CONF-970148--2

TASK SUMMARY

DEVELOPMENT AND TESTING OF SPHEROIDAL INORGANIC SORBENTS*

J. L. Collins, B. Z. Egan, and K. K. Anderson

Chemical Technology Division
Oak Ridge National Laboratory
Post Office Box 2008
Oak Ridge, Tennessee 37831-6223

December 3, 1996

Prepared for the
DOE Office of Science and Technology
Efficient Separations and Processing Crosscutting Program
Technical Exchange Meeting
January 1997
Gaithersburg, Maryland

---

*Research sponsored by Oak Ridge National Laboratory managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract DE-AC05-96OR22464.

DISCLAIMER

DEVELOPMENT AND TESTING OF SPHEROIDAL INORGANIC SORBENTS

J. L. Collins, B. Z. Egan, and K. K. Anderson

Technology Needs

Inorganic ion exchange materials have high selectivities and efficiencies for separating and removing fission products, actinides, and other elements from aqueous waste streams. However, in most cases, these sorbents are commercially available only as fine powders or as unstable granular particles that are not readily adaptable to continuous processes. Some of these powders are also made as pellets by using binding materials. However, the binders tend to lessen the number of exchange sites that are available for use by blocking pores and passage-ways to the exchange sites within the structures and adversely affect the loading and kinetic behavior of the exchangers.

Preparation of inorganic ion exchangers as microspheres improves the flow dynamics for column operations and expands their practical applications. One disadvantage of many of the inorganic ion exchangers that are made as powders, granular material, or as pellets is the lack of reproducibility as sorbents. These materials are prepared in batch processes in which chemical and physical gradients can occur that cause variances in the crystal morphology and compositions of the products. These same materials, when made by the internal gelation process, are more reproducible. Furthermore, in a few cases, the densities and porosities of an exchanger made as microspheres can be tailored by varying the chemical and physical process parameters; this allows some control over the selectivity and loading behavior of the exchanger.

Technology Description

The objectives of this task are to develop, prepare, and test spheriodal inorganic ion exchangers made by the HMTA (hexamethylenetetramine) internal gelation process to remove radionuclides and heavy metals from waste streams occurring at the various DOE sites. Inorganic ion-exchange materials, such as sodium silicotitanate, sodium titanate, ammonium molybdophosphate, phosphotungstic acid, hexacyanoferrates, titanium monohydrogen phosphate, hydrous titanium oxide, polyantimonic acid, magnesium oxide, etc. have high selectivities and efficiencies for separating and removing radionuclides (e.g., cesium, strontium, technetium, iodine, europium, cerium, ruthenium, and zirconium), actinides, and other elements (such as lead, mercury, silver, nickel, zinc, chromium, and fluoride) from aqueous waste streams.[1-4]

The initial task of this program involves the development of sodium titanate (ST) sorbents as microspheres by the HMTA internal gelation process. In previous studies at ORNL, PNNL, SNL, and SRTC, sodium titanate was found to be the best sorbent material for removing the strontium from alkaline supernatants of high ionic strength. Two types of composite materials are in the process of being developed and optimized. Initial preparations of several composite microspheres of hydrous titanium oxide (HTiO) and titanium monohydrogen phosphate (TiHP) that were homogeneously embedded with very fine particles of sodium titanate have been completed. Both sorbents are being optimized by empirically determining the amount of sodium titanate powder that can be embedded to obtain maximum strontium loading. These composite microspheres were chosen for development because both matrix materials (hydrous titanium oxide and titanium monohydrogen phosphate), as well as the sodium titanate, are good sorbents for removing strontium from alkaline supernatants.

Following the development of the spheroidal composite sorbents, attempts will also be made to make pure sodium titanate microspheres. Two chemical conversion methods will be tried; both require the use of hydrous titanium oxide gel spheres made by the HMTA internal gelation process. One method involves the hydrothermal conversion of hydrous titanium oxide gel spheres with sodium hydroxide. The other method utilizes an alkoxide conversion process for converting hydrous titanium oxide gel spheres to pure sodium titanate.

