. Watson, *Economic Evaluation for the Production of Sorbents and Catalysts Derived from Hydrous Titanium Oxide Microspheres Prepared by the HMTA Internal Gelation Process*, ORNL/TM-1999/212, April 2000.
13. R. J. Lauf, K. K. Anderson, F. C. Montgomery, J. L. Collins, and J. J. Felton, "Method for Preparing Dielectrics Composite Materials Use Thereof," U.S. Patent No. 2004/6,821,474, Nov. 23, 2004.
14. R. J. Lauf, K. K. Anderson, F. C. Montgomery, J. L. Collins, and J. J. Feldon, "Method of Preparing Spherical Ferrite Beads and Use Thereof," U.S. Patent No. 2003/0129387 A1, July 10, 2003.
15. R. J. Lauf, K. K. Anderson, F. C. Montgomery, and J. L. Collins, "Method of Preparing Spherical Ferrite Beads and Use Thereof," U.S. Patent No. 6,492,016 B1, Dec. 10, 2002.

APPENDIX A

BROTH STABILITY TESTS

A stable broth is one that remains clear and does not gel or precipitate for reasonable periods of time (usually about 1 h) at $\sim 0^{\circ}\text{C}$. Broths were prepared using hafnium stock solutions #1, #2 and #3, as described in Appendix C, and each was tested for broth stability. Calculated amounts of chilled HMTA/urea, stock solution, and water were mixed together as follows:

1. A rack for holding thin-walled glass centrifuge tubes was placed in the ice bath. Predetermined volumes of 3.2 *M* HMTA/3.2 *M* urea and acidified stock solutions of hafnium chloride were separately and carefully pipetted to these tubes with calibrated electronic pipettes, and the tubes were subsequently chilled for ~ 20 min. The centrifuge tubes containing the acidified hafnium stock solutions also served as the broth tubes and were labeled accordingly as to stock solution that was used and the HMTA/ H^{+} mole ratio.
2. When needed, calculated amounts of deionized water were added with a calibrated electronic pipette to the centrifuge tubes containing the acidified hafnium stock solutions to obtain the targeted concentrations for the broth.
3. To prepare a broth, a volume of chilled HMTA/urea was carefully removed with a pipette and transferred to a centrifuge tube containing the acidified hafnium stock solutions. Because of the small volumes involved, it was important that the transfer was complete. The broth was then mixed well with a Teflon stirring rod, and the broth temperature was maintained at 0°C . The time of mixing was recorded, and the broth was observed until the first sign of gelation or for 1 h. The time of gelation was recorded. Tests were done in duplicate. If gelation had not occurred after about 5 min of mixing, the pH of the broth for one of the samples was measured with a calibrated-temperature-compensated Ross electrode (Appendix B).

APPENDIX B

GELATION TESTS IN GLASS CENTRIFUGE TUBES

Apparatus

The apparatus used for the gel tests was simple and consisted of the following components:

- 2-L beaker containing ice water
- 4-L beaker containing heated water
- hot plate with stirring capability
- dial thermometer
- calibrated Metler DE 200 analytical balance (0- to 200-g range with a readability of 0.0001 g)
- calibrated, continuously adjustable digital pipette (100- to 1000- μ L range) or a calibrated Rainin EDP-Plus electronic pipette with interchangeable liquid ends that cover the 100- to 1000- μ L and 250- to 2500- μ L ranges, plus the concomitant disposable tips
- ROSS™ Sure-Flow combination pH electrode, which provides temperature compensation for temperatures in the range of 0–100°C
- in-date standard pH 7 and pH 4 buffer solutions
- 12-mL glass centrifuge tubes
- 8-in.-long Teflon-coated microspatulas

Testing Procedure

The gel test procedure was as follows.

1. A portion of the hafnium solution (at room temperature) and deionized water were carefully pipetted into the bottom of a glass centrifuge tube in an ice-bath. The required volume of HMTA/urea was pipetted into the bottom of a separate plastic centrifuge tube in an ice bath. Both were chilled for 10 min to attain ice-bath temperature. The chilled HMTA/urea was then quantitatively pipetted into the chilled

hafnium solution and well mixed. Care was taken not to splash the broth onto the test tube walls. The broth was maintained in the ice bath for an additional 5 min.

