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AEC Research and Development REPORT

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO COMPANY

MOUND LABORATORY

MIAMISBURG, OHIO

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SUMMARY

The preparation of plutonium-238 dioxide microspheres by the sol-gel process was evaluated. This process requires three major operations: the preparation of an aqueous sol, the removal of water to give a solid gelled microsphere, and the calcination of the gelled microsphere at 1200°C. Reproducible sols and microspheres were obtained on a laboratory scale, and various experimental parameters were studied.

INTRODUCTION

The preparation of plutonium-238 dioxide microspheres by the sol-gel process developed by Oak Ridge National Laboratory[1] was evaluated. This process requires three major operations, the preparation of an aqueous sol, the removal of water to give a solid gelled microsphere, and the calcination of the gelled microsphere at 1200°C.

AQUEOUS SOL PREPARATION

Plutonium(IV) polymer is precipitated from plutonium(IV) nitrate solution in excess HNO_3 by slow addition of the plutonium solution to a 100% excess of NH_4OH with rapid agitation. The polymer is filtered and washed to a wash solution pH of less than 8 in order to remove contaminants. The precipitated polymer is then digested by resuspending in water and refluxing. After a digestion time of not less than 1-1/2 hr the polymer is peptized by the addition of HNO_3. Complete peptization is characterized by a change from an opaque light-green slurry to a nearly transparent black-green colloid. The high nitrate sol is then evaporated to dryness and the nitrate concentration reduced to the desired level by baking the dried gel at 250°C for 2 to 3 hr. Due to the depolymerization of plutonium(IV) polymer in high nitrate environments, the high nitrate sol is immediately baked and not allowed to remain in this condition for any length of time. A uniform heating of the gel is necessary so that resuspension can be achieved by the addition of water to the gel. The detailed preparation of the aqueous sol is outlined in the following steps.

1) The valence of the plutonium in a solution of 10-12 g of $Pu(NO_3)_4$ in 250 ml of 2N HNO_3 is adjusted with 30% H_2O_2.*

2) The plutonium solution is added slowly to 2M NH_4OH (100% excess) with rapid stirring in order to precipitate the plutonium(IV) polymer.

3) The polymer is washed with water to a wash solution pH of less than 8. The precipitate is digested in boiling water (approximately 500 ml) for not less than 1-1/2 hr.

4) Concentrated HNO_3 is then added to the mixture of plutonium(IV) polymer and water to yield a nitrate-to-plutonium ratio of 2.5. The total acid concentration during peptization is maintained at approximately 0.25N, in order to prevent depolymerization of the polymer. Peptization to a dark-green colloid occurs in 15 to 30 min; however, the colloid is refluxed for an additional 30 min after peptization.

5) The peptized sol is vacuum distilled at 80°C to a volume of 15-20 ml to yield a black sol.

6) This black material is then baked at 240°C to remove nitrate until a nitrate-to-plutonium ratio of 0.10 to 0.15 is attained. Approximately 2 to 3 hr are necessary to obtain the desired ratio at this temperature.

7) The final sol is then prepared by resuspending the baked gel in water and evaporating to a plutonium concentration of approximately 1.5M. The resulting sol has a dark-green color and exhibits considerable stability if the colloid is not allowed to become too concentrated.

In order to achieve uniform heating during the baking step, a special baker was fabricated. The baker consisted of an aluminum block situated on the top of a hot plate. A well in the top of the block was fitted with a stainless steel pan. Thermocouples were located in the block in order to monitor the temperature with a recorder. A lid fashioned to fit the pan was fabricated so that decomposition gases could escape during the baking. The lid was removed while evaporating to dryness but replaced during baking.

*Studies of $Pu(NO_3)_4$ in 2M HNO_3, with the plutonium valence adjusted with a slight excess of H_2O_2, showed no valence change for as long as 96 hr at temperatures as high as 70°C. At the boiling point, however, the rapid growth of plutonium(VI) was observed.

MICROSPHERE PREPARATION

To produce a solid gelled microsphere water is removed in the manner outlined by Oak Ridge National Laboratory.[1] A diagram of the equipment used for sphere forming is illustrated in Figure 1. A two-fluid nozzle was used to disperse the sol into drops which are released into the enlarged top of the tapered column [1 in. (2.5 cm) at top and 1/2 in. (1.3 cm) at bottom, 11 in. (28 cm) length]. These drops are suspended by an up-flowing stream of organic liquid. The drying medium consists of 80% 2-ethyl-1-hexanol and 20% 2-octanol containing 0.15% Span 80 and 0.15% Amine-O surfactants. As the water is extracted and the drops gel into solid microspheres, they drop to the lower portion of the column. After approximately 30 min the tangential flow is reduced and the spheres are allowed to drop out of the column where they are collected on a glass frit.