As part of the optimization process, the prepared sorbents are being tested in batch experiments for the removal of strontium from both simulated and actual supernatant waste solutions. For comparison, commercial sodium titanate sorbents and other strontium-selective sorbents are also being tested. Based on the batch studies, the most promising microspheroidal materials will be selected for further evaluation using column chromatography studies. Bench-scale studies will be used to determine the radionuclide and metal removal efficiency, maximum loading, etc., in a continuous process. BET surface measurements will be made on the best microspherical sorbents.

Benefits

The internal gelation process was originally developed as a process for preparing UO_2 microspheres and nuclear fuels for Light Water and Fast Breeder Reactors. Making inorganic ion exchangers as microspheres by the internal gelation process is a "spin-off" of these highly developed fuel technologies. The major benefit of this program is to further develop the technology for use in making inorganic ion exchangers more usable for large scale column use. These materials could have several advantages in treating a variety of waste streams.

Numerous inorganic ion exchangers are being or have the potential of being used in treating supernate solutions, low-level liquid wastes, contaminated groundwater, contaminated surface water (including acid mine drainage), and soil leachates.

Some specific site applications include:
- removing cesium from acid solutions (Idaho),
- removing strontium, technetium, and cesium from tank supernatants (Hanford, Oak Ridge, Savannah River),
- treating contaminated wastewater to remove uranium, technetium, cobalt, lead, zinc, etc. (all sites),
- removing radioisotopes from groundwater (all sites),
- removing actinides and fission products from waste sludge leachate (Idaho, Hanford, Oak Ridge, Savannah River),
- removing heavy metals from acid mine drainage runoff (mine tailings, non-DOE sites),
- removing radionuclides such as Eu, Ce, and Pr from organic streams (solvent extraction processes, analytical wastes),
- removing fluoride from waste streams, and
- removing radionuclides, Cs, Co, Eu, etc., from liquid wastes generated in hot cell operations, to convert them to a more transportable, storable waste.

In addition to these applications, these inorganic sorbents also have high potential as *in situ* barrier materials to prevent the migration of metals and radionuclides from burial grounds, leaking tanks, and other sources of contamination.

The loaded inorganic ion exchangers might be appropriate as a final waste form or more amenable to incorporation into other inorganic waste forms such as glass, ceramics, or grouts. The inorganic ion exchangers are more resistant to ionizing radiation, high temperatures, and harsh chemical environments than the more common organic polymeric materials.

Technology Transfer

Information developed by this task will be submitted to the DOE Program Manager for dissemination. Results will be presented to Waste Management personnel at other DOE sites, and researchers at other sites will be kept informed of progress. Results will be presented at DOE workshops, program reviews, and technical meetings.

Making inorganic ion-exchangers in a more usable form as microspheres using the internal gelation process is amenable to commercialization. The large-scale engineering of the internal gelation process has already been developed for nuclear fuels. The same equipment designs with minor modifications could be used to make large quantities of the ion exchange microspheres. Two companies have expressed interest in licensing and expanding the use of the technology. A patent application entitled *Method for Preparing Hydrous Titanium Oxide Spherules and Other Gel Forms Thereof* was filed with the United States Patent and Trademark Office on November 1, 1996.

Scientific Background

The chemistry of the HMTA internal gelation process is described in detail in a report by J. L. Collins et al.[5] The results of those studies showed that there were four principal reactions involved in the hydrolysis and precipitation of uranyl nitrate hexahydrate and that the kinetics and equilibria of these reactions varied with temperature. The chemical behavior observed in that study should hold true for making microspheres of other hydrous metal oxides by the HMTA internal gelation process. The four reactions for making hydrous titanium oxide can be shown as follows:

complexation/decomplexation,

$$2CO(NH_2)_2 + Ti^{4+} \rightleftharpoons Ti[CO(NH_2)_2]_2^{4+}, \tag{1}$$

hydrolysis,

$$\begin{aligned} &Ti^{4+} + xH_2O \rightleftharpoons Ti(OH)_4 \bullet yH_2O\downarrow + 4H^+ \text{ and} \\ &TiO^{2+} + xH_2O \rightleftharpoons TiO(OH)_2 \bullet yH_2O\downarrow + 2H^+, \end{aligned} \tag{2}$$

