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September 2005

J. L. Collins

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Nuclear Science and Technology Division

EXPERIMENTAL METHODOLOGY FOR DETERMINING OPTIMUM PROCESS PARAMETERS FOR PRODUCTION OF HYDROUS METAL OXIDES BY INTERNAL GELATION

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1. OBJECTIVE

The objective of this report is to describe a simple but very useful experimental methodology that was used to determine optimum process parameters for preparing several hydrous metal-oxide gel spheres by the internal gelation process. The method is inexpensive and very effective in collection of key gel-forming data that are needed to prepare the hydrous metal-oxide microspheres of the best quality for a number of elements.

2. INTRODUCTION

The internal gelation process is one of the sol-gel processes developed for the preparation of microspheres of hydrous metal oxides in which chilled clear broth droplets containing the salt of the metal, hexamethylenetetramine (HMTA), and urea are heated, causing homogenous gelation and solidification of the droplets.[1-11] After washing treatments, the gel spheres can be either air dried for use as ion-exchange materials or, depending upon the metal, can be dried, calcined, and sintered to ceramic spheres for use as nuclear fuel, catalyst, dielectrics, or getters. A simple but effective experimental methodology was developed to determine the optimum process parameters for preparing a number of hydrous metal oxides using the internal gelation process. The methodology was designed to duplicate as closely as possible the typical procedures used in actual gel-sphere formation preparations.[5-9] Optimum process parameters were determined for hydrous metal oxides of Ti, Zr, Hf, Fe, Al, and Ce. The key factor in determining whether a hydrous metal oxide can be prepared is the pH at which a particular metal nitrate or chloride precipitates in an aqueous solution. Because of the buffering behavior of the HMTA, the pH of precipitation of each metal must be <7. For the above-mentioned elements, the pH of precipitation is in the range of 2 to 5. Plutonium, U, Th, Np, Am, and Cm also precipitate in this pH range; thus, their hydrous oxides can also be prepared by the internal gelation process.

The methodology that was used to determine the optimum process parameters for preparing hydrous zirconium oxide microspheres will be used as an example of the test tube methodology.[7] The major constituents of a broth for making microspheres of hydrous zirconium oxide are HMTA, urea, and a zirconium salt (in this example, either zirconyl nitrate ($ZrO(NO_3)_2 \bullet xH_2O$) or zirconyl chloride ($ZrO(Cl)_2 \bullet xH_2O$). Before describing the

methodology, it is important that the basic chemical reactions of the internal gelation process are understood.[5, 6]

Complexation/decomplexation:

$$2CO(NH_2)_2 + Zr^{4+} \leftrightarrow Zr[CO(NH_2)_2]_2^{4+} \quad (1)$$

Hydrolysis:

$$Zr^{4+} + xH_2O \leftrightarrow Zr(OH)_4 \bullet yH_2O9 + 4H^+$$

and

$$ZrO^{2+} + xH_2O \leftrightarrow ZrO(OH)_2 \bullet yH_2O9 + 2H^+ \quad (2)$$

HMTA protonation:

$$(CH_2)_6N_4 + H^+ \leftrightarrow (CH_2)_6N_4 \bullet H^+ \quad (3)$$

HMTA decomposition:

$$(CH_2)_6N_4 \bullet H^+ + 3H^+ + 6H_2O \leftrightarrow 4NH_4^+ + 6CH_2O \quad (4)$$

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 0EC. A stable broth is one that remains clear and does not gel or precipitate for reasonable periods of time (≥1 h). 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 zirconium 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 (≥95%) are protonated, they begin to decompose (reaction 4) into ammonia molecules, which make the system even more basic. Each protonated HMTA molecule can effectively remove three additional hydrogen ions. The reaction products are formaldehyde and ammonium nitrate or ammonium chloride. In addition to the role of urea as a complexing agent, it also functions as a catalytic agent, which accelerates the decomposition of the protonated HMTA molecules.[5, 6]

A number of process variables must be determined in order to effectively use the internal gelation process to make hydrous metal-oxide microspheres with desired properties. Such variables include optimum broth formulations and gel-forming temperatures that yield

structurally strong gel spheres. One of the most important factors in the formation of the gel spheres is the time needed for broth droplets to gel once they are introduced into the hot immiscible organic medium in the forming column. Ideally gelation should begin in ≤10 s. The following sections cover all the aspects required to make hydrous zirconium oxide microspheres.

3. PREPARATIONS OF STOCK SOLUTIONS USED FOR MAKING BROTHS

Before conducting any gel-forming experiments, solutions of 3.2 *M* HMTA and 3.2 *M* urea with a density of 1.14 g/mL and various concentrations of zirconyl nitrate were prepared. Generally, the rule of thumb was to make the solutions as concentrated as possible without being supersaturated.

3.1 Preparation of Zirconium Stock Solution

To prepare a stock solution, a soluble salt of zirconium had to be selected to begin the study. Two salts, zirconyl nitrate [$ZrO(NO_3)_2$] and zirconyl chloride [$ZrO(Cl)_2$], were chosen and purchased from Aldrich Chemical Company, Inc. Of the two, the nitrate salt was considered more nearly ideal. Generally, chloride salts are not chosen, because of the corrosive nature of the chloride. Zirconyl nitrate solutions were used in most of the tests. The molecular weight of $ZrO(NO_3)_2$ is 231.23 g/mol. To prepare a stock solution, the contents of a bottle containing 500 g of zirconyl nitrate were placed in a 3-L glass beaker, and a sufficient quantity of deionized water was added with good mixing to suspend the solids in the solution. Samples of the solution were analyzed by inductively coupled plasma (ICP) mass spectroscopy and gravimetric analyses. Figure 1 shows there is a linear correlation of solution density as a function of zirconium concentration that can be expressed by the following equation, where Zr is measured in grams per milliliter.

$$\text{Density} = 1.96 \times 10^{-3}(\text{Zr}) + 1.00476 \qquad (5)$$

The most-concentrated stock solution that was prepared had a density of 1.20 g/mL and a concentration of 1.09 *M* Zr (99.6 g Zr/L). A less-concentrated stock solution (labeled Zr-8) was used to conduct the gel-forming experiments that were needed to determine the

optimum process parameters for making hydrous zirconium oxide gel spheres. This solution had a density of 1.17 g/mL and a concentration of 0.925 *M* (84.4 g Zr/L).