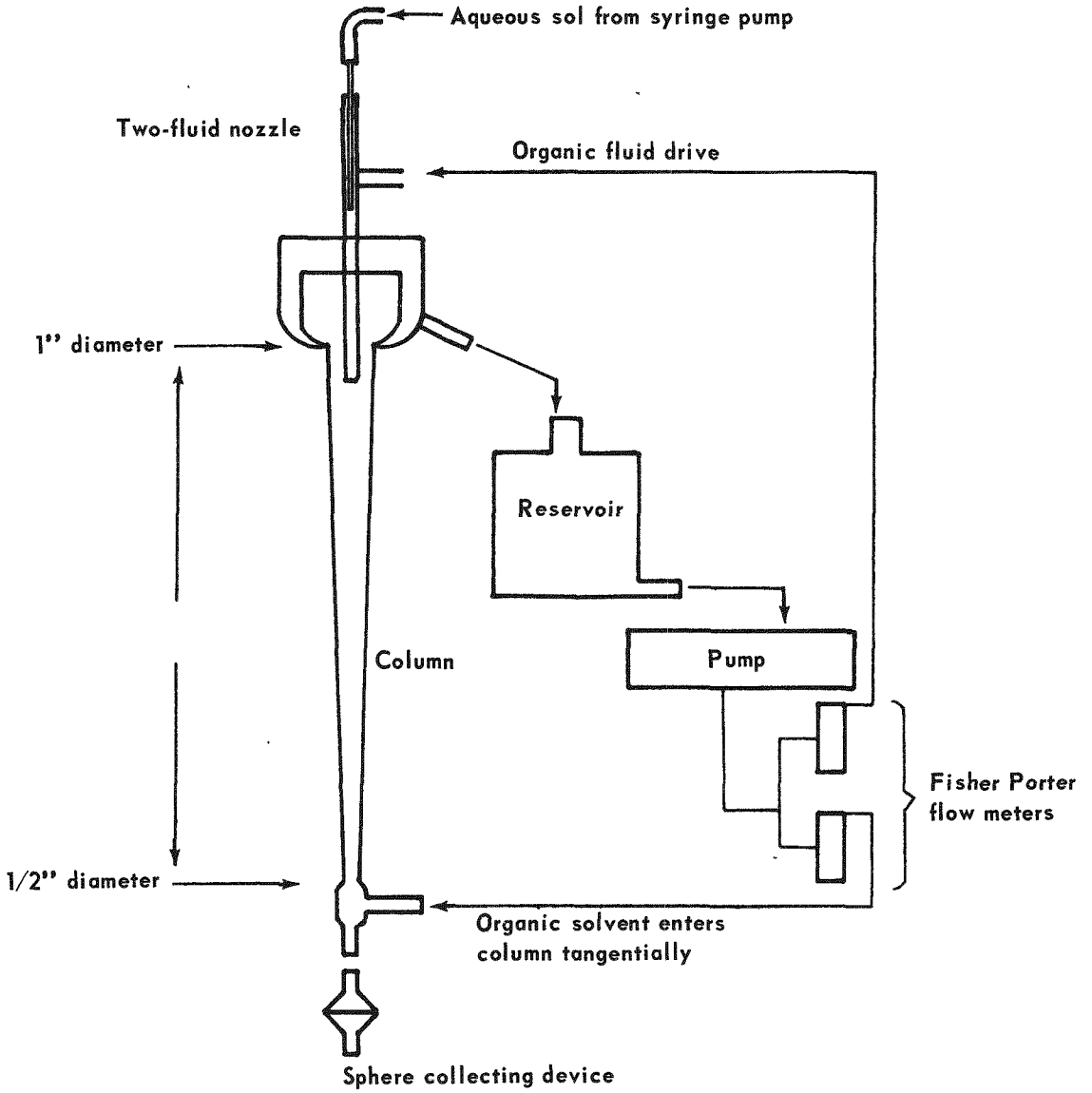

Figure 1. *Schematic Flow Diagram of Equipment for Forming Gelled Spheres.*

DRYING AND CALCINING

The gelled microspheres are dried and calcined in platinum boats in air as follows: (1) the spheres are air dried for 12-16 hr by self heating; (2) the spheres are fired from 25 to 500°C, at a heating rate of 120°C per hour; (3) from 500 to 1200°C, a heating rate of 300°C per hour is used; and (4) finally, the spheres are maintained at 1200°C for four hours. Calcined microspheres exhibit a hygroscopic nature and are stored in desiccators.

MICROSPHERE CHARACTERISTICS

Crush strength and apparent density of samples of plutonia microspheres prepared by the sol-gel process were measured. The results of these tests are listed in Table 1.

