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FORMATION OF COLLOIDAL SOLUTIONS OF Pu^{IV} AND THE CONVERSION INTO PuO_2 MICROSPHERES

by

K. P. LOUWRIER, T. STEEMERS and E. ZAMORANI

1968

Joint Nuclear Research Center
Karlsruhe Establishment - Germany

European Institute for Transuranium Elements

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Formation of microspheres with a tapered column and in a beaker is described.

Thermogravimetric analysis in connection with the drying procedure is discussed.

Metallographic inspection of the microspheres is presented.

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SUMMARY

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KEYWORDS

SOLS
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SPHERES
PRODUCTION
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COLLOIDS
SOLUTIONS
PLUTONIUM COMPOUNDS
VALENCE

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Formation of colloidal solutions of Pu^{IV} and the conversion into PuO_2 microspheres (+)

Introduction

Dense nuclear fuel of oxides and oxide mixtures can be produced through the sol-gel method. Powder, microspheres and shards can be produced at temperatures far below the generally accepted sintering temperatures. A considerable experience exists in the field of Th, U and Th-U fuel. Experience with Pu is rare. The two methods that are reported are :

1. Method developed in Oak Ridge National Laboratory (1). A high nitrate sol is made by digesting plutonium hydroxide in HNO_3. A baking step is applied to the high nitrate gel to obtain a powder that can be dispersed to give a low nitrate sol.

2. Procedure developed by CNEN (2) NO_3^- is removed from a Pu nitrate solution through solvent extraction and a sol with a NO_3/Pu ratio of 1 is obtained.

This report deals with different methods to make Pu colloidal solutions with the aim to make a sol with a low NO_3/Pu content.

(+) Manuscript received on November 27, 1967.

Formation of colloidal solutions

Different methods were used to obtain colloidal solutions and a great variety of solutions with different properties were made. It is known that the feasibility for the production of microspheres depends among other factors upon the NO_3 to Pu ratio in the sol. The aim of the work is the production of sols with a low NO_3 to Pu-ratio.

The methods used are :

1. Peptisation of a plutoniumhydroxide that is quickly precipitated from a Pu nitrate solution at a high pH. This forms a sol with a NO_3 to Pu ratio of 0.5 - 0.7 and about 2 M in Pu.

2. Dialysis of a sol with a NO_3 to Pu ratio of about 0.7. In this way we obtain sols 0.3 M in Pu with a NO_3 to Pu ratio of 0.35.

3. Baking of a gel formed from a sol with a high NO_3 to Pu ratio and redispersing the residue.

4. Precipitating a Pu hydroxide under such conditions that a conversion to a sol with a low NO_3 to Pu ratio is possible.

Ad 1. A solution containing about 30 gr of Pu/liter and a free acidity of 1.5 M HNO_3 was poured into 12 ½ % NH_4OH solution. The precipitate was filtered, washed and dispersed into a 10 fold excess of water (based on a final concentration of 2 M Pu). Enough HNO_3 was added to form a NO_3 to Pu ratio of 0.5 - 0.7. The mixture was evaporated in about 6 hours to a sol of 2 M. This sol was clear, green transparent and had a low viscosity. Very likely it consisted out of small particles.

X-ray measurements on the original precipitate or sol did not reveal any structure. An aging effect within some days on the precipitate was not observed. This is in contrast with similar experiments in which Ce^{IV} is converted into a sol and where the precipitate and sol have the structure of CeO_2 and where aging of the precipitate is important.

Ad 2. The sol described before was dialysed. This is carried out in a P.V.C. container separated by a semi-permeable membrane from a watery suspension of ion exchanger I.R.A. 400 in the alkaline form.

The sol and the ion exchanger suspension were constantly stirred and the pH of the sol is constantly measured.

The pH changes from 1.3. to 3.0 during 16 hours of dyalysis and the resulting liquid was so viscous that it had to be diluted to get a better streaming sol. The pH was measured directly with a glass electrode in the colloidal solution with a calomel electrode as reference. The measurements were not corrected for special effects. This sol was extremely tixotropic and rather unstable. Is gellyfied at 90° C and a small portion of Pu^{IV} precipitated irreversibly. This precipitation occured also after two weeks standing at room temperature. It was practically impossible to obtain a NO_3 to Pu ratio lower than 0.35 with this method and then the sol was already rather diluted, 0.36 M.