HMTA protonation,

$$(CH_2)_6N_4 + H^+ \rightleftharpoons (CH_2)_6N_4\bullet H^+, \text{ and} \tag{3}$$

HMTA decomposition,

$$(CH_2)_6N_4\bullet H^+ + 3H^+ + 6H_2O \rightleftharpoons 4NH_4^+ + 6CH_2O. \tag{4}$$

The major constituents of a broth for making microspheres of hydrous metal oxide are hexamethylenetetramine, urea, and the metal salt. Urea serves as a complexing agent for the metal (reaction 1) and at certain concentrations allows for stable broths to be prepared at 0°C that remain clear and free of gelation or precipitation for reasonable periods of time. As the temperature of the broth droplets rises in the hot organic medium, decomplexation occurs (reaction 1) allowing hydrolysis of the titanium to occur (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 make the system even more basic. Each protonated HMTA molecule can effectively remove three additional hydrogen ions. The reaction products are ammonium chloride and formaldehyde. In addition to being a complexing agent, urea also functions as a catalytic agent in the decomposition of protonated HMTA molecules.

One of the more interesting features of the chemistry of the process is the conversion of the reaction products back to HMTA in the basic wash step. When the microspheres are washed with NH_4OH to remove the reaction products (NH_4^+ and CH_2O), the reaction products react to reform HMTA[6] which is washed from the microspheres along with unreacted urea. This feature makes it possible, by chemical adjustments, to convert evaporator concentrates of the wash solutions back to process-usable HMTA/urea solutions. This feature aids in making the HMTA internal gelation process even more economically attractive.

Technical Approach

The HMTA internal gelation process being used in this task is similar to the process that was used in the development of light-water and breeder reactor microspheroidal fuels at ORNL and other laboratories worldwide.[7,8] A schematic of the lab-scale apparatus for making the microspheres is shown in Fig. 1. The procedure for making hydrous titanium oxide microspheres by this process involves first mixing formulated amounts of HMTA, urea, and titanium at temperatures near 0°C to form a broth. Broth formulations that remain clear and free of gel for reasonable periods of time ($\geq$1 h) at that temperature are used. To make the HTiO/ST microspheres, a predetermined amount of sodium titanate is also mixed into the broth. It is added as slurry of very fine hydrated sodium titanate particles. To keep particles of sodium titanate suspended, the broth is continuously mixed in the chilled broth tank while the broth is injected as droplets via a flat-tipped, stainless steel hypodermic needle into a flowing stream of heated organic medium. From there, the droplets are transported into the gel-forming apparatus. The size of the droplets is controlled by using a two-fluid nozzle concept and varying the gauge of the needle and the flow rate of the hot organic medium and the broth. Broth formulations with gel times of 8 to 12 s are used. About 35 s are required for the droplets to pass through the sphere-forming column and the serpentine residence tube to a collection basket (a cylindrical stainless steel-wire mesh basket). Once collected, the microspheres in the basket are lowered into the reservoir of hot organic medium and are aged for 10 to 30 min. The reaction impurities are removed from the microspheres by washing them several times with dilute NH_4OH and then with deionized water.

This project involves the development, preparation, characterization, and testing of sodium titanate (ST) sorbents made as microspheres by the HMTA internal gelation process. The goal is to develop spheriodal sodium titanate sorbents that are equal to or better than the commercially available engineered forms of sodium titanate in removing strontium from waste streams.

Composite microspheres of hydrous titanium oxide (HTiO) and titanium monohydrogen phosphate (TiHP) that are homogeneously embedded with very fine particles of sodium titanate are in the process of being developed and optimized. Optimization involves empirically determining the amount of sodium titanate that can be embedded to obtain maximum strontium loading. The HTiO and TiHP matrix materials were chosen because they are also good sorbents for removing strontium from alkaline supernatants of high ionic strength.