2. The broth tube was then placed in a hot water bath at the desired temperature. The test tube was gently swirled in the water bath to observe when the gel set. A stopwatch was used to measure the time in the bath needed for gelation to occur. When gelation began, the clear broth became viscous and motionless. The gel was then allowed to age for 10 min in the hot bath at the same temperature.

3. The test tube was then removed from the hot bath, and the gel was allowed to cool to room temperature. The transparency of the gel [on a scale of 1 (transparent) to 10 (opaque)] was subjectively determined and recorded. The rigidity of the gel was subjectively determined by inserting a spatula into the center of the gel and was quantified on a subjective scale of 1 (no resistance, almost like water) to 10 (high resistance, difficult to penetrate).

4. The gel was then broken up by stirring with the spatula. Next, the test tube was centrifuged to remove pockets of air and to compact the gel into the bottom of the tube. A calibrated pH probe was inserted into the gel to measure the pH. It took up to 30 s for the pH reading to stabilize.

At a minimum, duplicates of each broth were tested to ensure accuracy. If the gel times and properties matched, the test results were assumed to be acceptable. If the gel times did not match, additional tests were conducted to resolve the problem and obtain consistent values.

APPENDIX C

PREPARATION OF HAFNIUM TETRACHLORIDE STOCK SOLUTIONS

PROCEDURE

- Hafnium tetrachloride (lot #13236-1) and 5.626 M HCl (label #SS-BC-01) were used in preparing the stock solutions. HfCl_4 is a powder, and its molecular weight is 320.3 g/mol.
- Amounts of HfCl_4 and HCl needed were calculated for a particular stock preparation.
- HCl was transferred to beaker and then placed in ice bath on a stir plate with large stir bar.
- Chilled deionized water was added to HCl to achieve about three-fourths of total feed volume needed. For a 100-mL feed, ~75 mL of water-acid solution was made.*
- HfCl_4 was carefully weighed out into a small beaker taking special precautions (best if done in hood).
- HfCl_4 was added very slowly to the acid solution prepared above, and the solution was stirred manually several times during addition of powder.
- The wall of beaker containing the feed was rinsed with the solution using a small pipette.
- The same pipette was used to rinse out the hafnium beaker with water into the feed.
- The volume of the mixture was then brought up to a predetermined mark on the beaker.
- A stir bar was added, and solution was stirred overnight.
- If the volume dropped much below the mark, deionized water was added to bring the volume back up to the mark. At the mark, the hafnium concentration was near the predetermined molarity.
- When the HfCl_4 was totally into solution, the solution was carefully transferred into a tared volumetric flask with a funnel, being careful not to splash the sides of the funnel.
- Rinses from the funnel and beaker were added to flask, and volume was brought up to the meniscus.
- The flask was then weighed to determine the density of the solution.

* *Note: Mixing these chemicals is very exothermic. Lowering the temperature minimizes the amount of volatile HCl vapor released to the hood.*

DATA AND CALCULATIONS

Stock Solution #1	$[\text{HfCl}_4] = 1\text{ M}$	$[\text{HCl}] = 1.25\text{ M}$
Stock Solution #2	$[\text{HfCl}_4] = 1\text{ M}$	$[\text{HCl}] = 1.00\text{ M}$
Stock Solution #3	$[\text{HfCl}_4] = 1\text{ M}$	$[\text{HCl}] = 0.75\text{ M}$

Amounts HfCl_4 and HCl used to prepare 100 mL of stock solutions:



$$[(1.0 \text{ mol/L})(0.1 \text{ L})]/(320.3 \text{ g/mol}) = 32.03 \text{ g HfCl}_4$$

HCl (using a 5.625 *M* HCl stock solution)

for 1.25 *M* HCl stock solution,

$$[(1.25 \text{ mmol/mL})(100 \text{ mL})]/(5.625 \text{ mmol/mL}) = 22.2 \text{ mL was needed}$$

for 1.00 *M* HCl stock solution, 17.8 mL HCl was needed

for 0.75 *M* HCl stock solution, 13.3 mL HCl was needed

Amounts used:

	<u>HfCl₄</u>	<u>HCl</u>	<u>Total vol.</u>
Stock Solution #1	32.42 g	22.2 mL	103.55 mL
Stock Solution #2	32.43 g	17.8 mL	104.53 mL
Stock Solution #3	32.50 g	13.3 mL	100.45 mL

Concentrations of HfCl₄ and HCl used in stock solutions:

	<u>[HfCl₄]</u>	<u>[HCl]</u>
Stock solution #1	0.977 <i>M</i>	1.206 <i>M</i>
Stock solution #2	0.969 <i>M</i>	0.958 <i>M</i>
Stock solution #3	1.010 <i>M</i>	0.745 <i>M</i>

APPENDIX D
HEATING SCHEDULE USED TO HEAT, CALCINE, AND SINTER
HYDROUS HAFNIUM OXIDE GEL SPHERES

PROCEDURE

- Air-dried hydrous hafnium oxide gel spheres in stainless steel pans and at ambient temperature for ~48 h. The maximum number of layers of gel spheres was 3.
- Sieved the air-dried microspheres using 8-in.-diam stainless steel sieves.
- Placed desired fraction of microspheres in an alumina or platinum boat and heated at 80°C in a flowing steam and O₂ (30 mL/min) atmosphere for 2 h.^{*}
- Heated at 190°C in a flowing steam and O₂ (30 mL/min) atmosphere for 3 h.^{*}
- Heated at 400°C in flowing O₂ (30 mL/min) atmosphere for 2 h.^{*}
- Heated at 1046°C in flowing O₂ (30 mL/min) atmosphere for 4 h.^{**}
- Turn furnace off and let cool to ambient temperature.
- Remove boat from furnace, weigh, and sieve microsphere to determine size range.
- Measure the slow-pour density and crush strength.[†]

^{*}*The heat-up ramp was 60 °C/h.*

^{**}*The heat-up ramp was 180 °C/h.*

[†]*The methodologies are described in detail in Ref. 7.*

APPENDIX E

WASHING AND SINTERING PROCEDURE DEVELOPED TO PRODUCE HYDROUS HAFNIUM OXIDE MICROSPHERES WITH HIGH CRUSH STRENGTH

PROCEDURE (Developed by F. C. Montgomery of the Materials Science and Technology Division)

- Wash gel spheres with deionized water until the pH of the wash solution is <5.
- Washed gel spheres with five separate portions of Dowanol PM glycol ether* for ~30 min/wash. Make sure enough volume is used to cover all the gel spheres.
- To sinter, follow the procedure in Appendix D; however, sinter the microspheres at 1350°C for 5 h rather than at 1050°C for 4 h.
- The sintered HfO₂-Y₂O₃ did not develop cracks and had a crush strength >1200 g. The gel spheres prepared in Example 3 were used in this work (see page 14).

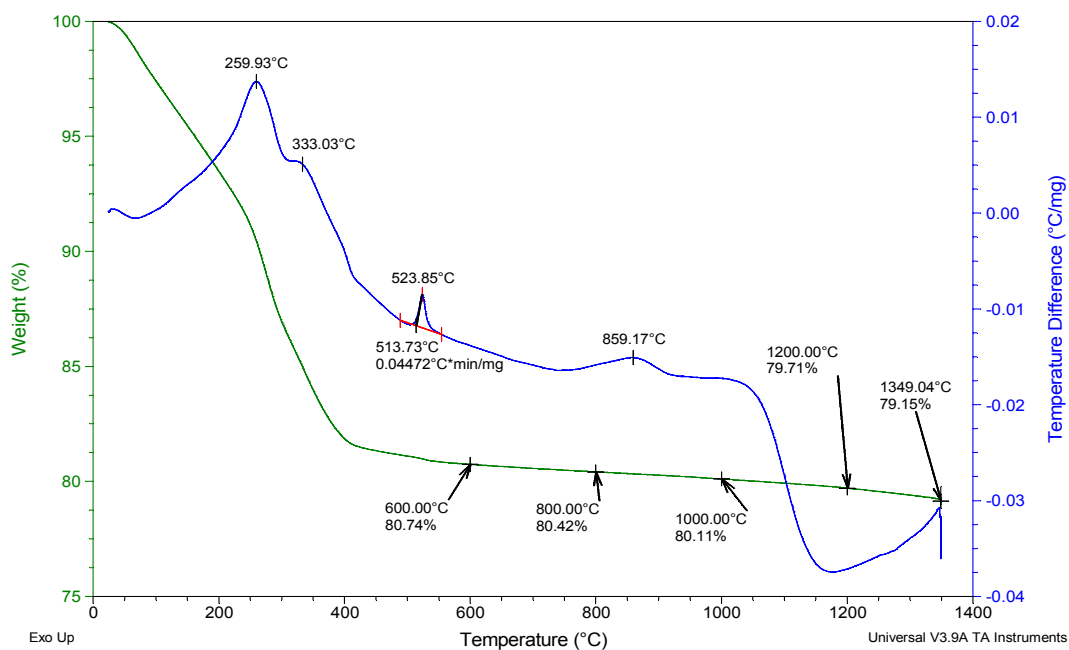
*Dowanol PM glycol ether
1-methoxy-2-propanol (99.5%)
CH3OCH2CH(OH)CH3