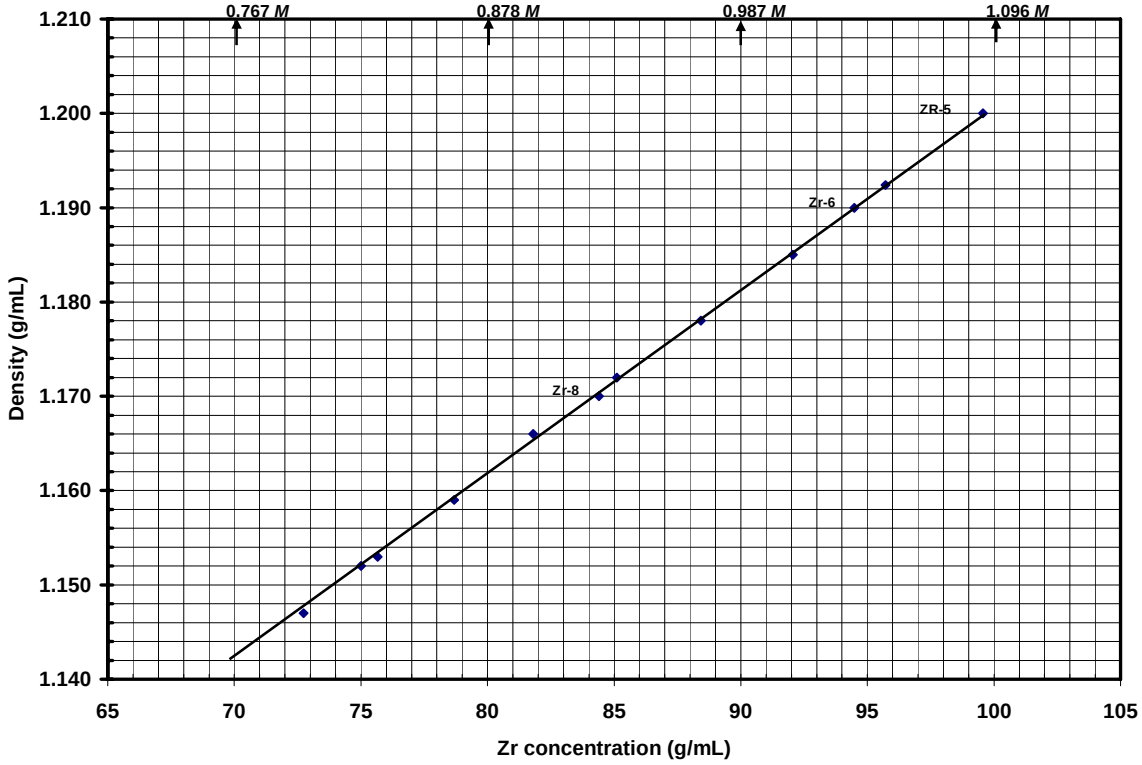

Fig. 1. Density of zirconyl nitrate solution as a function of zirconium concentration.

3.2 Preparation and Acidification of Stock Solution

Scouting tests quickly determined that stable broths could not be prepared using acid-deficient (partially hydrolyzed) or stoichiometric zirconyl nitrate stock solutions. Thus, the goal of the optimization study was to determine the required acidification for these solutions.

Three acidified stock solutions were prepared in which each contained 10 mL of Zr-8 stock solution. Reagent-grade 15.8 *M* HNO_3 was used for acidification. The following stock solutions were prepared:

- **Zr-8 (2.0 *M* HNO_3) stock solution** was prepared by mixing 1.449 mL of 15.8 *M* HNO_3 with 10 mL (11.702 g) of the Zr-8 stock solution. The zirconium concentration was 0.81 *M*.

- **Zr-8 (1.5 *M* HNO_3) stock solution** was prepared by mixing 1.049 mL of 15.8 *M* HNO_3 with 10 mL (11.702 g) of the Zr-8 stock solution. The zirconium concentration was 0.84 *M*.

- **Zr-8 (1.0 *M* HNO_3) stock solution** was prepared by mixing 0.673 mL of 15.8 *M* HNO_3 with 10 mL (11.702 g) of the Zr-8 stock solution. The zirconium concentration was 0.87 *M*.

3.3 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*. The maximum solubility of HMTA in a solution containing 3.2 *M* urea was only about 3.2 *M*. In this work, only 3.2 *M* HMTA plus 3.2 *M* urea solutions were used, which had a density of 1.14 g/mL. An important discovery was that a good technical grade of *crystalline* HMTA needs to 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 (NH_2CONH_2) and 892.22 g HMTA ($C_6H_{12}N_4$) to a clean 3-L beaker and dissolving with chilled (5 ± 5°C) deionized water. The volume was brought up to about 2 L via slowly adding the DI water and mixing. Once the solids were in solution, the solution 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.