The colour of the sol was unchanged. It was still a dark green transparent solution.

Ad 3. Several experiments were made with the aim of decreasing the NO_3 to Pu ratio by heating the gel.

The gel was heated for different times at temperatures ranging from 180° - 230° C under normal and reduced pressure. The remaining powder was dispersed in water. When the solid was still dispersable we again obtained transparent sols with a slightly lower NO_3 to Pu ratio than initially. Practically always an insoluble heel was left behind. It was difficult to reproduce the experiments.

It is known that plutonium ions in aqueous solution are already considerably hydrolysed at a pH of 1 - 2 (3, 4, 5,). A slower hydrolysis may result in a larger initial particle and this can result in a sol with a lower nitrate content. A series of Pu precipitations at different pH's was made. The oxihydrate was dispersed in HNO_3 and the possibility to form a low nitrate sol was checked by heating the mixture. The next method was the most successful. A Pu nitrate solution containing 30 g Pu/L and 1,5 N in free HNO_3 was brought at a pH of 1,1 - 1,2 with ammonia by pouring the Pu solution into a solution of pH 1,1 - 1,2 that was kept at this pH by simultaneously adding of ammonia. At this point the colour of the mixture was greenish and the solution became cloudy. The next step was precipitation at pH 7. This precipitate was washed with water and with diluted ammonia. The washing with diluted ammonia was necessary to remove all nitrate. The NO_3 to Pu ratio in precipitate which is only washed with water remains constant at 0.2.

The precipitate again was dispersed in an excess of water to which HNO_3 was added to give a NO_3 to Pu ratio of 0.1 - 0.2.

The mixture was evaporated with continuous stirring until a volume corresponding with 2 M Pu sol resulted. After 8 hours of heating the resulting product was a course sol with an appearance different from those mentioned before. It had a low viscosity, was lighter green in colour and was not transparent. After standing for one day a more viscous part settled. This sol consisted clearly out of particles that were considerably larger than those mentioned before.

Production of microspheres

The methods for the production of microspheres was based on the one developed at Oak Ridge National Laboratory. It is based on water extraction of a sol low in nitrate with a long chain alcohol. Depending on the required size the beads can be produced in a beaker or in a tapered column. Beads of a size of ca. 50 μ were made by pouring the sol into a beaker filled with 2 - aethylhexanol that is stirred at constant speed. With this method, the dispersion in size is considerable. Beads up to 500 μ were produced in the tapered column.

The sol was dispersed through a double nozzle system into a counter current of eathylhexanol in the column (Fig. 1 and 2). The water content of the aethylhexanol was kept at ca. 1% by constantly distilling a water aethylhexanol mixture at ca. 150° C in a side loop. The temperature of the aethylhexanol was kept at ca. 20° C. At higher temperatures the viscosity is too low and the counter current must be too strong. We have added different surfactants such a sarkesyl-O, primene and oil BX 5 to the aethylhexanol. The last was considered the best since we could use it in very low concentration, depending on the sol used 0.1 °/oo - 1 °/oo. (Oil BX 5 is a lauryl (poly - 1 - oxapropene), oxaethane carboxylic acid made by Chemy, Bodegraven, Holland).

The aethylhexanol should contain about 1 % of water. If it is too dry, the beads gel too fast and will fracture. During the production of microspheres once in a while we added surfactant when the beads showed a tendency to stick together. Sticking of beads to the glass wall of the column was eliminated by treating glass with chlorsilan. Beads made of sols with a NO_3/Pu ratio of 0,5 show also a strong tendency to agglomerate. Higher surfactant concentrations have to be used in that case. The sol was dispersed into the aethylhexanol and after about 20 min. the beads were collected and washed with petroleumaether. Washing with aceton resulted in the breaking of the spheres. Carbontetrachloride was not used in order to avoid Cl contamination. They were kept in air at room temperature for 8 hours.

