MASTER

Sol-Gel Processes for Ceramic Nuclear Fuels

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PROCEEDINGS OF A PANEL, VIENNA, 6-10 MAY 1968

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INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1968

SOL-GEL PROCESSES
FOR CERAMIC NUCLEAR FUELS

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ON SOL-GEL PROCESSES FOR CERAMIC NUCLEAR FUELS
HELD IN VIENNA, 6 - 10 MAY 1968

INTERNATIONAL ATOMIC ENERGY AGENCY
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SOL-GEL PROCESSES FOR CERAMIC NUCLEAR FUELS
(Panel Proceedings Series)

ABSTRACT. Proceedings of a Panel convened by the IAEA and held in Vienna from 6 to 10 May 1968. The meeting was attended by 25 participants and observers from 11 countries and two international organizations.

Contents: Status reports; Basic research; Development of processes and equipment; Irradiation and cost; Summary of the Panel; List of participants.

Entirely in English.

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SOL-GEL PROCESSES FOR CERAMIC NUCLEAR FUELS
IAEA, VIENNA, 1968
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FOREWORD

Both advanced and developing countries are at present intensifying their nuclear power programs. The total installed nuclear capacity in 1968 was equal to 11 000 MW(e) and it is anticipated that by 1975 it will be about 100 000 MW(e).

Among the most important decisions to be faced is the choice of the best and most economical way to produce ceramic nuclear fuels. The International Atomic Energy Agency therefore convened a Panel on Sol-Gel Processes for Ceramic Nuclear Fuels, which was held at the IAEA Headquarters in Vienna from 6 to 10 May 1968.

Sol-gel processes have been developed primarily for recycling thorium reactor fuels and they promise to become an almost universal method of preparing ceramic fuels for reactors. When compared with more conventional methods, the processes have the advantage of simplicity, flexibility, easy control of the size and shape of product particles, a much lower calcination temperature required for densification, and superior adaptability to remote operation in a shielded facility. This last advantage is most important in recycling uranium-233 and thorium fuels, where handling is complicated by the gamma activity from the decay products of uranium-232 and thorium-228.

Initially, the sol-gel processes were developed to produce high-density thorium-uranium oxide powder suitable for aqueous suspension reactors and for vibratory compaction in metal tubes. More recently, the processes have been adapted to the preparation of nuclear fuels with a variety of compositions, such as carbides of thorium and thorium-uranium mixtures, and with a variety of shapes, for example microspheres.

Many countries are now making great efforts to develop the process further, and seventeen scientific papers and status reports on important aspects of the subject were presented at the Panel. It is hoped that the publication of these papers will be of interest to chemists and nuclear engineers engaged in this work.

The Agency is grateful to the authors and rapporteurs, and to the chairmen, Dr. C.J. Hardy and Prof. M. Zifferero, for guiding the work of the Panel.

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Wet way processes for preparing nuclear ceramic materials

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Abstract

STATUS REPORT FROM THE CZECHOSLOVAK SOCIALIST REPUBLIC: WET WAY PROCESSES FOR PREPARING NUCLEAR CERAMIC MATERIALS. The basic premise for the Czechoslovak investigations of wet way processes is given and the following main lines of research are proposed: (a) Reviews of selected topics and analysis of published results; (b) The chemical state of uranium (IV) hydroxide precipitate; (c) Chemical and granulometric changes during the growth of particles; (d) Interaction of valence states of uranium ions; (e) Some aspects of electro-reduction. In addition to completed work, current investigations and proposed experiments are briefly described.

1. INTRODUCTION

Czechoslovakia is an industrial country with significant resources of uranium and intends to increase its production of nuclear fuel materials. This increase must be achieved logically, i.e. it must develop the given possibilities on a natural basis with economic and other conditions being taken into account. Within this scope, both the classical technological procedures and the newly proposed methods have their significance. Among the wet way methods of preparing ceramic materials the most important are the so-called sol-gel processes. At present there is no urgent need for the technological application of these processes, and emphasis is therefore laid on keeping close track of world development as well as on preparing well-trained specialists by means of rationally conducted fundamental research.