4. BROTH STABILITY TESTS

A stable broth is one that remains clear and does not gel or precipitate for reasonable periods of time at ~0°C (usually about 1 h). Broths were prepared using the Zr-8 (2 *M* HNO_3), Zr-8 (1.5 *M* HNO_3), and Zr-8 (1.0 *M* HNO_3) stock solutions described in Sect. 3.2, and each was given a simple broth stability test. Calculated amounts of chilled HMTA/urea, stock solution, and water were mixed together to produce each broth. The stability test procedure was as follows.

1. A rack for holding thin-walled glass centrifuge tubes was placed in an ice bath. Predetermined volumes of 3.2 *M* HMTA/3.2 *M* urea and acidified stock solutions were separately and carefully pipetted into these tubes via calibrated electronic pipettes, and the tubes were subsequently chilled for ~20 min. The centrifuge tubes containing the acidified

zirconium 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 (1.2, 1.1, 1.0, 0.9, 0.8, 0.7, or 0.6).

2. When needed, a calibrated electronic pipette was used to add calculated amounts of deionized water to the centrifuge tubes containing the acidified zirconium 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 zirconium stock solutions. Because of the small volumes involved, it was important that the transfer was quantitative. The broth was then mixed well with a Teflon stirring rod. The time of mixing was recorded, and the broth was observed until there was the first visual sign of gelation, or for 1 h. The time of gelation was recorded. Tests were performed in duplicate. About 5 min after mixing, if gelation had not occurred, the pH of the broth for one of the samples was measured with a calibrated temperature-compensated ROSS™ electrode.

None of the Zr-8 broths (2, 1.5, or 1 *M* HNO_3) with the $HMTA/H^+$ mole ratios tested (1.2, 1.1, 1.0, 0.9, 0.8, 0.7, or 0.6) gelled in less than 1 h. All were considered stable.

5. GEL TESTS IN GLASS CENTRIFUGE TUBES

5.1 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;
- hotplate 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-µL range) or a calibrated Rainin EDP-Plus electronic pipette with interchangeable liquid ends that cover the 100- to 1000-µL and 250- to 2500-µL ranges, plus the concomitant disposable tips;

- ROSS™ Sure-Flow combination pH electrode, which provides temperature compensation for temperatures in the 0 to 100°C range;
- in-date standard pH 7 and pH 4 buffer solutions;
- 12-mL glass centrifuge tubes; and
- 8-in.-long Teflon-coated microspatulas.

The techniques used to ensure good quality are described in Appendix A.

5.2 Testing Procedure

The gel test procedure was as follows.

1. A portion of the zirconium feed 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 zirconium 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 sets. 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.

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. Afterward, 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.

As 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.

6. TESTING RESULTS

Appendix B contains tabulated results for the different broths that were tested at 70, 80, and 90°C. Gel time as a function of HMTA/H^+ mole ratio is given in Figs. 2–5. Broths with gel times of 10 s or less are clearly shown. These data allow sound decisions to be made regarding the broth concentrations and forming temperature that are needed to prepare hydrous zirconium oxide microspheres. The gel times shown in Figs. 2–5 are corrected values (i.e., the actual gel time in a forming column at the designated temperature). The test tube gel times were about twice those observed for broth droplets gelling in a forming column at the same temperature. Runs were made with several broth formulations to obtain the gel-time conversion factor.

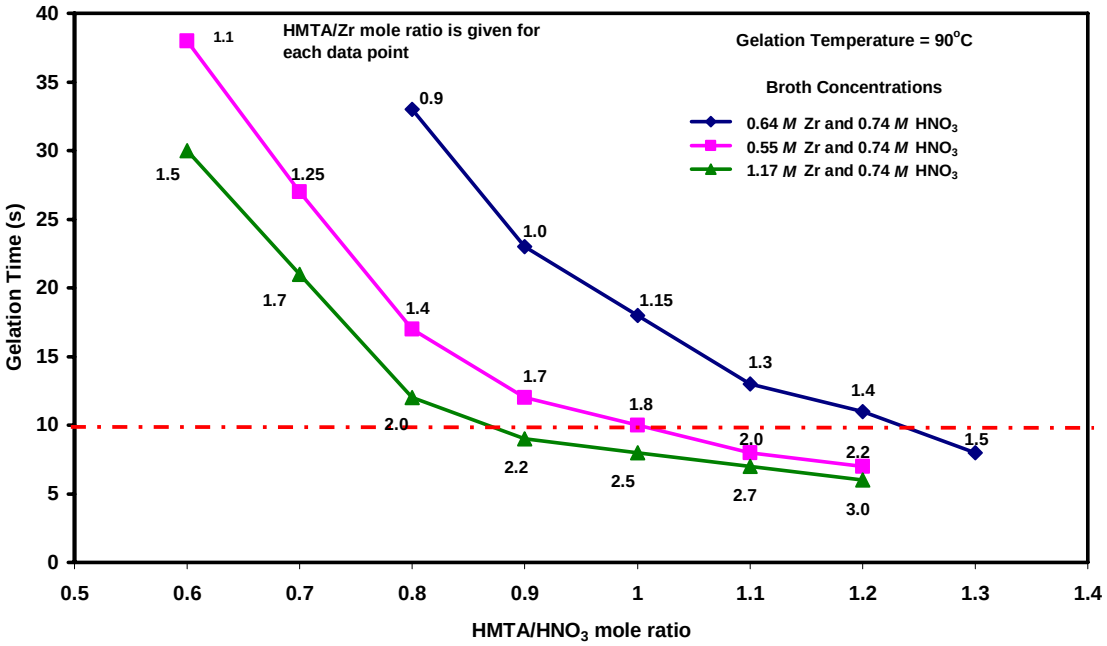

Fig. 2. Gel time as a function of broth formulation at 90°C.