Table 1

Crush Strength and Apparent Density of Plutonium-238 Dioxide Microspheres

	Calcining Environment	NO_3/Pu Ratio of Sol	Size (microns)	Crush Strength (g)	Apparent Density (g/cc)
1.	1200°C	0.12	250-400	1260	10.8
2.	1200°C + plasma	0.12	250-400	1310	10.8
3.	1400°C + plasma	0.12	250-400	1270	10.8
4.	1200°C	0.15	50-250	926	10.4
5.	1600°C	0.15	50-250	969	–
6.	1200°C	0.20	250-400	938	10.7

Figure 2 is a photograph of typical plutonium-238 dioxide microspheres. Figure 3 shows polished sections of these same spheres.

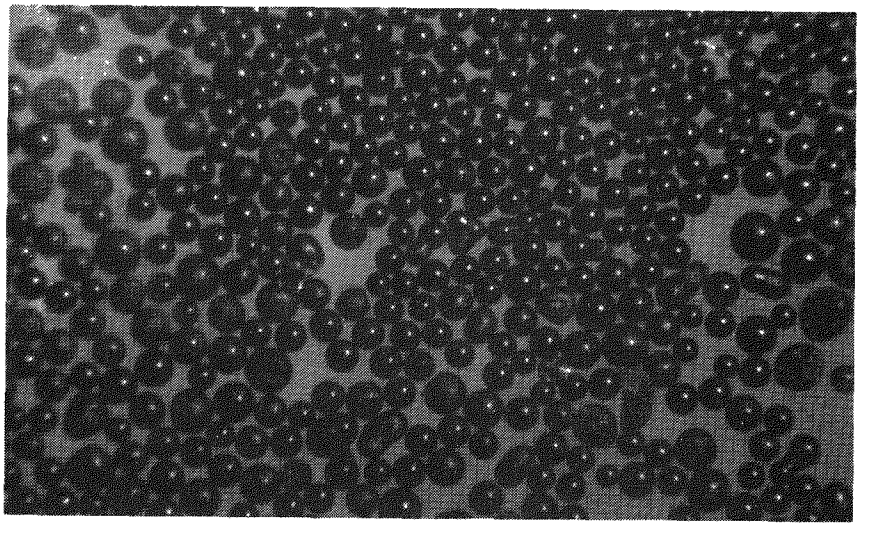

Figure 2. *Typical Plutonium-238 Dioxide Microspheres.*

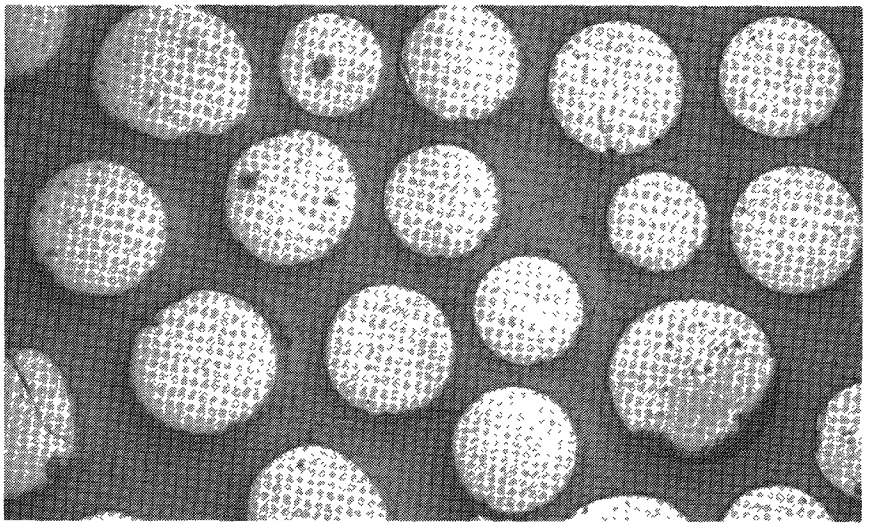

Figure 3. *Sections of Plutonium-238 Dioxide Microspheres.*

RECOVERY

The recovery of bad gels was also briefly investigated. The depolymerization and dissolution of gels and uncalcined microspheres was accomplished successfully in boiling 8M HNO_3 in approximately 30 min. Calcined spheres, however, are not soluble in HNO_3.

The solubility of plutonium dioxide in the organic drying medium was also investigated. Samples of the alcohol after filtration through a fine frit contained only 7×10^{-5} g/l of plutonium.