Parallel to the development of the spheroidal composite sorbents, attempts will be made to make pure sodium titanate microspheres by chemical conversion of hydrous titanium oxide microspheres. Two methods will be employed. One method involves the hydrothermal conversion of HTiO microspheres with sodium hydroxide and the other utilizes an alkoxide conversion of the HTiO microspheres. As proof of principle, a batch of sodium titanate microspheres was successfully prepared by an alkoxide conversion method. Analyses showed that ~70% of the hydrous titanium oxide was converted to sodium titanate.

The broth formulations and process conditions which are essential for making hydrous titanium oxide microspheres by the HMTA internal gelation method were determined in earlier work at ORNL by this research team. Being able to make hydrous titanium oxide as microspheres is the key to making all of the sorbents. Furthermore, the chemical procedure for converting hydrous titanium oxide microspheres to either the amorphous semicrystalline and crystalline spheroidal forms of titanium monohydrogen phosphate, also good sorbents for removing strontium, have been determined. In many cases the crystalline form determines the type of ions that are sorbed.

The prepared sorbents are being tested in batch experiments to determine their effectiveness in removing strontium from both simulated and actual MVST supernatants. The most promising materials, based on the batch tests, will be selected for column chromatography studies.

Accomplishments

As an initial exploratory step to determine the optimum amount of sodium titanate that can be embedded in hydrous titanium oxide microspheres, several batches of the composite microspheres were made. Weight percentages of sodium titanate of 9.2%, 13.2%, 16.8%, 20.2%, and 23.3% in hydrous titanium oxide were prepared. The size of the composite microspheres ranged from 28 to 48 mesh. The sodium titanate was obtained as a slurry of hydrated sodium titanate particles from Boulder Scientific Company, Mead, Colorado. An additional batch of the microspheres containing 13.2% sodium titanate was prepared in which the hydrous titanium oxide matrix material was converted to the titanium monohydrogen phosphate. Samples of the composite microspheres that were not dried, some that were air dried to a constant weight, and some that were air dried to a constant weight and then dried at 110°C for 24 h are being characterized.

The average crush strength for each composite microsphere composition was determined dynamometrically. This is the force in grams needed to crush the microsphere. For these measurements, ten microspheres were randomly chosen from each composition. The average crush strength of the microspheres before they were dried was 58±3 g. In general, the crush strength of air-dried microspheres was much higher, an average of 2500 g for the sodium titanate/hydrous titanium oxide microspheres, and 275 g for the sodium titanate/titanium monohydrogen phosphate microspheres. For comparison, the average crush strength for the commercially available granular sodium titanate was 425 g, and for the IONSIV IE-911 was 105 g.

To determine the effectiveness of the composite microspheres for strontium removal, batch tests were conducted using simulated MVST W-29 supernatant of the following composition: 3.9 M $NaNO_3$, 1.0 M NaOH, 0.14 M Na_2CO_3, 0.1 M NaCl, 0.25 M KNO_3, 1.0×10^{-4} M $CaCO_3$, and 1.1×10^{-5} M Sr (1 ppm). The strontium was added as strontium nitrate which was traced with the gamma-emitter, ^{85}Sr ($t_{1/2} = 64.8$ d). Batch tests were conducted by mixing masses of exchanger equivalent to about 0.025 g of air-dried exchanger with ~5 mL volumes of supernatant simulant for 1 h and 24 h periods. To establish a baseline for comparison for the optimization process, batch tests were also conducted with pure hydrous titanium oxide and titanium monohydrogen phosphate microspheres; sodium titanate that was obtained from Boulder Scientific Company as a powder slurry; granular sodium titanate that was obtained from Allied-Signal Corp.; and granular crystalline silicotitanate (IONSIV IE-911) that was obtained from UOP.