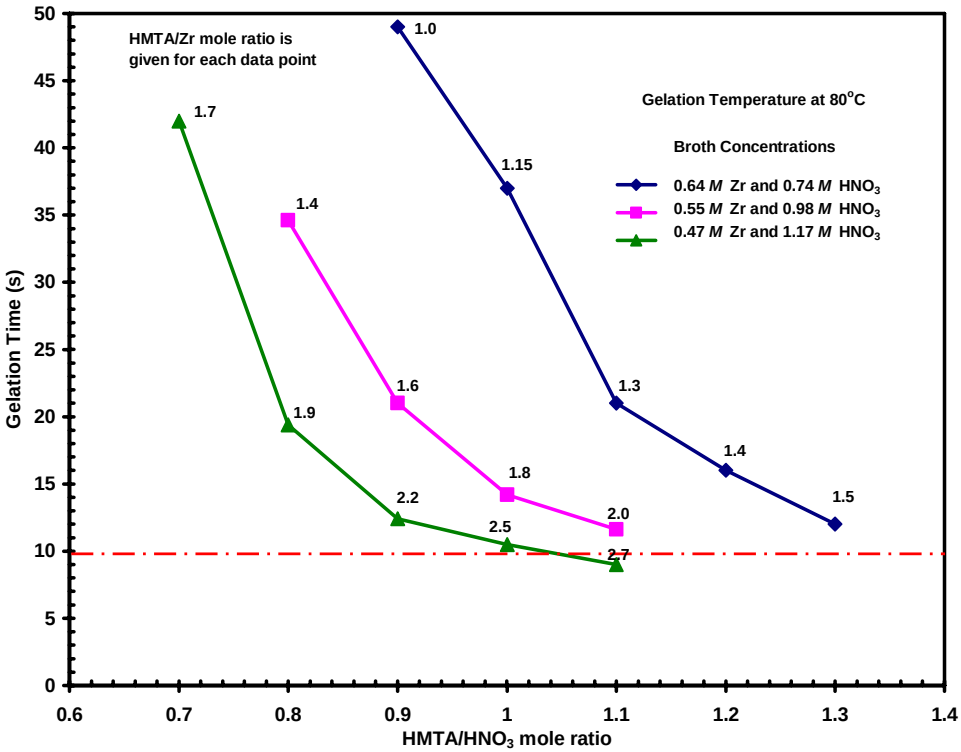

Fig. 3. Gel time as a function of broth formulation at 80°C.

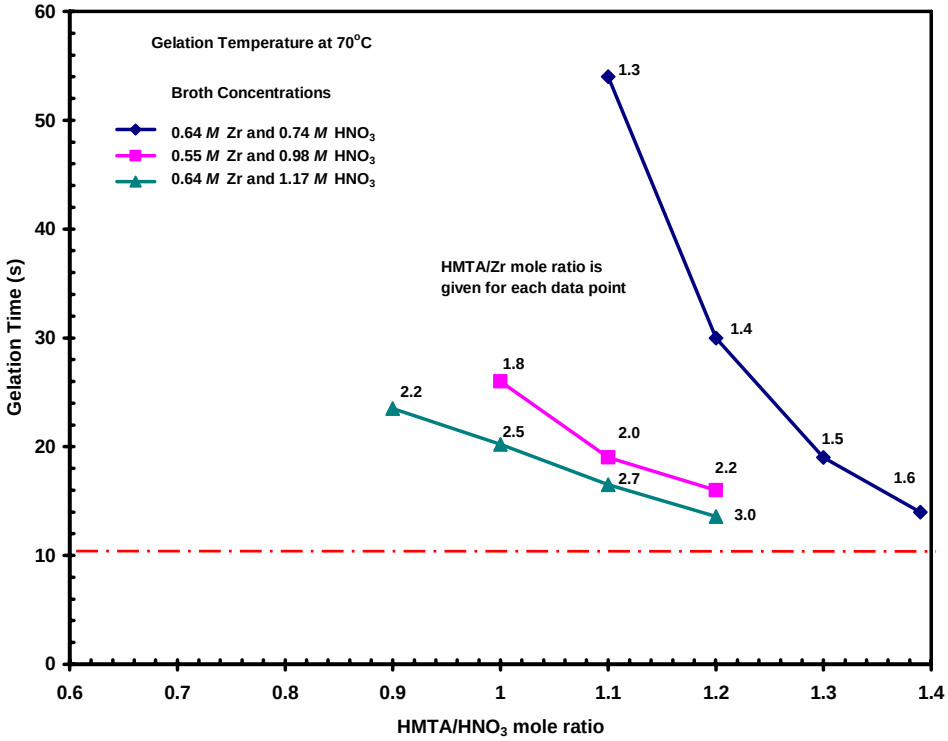

Fig. 4. Gel time as a function of broth formulation at 70°C.