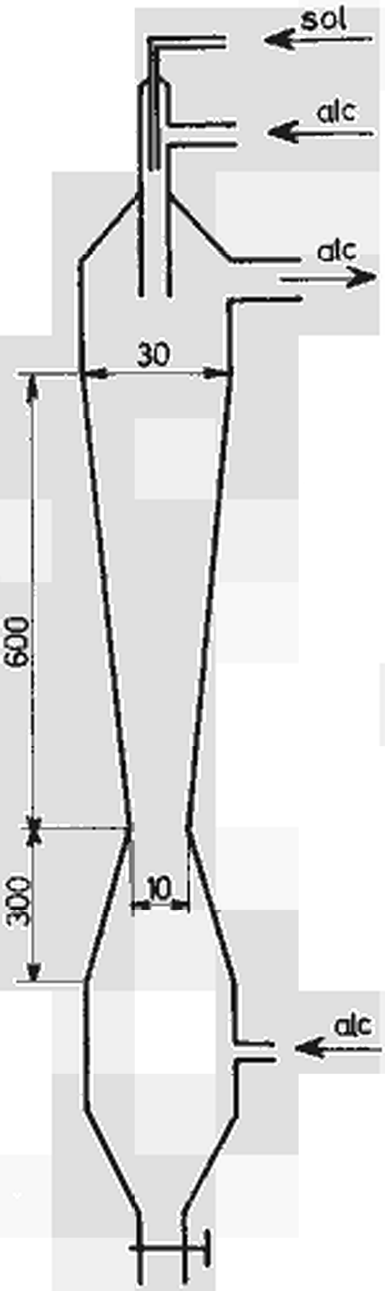

Fig. 1 Tapered Column as used in the experiment

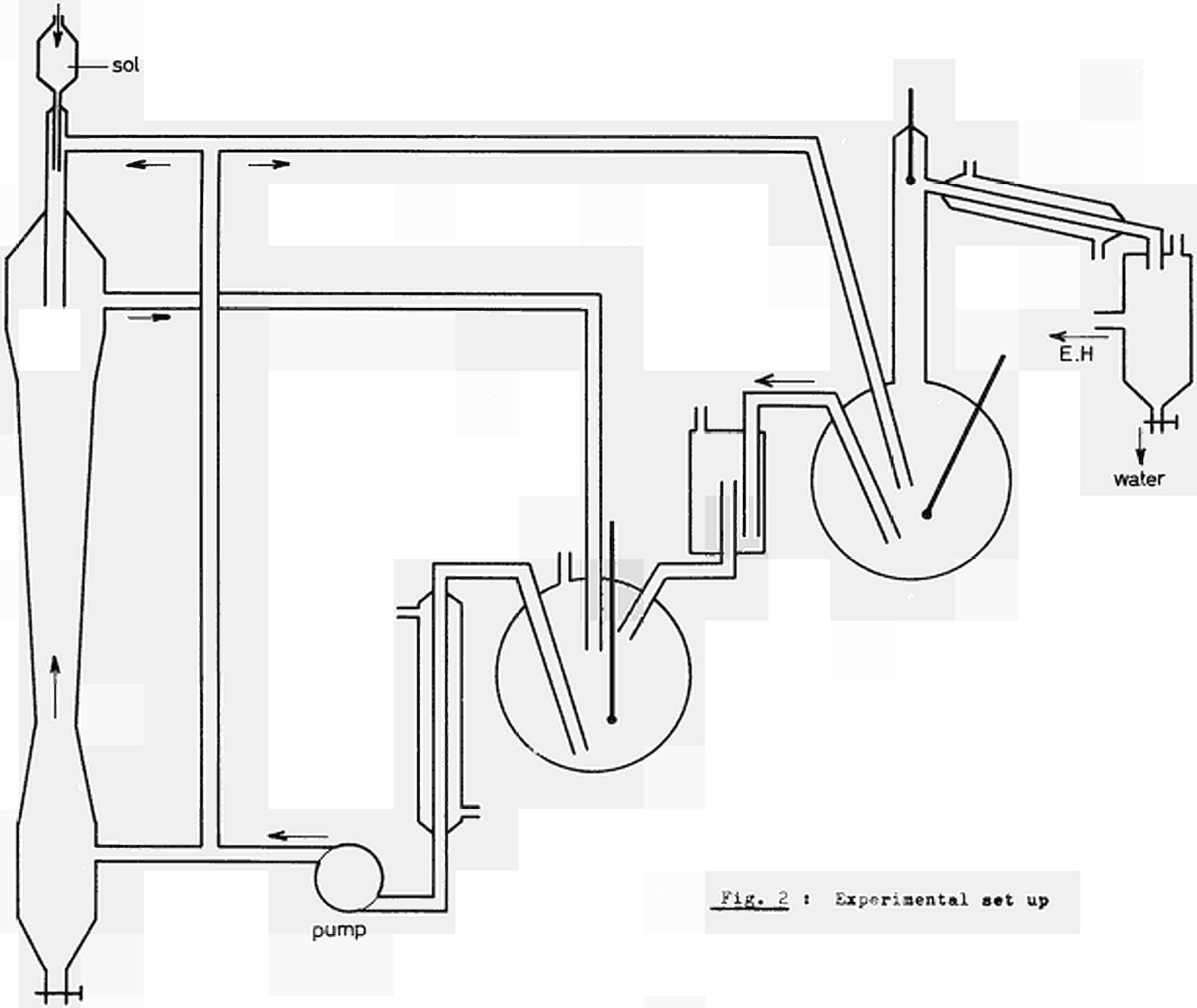

Fig. 2 : Experimental set up

To have an idea of optimal conditions we dried some beads in a thermobalance. A considerable loss of weight was seen up until ca. 170° C and with a higher NO_3^- content a weight loss around 260° C was observed. The first loss may correspond with release of water and aethylhexanol and the last may be due to decomposition of nitrate. The initial drying process was as follows. The temperature was raised to 110° C in 5 hours, kept at this temperature, raised to 170° C in 3 hours, kept for 5 hours at this temperature, raised in 2 hours to 250° C and kept overnight at this temperature. The beads made with a sol that had a NO_3 to Pu ratio higher than 0.35 break in this process and after calcination showed many cracks (fig. 3) or, even worse fell to pieces.

If the drying time at 170° C was shortened the beads became powder, probably because of a sudden release of aethylhexanol. Preliminary experiments have shown a faster way of drying. This was done with hot air which is nearly saturated with water vapour. After the beads are dried, they are calcinated in air at 900° C for 3 hours. The metallographic cuts through beads produced with method No. 4 are shown in fig. 4 and 5. The diameter of the beads in about 250/u.

In an attempt to use directly a sol with a NO_3 to Pu ratio of 0,5 we added ammonia to the aethylhexanol. During the drying, a considerable amount of beads broke, but those that remained showed no pores (fig. 6). Pycnometer densities obtained from powder produced through sol gel method were 10,3 for powder heated at 600° C and 11,3 for powder heated at 1200° C. The density of beads heated at 900° C is about 10,8. It does not change significantly during heating at higher temperatures. Differences of several percentages are found in the densities of different batches due to different porosity.