Strontium was effectively removed from the simulated MVST W-29 supernatant by all of the samples of composite microspheres. For mixing times of 1 h, the composite samples with 13.2% ST/HTiO that were not dried seemed to work best, removing 98.9% of the strontium with an average distribution ratio (D) of 18,200 mL/g. For tests with mixing times of 24 h, the values were much higher; most of the D values were greater than 100,000 mL/g with ≥99.8% of the strontium removed. Samples of the 13.2% ST/TiHP microspheres gave Ds of 150,000 mL/g and removed 99.9% of the strontium. These values were similar to those obtained for the sodium titanate slurry.

Of the ST/HTiO composite microspheres that were air dried, the one with 13.2% ST worked best in the 1-h tests, removing about 95.9% of the strontium. The average distribution ratio was 4800 mL/g, which was similar to the value that was obtained for the commercial, granular ST. The pure TiHP and HTiO microspheres removed 92.2 and 93.2% of the strontium with Ds of 2400 and 2800 mL/g. For the 24-h tests, the strontium distribution ratio for the composite microspheres ranged from 4500 to 7800 mL/g, resulting in the removal of 95.5 to 97.3% of the strontium. The samples containing 16.8% ST had the highest D. The granular ST removed 98.3% of the strontium with a D of 12,600 mL/g. Samples of the IONSIV®IE-911 removed 93.4% (D = 2900 mL/g) of the strontium in 1-h tests and 92.2% (D = 2400 mL/g) in the 24-h tests.

Interesting results were obtained with samples of composite microspheres that were heated for ~24 h at 110°C. More strontium was removed by these microspheres than by the air-dried microspheres. The distribution ratios ranged from 12,200 to 17,300 mL/g, corresponding to 98.3 to 98.8% strontium removal.

Keywords

hydrous titanium oxide, ion exchange, internal gelation, microspheres, separations, sodium titanate, sorbents, strontium, supernatant, tank waste, titanium monohydrogen phosphate, strontium

For further information, please contact:

J. L. Collins
Lockheed Martin Energy Systems
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, Tennessee 37831-6221
(423) 574-6689, fax (423) 574-6872
E-mail: lns@ornl.gov

B. Z. Egan
Lockheed Martin Energy Systems
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, Tennessee 37831-6223
(423) 574-6868, fax: (423) 574-6870
E-mail: eganbz@ornl.gov

TTP Number: OR16C342

References

1. A. K. De and A. K. Sen, "Synthetic Inorganic Ion-Exchangers," *Separation Science and Technology*, **13**(6), 517-540, 1978.
2. A. Clearfield, ed., *Inorganic Ion Exchange Materials*, CRC Press, 1982.
3. E. W. Hooper, B. A. Phillips, S. P. Dagnall, and N. P. Monckton, *An Assessment of the Application of Inorganic Ion Exchangers to the Treatment of Intermediate Level Wastes*, AERE-R-11088, Atomic Energy Research Establishment, Harwell, 1984.
4. J. L. Collins, B. Z. Egan, K. K. Anderson, C. W. Chase, J. E. Mrochek, J. T. Bell, and G. E. Jernigan, *Evaluation of Selected Ion Exchangers for the Removal of Cesium from MVST W-25 Supernate,* ORNL/TM-12938, April 1995.
5. J. L. Collins, M H. Lloyd, and R. L. Fellows, "The Basic Chemistry Involved in the Internal-Gelation Method of Precipitation of Uranium as Determined by pH Measurements," *Radiochimica Acta*, **42**, 121-134 (1987).
6. J. R. Polley, C. A. Winkler, and R. V. V. Nicholls, "Studies of the Formation of Hexamine from Formaldehyde and Ammonium Salts in Aqueous Solution," *Canadian Journal of Research*, **25**, Sect. B., 525-534, 1947.
7. P. A. Haas, J. M. Begovich, A. D. Ryon, and J. S. Vavruska, "Chemical Flowsheet Conditions for Preparing Urania Spheres by Internal Gelation," *I&EC Product Research & Development*, **19**, No. 3, 459-467, September 1980.
8. 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.