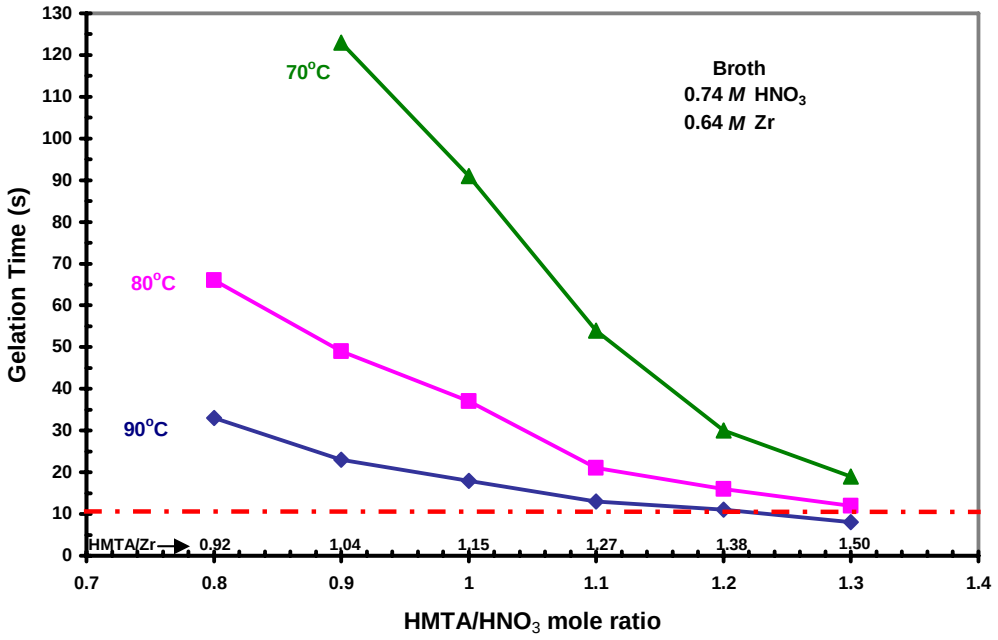

Fig. 5. Gel time as a function of broth formulation and temperature.

The results shown in Figs. 3 and 4 indicate that hydrous zirconium oxide gel spheres can be prepared with certain broth formulations in which the acidity of the broth is varied from 0.74 to 1.17 *M*. Generally, lower acidity is better while still maintaining broth stability. Figure 5 compares the gel times for broth concentrations of 0.74 *M* HNO_3 and 0.64 *M* Zr at various forming temperatures and HMTA/HNO_3 mole ratios. To obtain a gel time of ≤10 s, the HMTA/HNO_3 mole ratio needs to be ≥1.2 for a forming temperature of 90°C. At 80 and 70°C, it should be about ≥1.3. To increase the concentration of zirconium in the broth, a broth could be prepared with a HNO_3 concentration of 0.5 *M*, but an HMTA/HNO_3 mole ratio of 1.5 to 1.6 would be needed. Broth stability becomes a problem if the acidity is decreased too much. All of the formulations give amorphous gel spheres, so the best broth is one with the least amount of HMTA, urea, and acid that gels in ≤10 s.

7. BROTH DILUTION EXPERIMENTS

The effects of dilution of the stock solutions with water on the gel times and characteristics of the hydrous zirconium oxide were also studied. Broth formulations that had gel times of approximately 20 s (when not diluted) were used because these

formulations were the easiest to time; the gelation reaction was neither too fast nor too slow (gradual) to be distinctive. Volume dilutions of 20, 40, and 60% using deionized water were tested. The formulations chosen were Zr-8 (2 *M* HNO_3) with HMTA/H^+ mole ratio of 0.72 at 90°C, Zr-8 (1.5 *M* HNO_3) with HMTA/H^+ mole ratio of 0.82 at 90°C, and Zr-8 (1.0 *M* HNO_3) with HMTA/H^+ mole ratio of 0.93 at 90°C. Tables 1, 2, and 3 show the makeup of the diluted broths that were prepared and tested. In general, all three feeds were affected about the same by the water dilution (see Tables 4–6), showing the same general pattern with regard to gel time and rigidity changes. The gel times were increased by as much as 3 to 8 s with (in each case) the largest increase in gel time caused by the largest dilution (60%).

Table 1. Dilutions prepared with a Zr-8 (2 *M*) broth formulation with HMTA/H^+ and HMTA/Zr mole ratios of 0.72 and 1.78, respectively

Volume of undiluted broth				Added	Total		
Zr-8 (2 *M*) (mL)	H_2O (mL)	HMTA/urea (mL)	Dilution (%)	H_2O (mL)	volume (mL)	H^+ (*M*)	Zr (*M*)
0.200	0.052	0.090	0	0	0.342	1.170	0.474
0.200	0.052	0.090	20	0.068	0.410	0.976	0.395
0.200	0.052	0.090	40	0.137	0.479	0.838	0.338
0.200	0.052	0.090	60	0.205	0.547	0.731	0.296

Table 2. Dilutions prepared with a Zr-8 (1.5 *M*) broth formulation with HMTA/H^+ and HMTA/Zr mole ratios of 0.82 and 1.47, respectively

Volume of undiluted broth				Added	Total		
Zr-8 (1.5 *M*) (mL)	H_2O (mL)	HMTA/urea (mL)	Dilution (%)	H_2O (mL)	volume (mL)	H^+ (*M*)	Zr (*M*)
0.200	0.029	0.077	0	0	0.306	0.980	0.548
0.200	0.029	0.077	20	0.061	0.367	0.817	0.457
0.200	0.029	0.077	40	0.122	0.428	0.701	0.392
0.200	0.029	0.077	60	0.184	0.490	0.612	0.342

Table 3. Dilutions prepared with a Zr-8 (1.0 *M*) broth formulation with HMTA/H^+ and HMTA/Zr mole ratios of 0.928 and 1.067, respectively

Volume of undiluted broth				Added	Total		
Zr-8 (1 *M*) (mL)	H_2O (mL)	HMTA/urea (mL)	Dilution (%)	H_2O (mL)	volume (mL)	H^+ (*M*)	Zr (*M*)
0.200	0.013	0.058	0	0	0.271	0.738	0.642
0.200	0.013	0.058	20	0.054	0.325	0.615	0.535
0.200	0.013	0.058	40	0.108	0.379	0.528	0.459
0.200	0.013	0.058	60	0.163	0.424	0.473	0.411