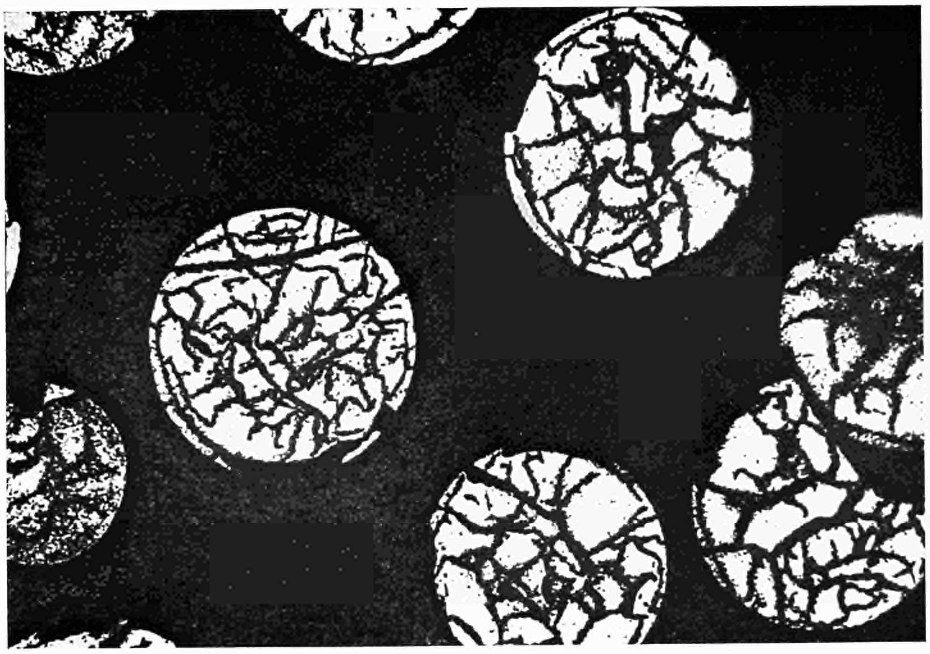

FIG. 3

Microspheres from a sol with a Pu/NO_3 ratio of ca. 0,5 — diameter ca. 250 μ

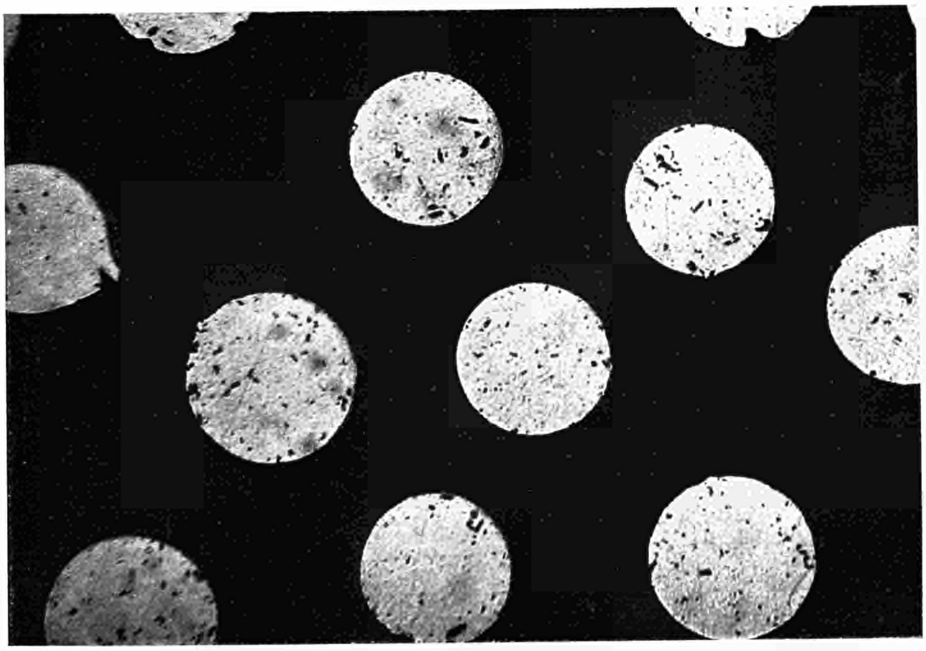

FIG. 4

Microspheres from a sol with a Pu/NO_3 ratio of 0,2 — diameter 250 μ

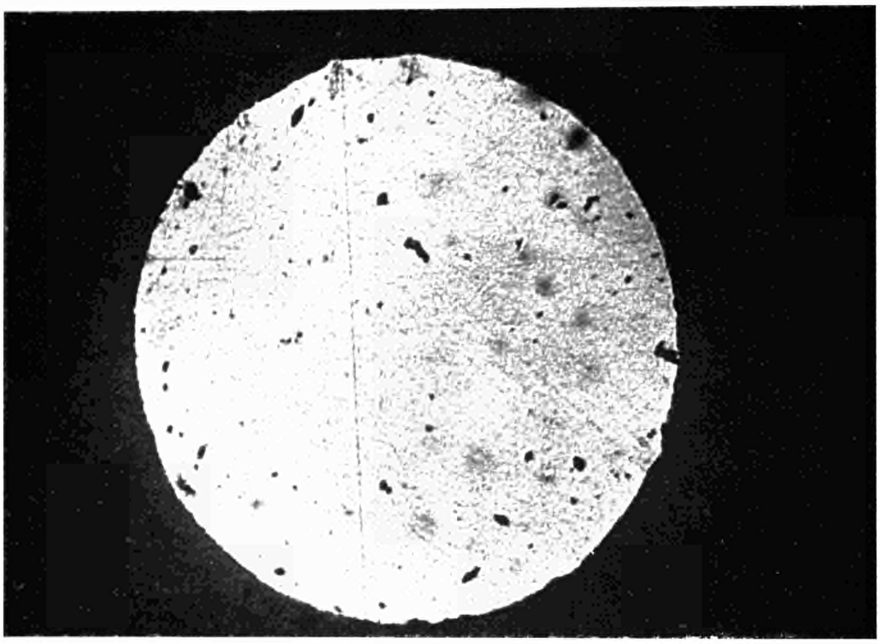

FIG. 5

Microsphere from a sol with a Pu/NO_3 ratio of 0,2 — diameter ca. 250 μ

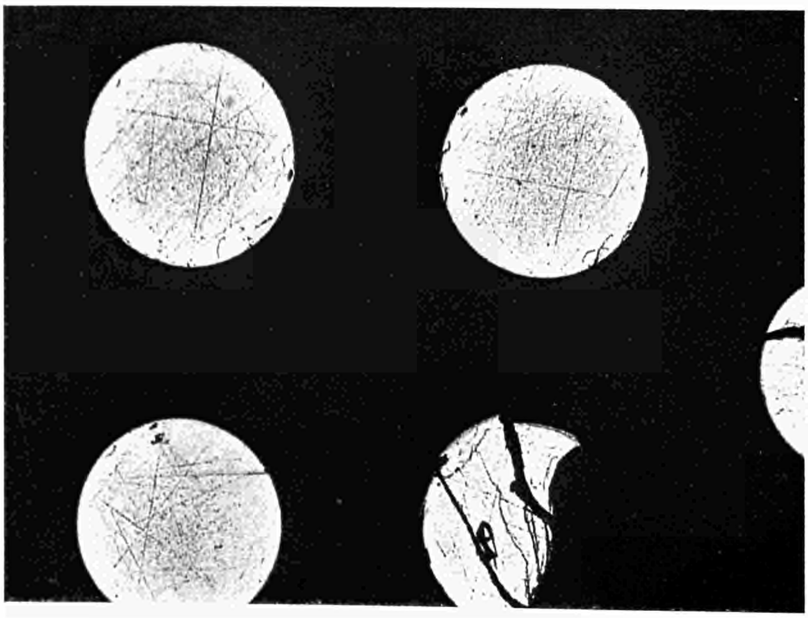

FIG. 6

Microsphere obtained from a sol with a Pu/NO_3 ratio of ca. 0,5 and NH_3 dissolved in the 2 EH — diameter ca. 250 μ

Production of 100 gr. microspheres

100 gr. of PuO_2 beads were reduced in an H_2 atmosphere from 1600 - 1700°C resulting in microspheres with an average diameter of 285 µ. The structure of the beads did not change much in this step. Porous beads obtained a more closed porosity. The beads will be covered with different layers of pyrolytic carbon and a layer of silic carbide. The first layer of pyrolytic carbon will be a porous layer. Pu_2O_3 was chosen as fuel since a lower CO pressure will be built up in the covered particle.

The beads were examined after reduction for different caracteristics. The results are presented in table I. The O/Pu ratio was determined from the weight difference before and after calcination in air. The crystallographic density was determined after X-ray analysis. There also the crystallographic O/Pu ratio was obtained (6).

Specimens	Weight of Pu (gs)	X-ray analysis		O/M gravimetric	Picnometer density (g/cc)	Temperature of reduction (°C)	Time of reduction (hours)
		O/Pu	Density (g/cc)				
PuS017	23,575	1,74	10,90	1,759	10,38	1600	4
PUS018	11,478	1,67	10,74	1,679	10,05	1720	4
PuS019	26,679	1,76	10,94	1,772	10,69	1700	4
PuS020	18,641	1,73	10,87	1,721	10,50	1600	4

Table I

Physical characteristics of Pu_2O_3 microspheres

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C.E.A. - R - 3092, 1966.

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To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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