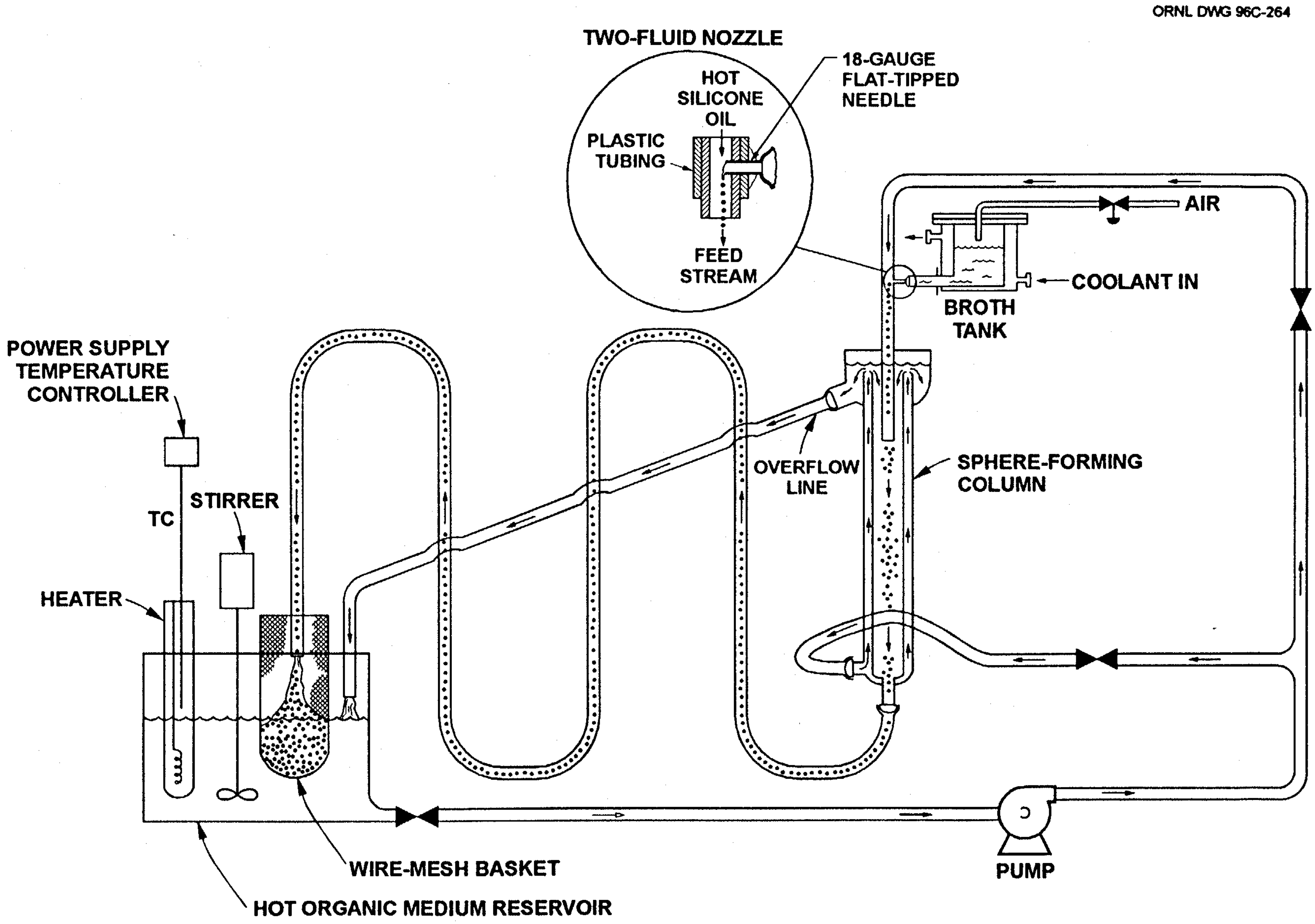

Fig. 1. Schematic of HMTA internal gelation process experimental apparatus