Table 4. Effects of dilution on a broth with the following characteristics at 90°C: HMTA/H^+ mole ratio = 0.72; HMTA/Zr mole ratio = 1.78; [Zr] = 0.47 *M*; [H^+] = 1.17 *M*; [HMTA or urea] = 0.84 *M*

Dilution (%)	Gelation start time (s)	Color	Rigidity	Gel condition
0	21	10	8	Moist
20	21	10	7	Wet
40	22	10	4	Wet
60	24	10	2	Very wet

Table 5. Effects of dilution on a broth with the following characteristics at 90°C: HMTA/H^+ mole ratio = 0.82; HMTA/Zr mole ratio = 1.47; [Zr] = 0.55 *M*; [H^+] = 0.98 *M*; [HMTA or urea] = 0.805 *M*

Dilution (%)	Gelation start time (s)	Color	Rigidity	Gel condition
0	17	10	9	Dry
20	20	10	7	Damp
40	21	10	4	Wet
60	24	10	1	Very wet

Table 6. Effects of dilution on a broth with the following characteristics at 90°C: HMTA/H^+ mole ratio = 0.93; HMTA/Zr mole ratio = 1.07; [Zr] = 0.64 *M*; [H^+] = 0.74 *M*; [HMTA or urea] = 0.69 *M*

Dilution (%)	Gelation start time (s)	Color	Rigidity	Gel condition
0	22	10	9	Slightly moist
20	23	9	7	Moist
40	27	9	4	Wet
60	30	9	1	Very wet

Color/transparency remained fairly unaffected. [This was observed for the Zr-8 (2.0 *M*) with HMTA/H^+ = 1.0 and Zr-8 (1.5 *M*), HMTA/H^+ = 1.1, broths that were heated at 70°C.] The greatest change caused by dilution was observed in the rigidity of the gels that formed. At 20% dilution, the rigidity was only slightly decreased. At 40% dilution, the rigidity was decreased by more than half; and at 60% dilution, the rigidity was about 1–2 on a scale of 1 to 10 (1 being the softest). This was observed in each formulation and at all temperatures. In addition, dilute broths also exhibit larger shrink factors. The ability to formulate workable broths to control shrinkage and yield smaller dried microspheres has a variety of practical uses in the production of fuels, sorbents, catalysts, and other products.

8. ACKNOWLEDGMENTS

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APPENDIX A

QUALITY ASSURANCE TECHNIQUES USED IN TESTING

For quality assurance purposes, the equipment used during the experiments was calibrated according to established laboratory guidelines and procedures for accuracy. Temperature measurements were to be within ±1^{o}C; pH measurements, within ±0.02 units; mass, within ±0.001 g (depending on the balance used); and volume, within ±0.001 mL. These calibrations were designated to be carried out at specified time intervals to ensure accuracy.

The pH meter and electrode were calibrated using in-date buffer solutions of pH 4 and pH 7.02 (since the gels we will be testing will be within this range). The "% slope" dial was set at 100%, and the calibration knob was adjusted to 7.02 when the electrode was placed in the 7.02 buffer solution. The electrode was then rinsed in ultrapure deionized distilled water and placed in the pH 4 buffer solution. The "% slope" dial was adjusted until the meter read pH 4. It must be noted that this "adjustment" was to the limits of the meter's capabilities for accuracy. The electrode was again rinsed and placed in the pH 7.02 solution and then in the pH 4 solution to ensure reproducibility. The pH meter was calibrated with every use.

Calibration of the electronic pipette was done by tarring a beaker and then delivering a set volume of distilled water into the beaker and weighing. This procedure was performed ten times for each selected setting, and an average was then calculated. The pipettes were always calibrated before testing.

APPENDIX B

TABULATION OF RESULTS FOR BROTHS TESTED

Zr-8(2.0M HNO3):