DISCUSSION

During baking, the rate of nitrate removal varies widely with temperature and excessive baking will result in a material which will not resuspend. Therefore, nitrate removal rates as a function of temperature are necessary to control the preparation of sols. The nitrate removal is monitored by titration of the dispersed sol with base. Work performed at Oak Ridge National Laboratory indicates that the milliequivalents of nitrate present in the sol is equal to the milliequivalents of base required to titrate the sample to pH 9.[2] Experimentally, samples of 30 to 50 mg of sol were resuspended and titrated with 0.02N KOH to pH 9 using a pH meter. Kinetic data were collected by determining the NO_3/Pu mole ratios as a function of baking time at constant temperature. The decomposition shows a second-order dependence on nitrate concentration and is independent of the plutonium concentration.[3] A plot of $1/NO_3$ as a function of time should give a straight line for a second order reaction. A plot of NO_3/Pu as a function of time was made for convenience and shows a straight line in Figure 4. Baking times of 2.5 to 3 hr at 240-250°C are sufficient to yield the desired NO_3/Pu ratio. After the sols were dried and heated to the baking temperature the NO_3/Pu mole ratio decreased from 2.5 to approximately 0.3.

Failures which were encountered initially in the preparation of sols cannot be related to the presence of impurities. Silicon analysis of both good and bad sols showed no significant difference (approximately 0.01%). The presence of fluoride ion also does not inhibit the formation of a good sol. Plutonium nitrate solutions from Mound's recovery system which may contain organic nitrates form satisfactory sols.

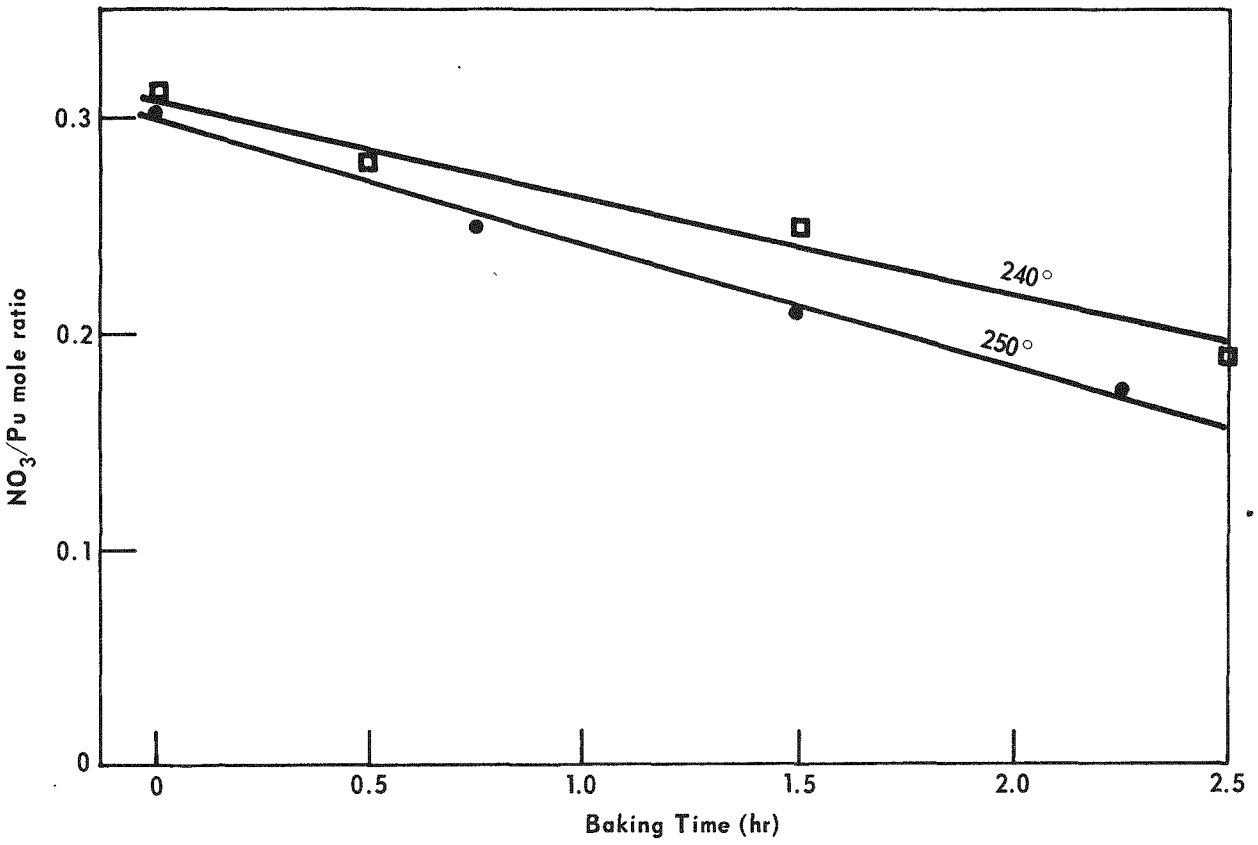

Figure 4. *Denitration of Plutonium-238 Dioxide Sols.*

ACKNOWLEDGMENT

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