Mol. wt. = 90.12 g/mol
Density = 0.962 g/mL
Boiling point = 118°C

Made by ENTAONE-OMI, Inc.
P.O. Box 1900
New Haven, CT 06508

The following figure is a differential scanning calorimetry (DSC)/DTA analytical plot for a 29.8890-mg sample of the HHfO-HYO gel spheres from Example 3 washed with Dowanol PM glycol ether which was provided by F. C. Montgomery. The gel spheres were dried at 60°C and then heated in the DSC/DTA furnace at a rate of 60°C/h to 1350°C.

File: C:\TA\Data\SDT\FMData.041
Operator: montgomery
Run Date: 10-Apr-04 05:38
Instrument: SDT Q600 V6.1 Build 72



APPENDIX F

PROCEDURE FOR CONVERTING HYDROUS HAFNIUM OXIDE GEL SPHERES TO HAFNIUM MONOHYDROGEN PHOSPHATE SPHERES

PROCEDURE (Developed with the help of a former University of Tennessee at Chattanooga co-op student, S. G. Simmerman)

- Put washed hydrous hafnium oxide gel spheres in a glass fleaker and cover and soak for about 10 min in 0.5 M H_3PO_4 . This step converts the surface to hafnium monohydrogen phosphate and prevents dissolution of the spheres. The monohydrogen phosphate is insoluble in strong acid.
- Pour off solution and then cover spheres again with fresh 0.5 M H_3PO_4 and let them soak for ~24 h at ambient temperature. This step adds depth to the monohydrogen phosphate layer.
- Pour off the liquid and cover the spheres with 6.0 M H_3PO_4 .
- Place fleaker in stainless steel pressure vessel and add deionized water to the vessel but outside the fleaker.
- Seal the vessel and place in an oven and heat to 125°C and hold at that temperature for 3 h. The vessel employed in this work had a stainless steel thermowell, and all temperatures were based on a thermocouple in the thermowell.
- Remove vessel and place in an ice bath to quickly cool vessel.
- Once the temperature drops to 25°C, carefully open vessel and remove fleaker.
- Pour off liquid and then wash the spheres with deionized water until the pH is >3.
- The spheres should be white crystalline and can be air dried for use as sorbents.

Note. In separate conversions using the same procedure, it was found that hafnium monohydrogen phosphate spheres prepared with 5 M H_3PO_4 were amorphous or glassy in appearance. Ones converted with 5.25 M H_3PO_4 , 5.50 M H_3PO_4 , and 5.75 M H_3PO_4 were about 90, 95, and 99% converted to the white crystalline form, respectively, the remainder being glassy. None of the spheres, including the 6.0 M H_3PO_4 treated spheres, degraded when soaked in 8 M HNO_3 for 24 h. It was also found that a H_3PO_4 concentration of 6.25 M or greater could not be used because the spheres became too crystalline and were not strong enough to use in ion exchange columns.