HMTA/H	Broth Formulations				Conc. Of Species in Broth				Stable		Gel Test Results for Zr-8(2.0M HNO3)					
	mL H20	mL Zr-8	mL HMTA	Total mL	[HMTA]	[H]	[Zr]	Zr g/L	HMTA/Zr	Broth	pH (broth)	Temp	Gel time(s)	color	rigidity	Sticky?	pH(gel)
1.2	none	0.20	0.154	0.354	1.35	1.13	0.46	41.7	2.96	Y		90	not run				
1.1	none	0.20	0.071	0.342	1.29	1.17	0.47	43.2	2.73	Y	1.28	90	7	8	7	little	5.00
1.0	0.013	0.20	0.064	0.342	1.17	1.17	0.47	43.2	2.47	Y	1.16	90	8	9	7	little	4.66
0.9	0.026	0.20	0.058	0.342	1.05	1.17	0.47	43.2	2.22	Y	1.08	90	9	9	8	little	4.17
0.8	0.039	0.20	0.051	0.342	0.94	1.17	0.47	43.2	1.98	Y	0.93	90	12	10	9	dry	3.80
0.7	0.052	0.20	0.090	0.342	0.67	1.17	0.47	43.2	1.41			90	21	10	8	wet	2.39
0.6	0.065	0.20	0.077	0.342	0.59	1.17	0.47	43.2	1.25			90	30	10	8	moist	1.68
1.2	none	0.20	0.154	0.354	1.35	1.13	0.46	41.7	2.96	Y		80	not run				
1.1	none	0.20	0.071	0.342	1.29	1.17	0.47	43.2	2.73	Y	1.28	80	9	8	5	damp	5.19
1.0	0.013	0.20	0.064	0.342	1.17	1.17	0.47	43.2	2.47	Y	1.16	80	11	8	3	wet	4.93
0.9	0.026	0.20	0.058	0.342	1.05	1.17	0.47	43.2	2.22	Y	1.08	80	12	9	7	little	4.29
0.8	0.039	0.20	0.051	0.342	0.94	1.17	0.47	43.2	1.98	Y	0.93	80	19	10	7	little	3.50
0.7	0.052	0.20	0.090	0.342	0.67	1.17	0.47	43.2	1.41			80	58	10	7	wet	1.94
0.6	0.065	0.20	0.077	0.342	0.59	1.17	0.47	43.2	1.25			80	84	10	4	real wet	1.54
1.2	none	0.20	0.154	0.354	1.35	1.13	0.46	41.7	2.96	Y		70	14	6	4	wet	5.16
1.1	none	0.20	0.071	0.342	1.29	1.17	0.47	43.2	2.73	Y	1.28	70	17	5	3	wet	4.93
1.0	0.013	0.20	0.064	0.342	1.17	1.17	0.47	43.2	2.47	Y	1.16	70	20	5	4	wet	4.58
0.9	0.026	0.20	0.058	0.342	1.05	1.17	0.47	43.2	2.22	Y	1.08	70	24	6	3	wet	4.26
0.8	0.039	0.20	0.051	0.342	0.94	1.17	0.47	43.2	1.98	Y	0.93	70	43	8	6	damp	3.34
0.7	0.052	0.20	0.090	0.342	0.67	1.17	0.47	43.2	1.41			70	108	10	8	moist	3.77
0.6	0.065	0.20	0.077	0.342	0.59	1.17	0.47	43.2	1.25			70	141	10	7	wet	2.33
1.2	none	0.20	0.154	0.354	1.35	1.13	0.46	41.7	2.96	Y		60	22	6	3	moist	5.81
1.1	none	0.20	0.071	0.342	1.29	1.17	0.47	43.2	2.73	Y	1.28	60	27	5	6	damp	5.10
1.0	0.013	0.20	0.064	0.342	1.17	1.17	0.47	43.2	2.47	Y	1.16	60	36	5	6	wet	4.36
0.9	0.026	0.20	0.058	0.342	1.05	1.17	0.47	43.2	2.22	Y	1.08	60	54	5	5	damp	3.80
0.8	0.039	0.20	0.051	0.342	0.94	1.17	0.47	43.2	1.98	Y	0.93	60	120	6	5	wet	3.14
0.7	0.052	0.20	0.090	0.342	0.67	1.17	0.47	43.2	1.41			not run					
0.6	0.065	0.20	0.077	0.342	0.59	1.17	0.47	43.2	1.25			not run					

Zr-8(1.5M HNO3):

	Broth Formulations				Conc. of Species in Broth					Stable		Gel Test Results	for Zr-8(1.5M HNO3)				
HMTA/H	mL H20	mL Zr-8	mL HMTA	Total mL	[HMTA]	[H]	[Zr]	Zr g/L	HMTA/Zr	Broth	pH (broth)	Temp	Gel time(s)	color	rigidity	Sticky?	pH(gel)
1.2	none	0.20	0.116	0.316	1.14	0.95	0.51	46.7	2.23	Y		90	not run				
1.1	none	0.20	0.106	0.306	1.08	0.98	0.55	49.9	1.96	Y	0.88	90	8	7	8	little	4.98
1.0	0.009	0.20	0.097	0.306	0.99	0.98	0.55	49.9	1.79	Y	0.80	90	11	7	7	damp	4.55
0.9	0.019	0.20	0.087	0.306	0.88	0.98	0.55	49.9	1.62	Y	0.68	90	12	9	8	little	3.76
0.8	0.029	0.20	0.077	0.306	0.78	0.98	0.55	49.9	1.43	Y	0.58	90	17	10	9	dry	2.96
0.7	0.038	0.20	0.068	0.306	0.69	0.98	0.55	49.9	1.26			90	27	10	7	moist	1.88
0.6	0.048	0.20	0.058	0.306	0.59	0.98	0.55	49.9	1.07			90	38	10	5	wet	1.48
1.2	none	0.20	0.116	0.316	1.14	0.95	0.51	46.7	2.23	Y		80	not run				
1.1	none	0.20	0.106	0.306	1.08	0.98	0.55	49.9	1.96	Y	0.88	80	12	8	9	little	4.92
1.0	0.009	0.20	0.097	0.306	0.99	0.98	0.55	49.9	1.79	Y	0.80	80	14	8	9	little	3.99
0.9	0.019	0.20	0.087	0.306	0.88	0.98	0.55	49.9	1.62	Y	0.68	80	21	8	9	little	3.42
0.8	0.029	0.20	0.077	0.306	0.78	0.98	0.55	49.9	1.43	Y	0.58	80	35	9	9	little	3.22
0.7	0.038	0.20	0.068	0.306	0.69	0.98	0.55	49.9	1.26			80	58	10	7	wet	1.94
0.6	0.048	0.20	0.058	0.306	0.59	0.98	0.55	49.9	1.07			80	84	10	4	real wet	1.54
1.2	none	0.20	0.116	0.316	1.14	0.95	0.51	46.7	2.23	Y		70	16	6	4	wet	5.91
1.1	none	0.20	0.106	0.306	1.08	0.98	0.55	49.9	1.96	Y	0.88	70	19	5	5	damp	4.76
1.0	0.009	0.20	0.097	0.306	0.99	0.98	0.55	49.9	1.79	Y	0.80	70	26	5	4	damp	4.37
0.9	0.019	0.20	0.087	0.306	0.88	0.98	0.55	49.9	1.62	Y	0.68	70	44	5	6	damp	3.44
0.8	0.029	0.20	0.077	0.306	0.78	0.98	0.55	49.9	1.43	Y	0.58	70	94	9	8	damp	2.61
0.7	0.038	0.20	0.068	0.306	0.69	0.98	0.55	49.9	1.26			70	not run				
0.6	0.048	0.20	0.058	0.306	0.59	0.98	0.55	49.9	1.07			70	not run				
1.2	none	0.20	0.116	0.316	1.14	0.95	0.51	46.7	2.23	Y		60	74	5	7	damp	4.91
1.1	none	0.20	0.106	0.306	1.08	0.98	0.55	49.9	1.96	Y	0.88	60	34	5	5	wet	4.68
1.0	0.009	0.20	0.097	0.306	0.99	0.98	0.55	49.9	1.79	Y	0.80	60	56	5	6	wet	3.97
0.9	0.019	0.20	0.087	0.306	0.88	0.98	0.55	49.9	1.62	Y	0.68	60	125	5	6	wet	3.21
0.8	0.029	0.20	0.077	0.306	0.78	0.98	0.55	49.9	1.43	Y	0.58	60	262	9	5	wet	2.60
0.7	0.038	0.20	0.068	0.306	0.69	0.98	0.55	49.9	1.26			60	not run				
0.6	0.048	0.20	0.058	0.306	0.59	0.98	0.55	49.9	1.07			60	not run				

Zr-8(1.0M HNO3):

	Broth Formulations				Conc. of Species in Broth					Stable		Gel Test Results for Zr-8(1.0M HNO3)					
HMTA/H	mL H20	mL Zr-8	mL HMTA	Total mL	[HMTA]	[H]	[Zr]	Zr g/L	HMTA/Zr	Broth	pH (broth)	Temp	Gel time(s)	color	rigidity	Sticky?	pH(gel)
	none	0.20	0.077	0.277	0.86	0.72	0.58	53.2	1.48	Y		90	11	5	9	little	3.88
	none	0.20	0.071	0.271	0.81	0.74	0.64	58.3	1.27	Y	0.80	90	13	7	9	little	3.66
1.0	0.007	0.20	0.064	0.271	0.73	0.74	0.64	58.3	1.15	Y	0.77	90	18	9	9	dry	2.98
0.9	0.013	0.20	0.058	0.271	0.67	0.74	0.64	58.3	1.04	Y	0.72	90	23	10	9	little	2.83
0.8	0.020	0.20	0.051	0.271	0.59	0.74	0.64	58.3	0.92	Y	0.54	90	33	10	7	damp	2.72
0.7	0.026	0.20	0.045	0.271	0.52	0.74	0.64	58.3	0.81			90	45	10	7	moist	2.09
1.2	none	0.20	0.077	0.277	0.86	0.72	0.58	53.2	1.48	Y		80	16	5	9	little	3.73
1.1	none	0.20	0.071	0.271	0.81	0.74	0.64	58.3	1.27	Y	0.80	80	21	5	9	little	3.72
1.0	0.007	0.20	0.064	0.271	0.73	0.74	0.64	58.3	1.15	Y	0.77	80	37	6	9	little	3.36
0.9	0.013	0.20	0.058	0.271	0.67	0.74	0.64	58.3	1.04	Y	0.72	80	49	9	8	moist	3.21
0.8	0.020	0.20	0.051	0.271	0.59	0.74	0.64	58.3	0.92	Y	0.54	80	66	10	7	moist	2.78
0.7	0.026	0.20	0.045	0.271	0.52	0.74	0.64	58.3	0.81			80	not run				
1.2	none	0.20	0.077	0.277	0.86	0.72	0.58	53.2	1.48	Y		70	30	5	8	damp	5.50
1.1	none	0.20	0.071	0.271	0.81	0.74	0.64	58.3	1.27	Y	0.80	70	54	5	9	little	4.03
1.0	0.007	0.20	0.064	0.271	0.73	0.74	0.64	58.3	1.15	Y	0.77	70	91	7	9	little	2.84
0.9	0.013	0.20	0.058	0.271	0.67	0.74	0.64	58.3	1.04	Y	0.72	70	123	10	8	moderate	3.10
0.8	0.020	0.20	0.051	0.271	0.59	0.74	0.64	58.3	0.92	Y	0.54	70	175	10	7	wet	2.95
0.7	0.026	0.20	0.045	0.271	0.52	0.74	0.64	58.3	0.81			70	not run				
1.2	none	0.20	0.077	0.277	0.86	0.72	0.58	53.2	1.48	Y		60	74	5	7	damp	4.91
1.1	none	0.20	0.071	0.271	0.81	0.74	0.64	58.3	1.27	Y	0.80	60	145	4	6	damp	3.54
1.0	0.007	0.20	0.064	0.271	0.73	0.74	0.64	58.3	1.15	Y	0.77	60	303	9	6	damp	3.00
0.9	0.013	0.20	0.058	0.271	0.67	0.74	0.64	58.3	1.04	Y	0.72	60	421	10	6	wet	2.09
0.8	0.020	0.20	0.051	0.271	0.59	0.74	0.64	58.3	0.92	Y	0.54	60	not run				
0.7	0.026	0.20	0.045	0.271	0.52	0.74	0.64	58.3	0.81			60	not run				

ELECTRONIC DISTRIBUTION

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