2. CHARACTERISTIC RESULTS AND PROPOSALS

(a) Reviews of selected topics and analysis of published data

Accessible references on wet way methods, especially sol-gel processes, were summarized up to the end of 1966 (about 200 references) [1] and provided basic orientation. Metal hydroxy complexes are reviewed from the viewpoint of co-ordination chemistry in the paper "Hydroxyl ion as a ligand" (about 200 references)[2]. Their importance in wet way chemistry is clearly demonstrated.

(b) Chemical state of U (IV) hydroxide precipitate

The description of many properties is inconsistent as a result of problems arising from preparation (sufficiently low U (VI) content, exact content of water, etc.) or of changes during measurement, if the product comes into contact with air. For example, the colour of the hydroxide precipitate is described in most cases as being black [1, 3, 4], which is true only for insufficiently reduced solutions, since at a concentration of $U(VI) < \sim 3\%$ of U_{total}, green precipitate is obtained. It is, however, very sensitive to oxidation which changes its colour to black. As the hydroxidic precipitate of U(IV) is green and that of U(VI) yellow, a question arises: namely, what is the nature of the black precipitate? It may be, for example, a precipitate of U in the valence states four and six or the hydroxide of pentavalent uranium formed as a consequence of the interaction of U(IV) and U(VI). Since the pure hydroxidic precipitate of U(VI), i.e. 'hydrolytic' uranium acid [5], is the so-called $UO_3 \cdot 2H_2O$ (a relatively well-known substance), the first step is to investigate the chemical constitution of the green hydroxide of U(IV). For the present time, the formula $UO_2 \cdot 2H_2O$ or $U(OH)_4$ is assigned to it [3-7]; as it is a hydrolytic precipitate, it may be a polynuclear oxyhydroxy complex [8, 9] of the $UO(OH)_2 \cdot xH_2O$ type.

The resemblance in the properties of hydroxy complexes both in liquid and solid phases became evident after a study of the absorption spectra of $U(OH)_x^{(4-x)+}$ in solution and the reflection spectra of the precipitate. The former were observed by means of differential spectrophotometry [10] and contain a number of absorption bands similar to the spectra of U^{4+}_{aq} ion, but with lower intensity and shifted towards higher energies. The reflection spectra were not measured because of experimental difficulties caused by the extreme sensitivity of the precipitate to oxidation; these difficulties should be overcome in the near future.

For direct chemical identification of the green precipitate we had first of all to prepare it correctly. For this purpose an apparatus was developed (by M. Tympl) with a perfectly pure nitrogen atmosphere, enabling preparation of the precipitate to be done by means of alkalization with ammonia, filtration and washing by water or organic solvents, drying in vacuo and sealing into ampoules. The key problem of this preparation is good filterability of the precipitate, which may be achieved by a special alkalization method. The product is not crystalline but composed of firm macroaggregates that permit sufficient washing to be performed without peptization (e.g. a precipitate prepared from UCl_4 solutions contains only traces of chloride ions after ordinary washing).

We also tried to prepare a precipitate by alkalizing the solution by decomposing urea; our results essentially agree with the data in the literature [1]. Direct preparation of sols by means of electrodialysis was carried out in a two-compartment cell equipped with an anion resin membrane (a homogeneous as well as a heterogeneous one).

The basic aspects of this process are:

(1) Combination of electro-reduction, neutralization of the acid, formation of stable sol, and removal of the electrolytes, which is advantageous.

(2) Each membrane presents, from the electrodynamic point of view, a barrier acting as an interelectrode [11], which means, for example, that the membrane side washed by the catolyte behaves somewhat like an

anode, so that uranium (IV) ions are reoxidized and the current efficiency is reduced. The fraction of this current is relatively lower at higher total current, but at inevitably low conductivity of the final sol the considerable effect of this membrane acting as the interelectrode cannot be avoided, which is disadvantageous.

The following technical aspects may be mentioned: high mechanical resistance of the membranes is required; slow kinetics of the process [1] from the viewpoint of production on a larger than laboratory scale; neutralization of free acid by electric current is not, as a rule, economical; adhesion of finely dispersed solid phase on some surfaces takes place and cannot be inhibited even by short overpoling[1], successful in the seawater desalination process [12].

For the reasons mentioned, we are rather sceptical about the practical preparation of the precipitate (sols) by means of this procedure.

We have not yet completed direct identification of the chemical state of the green precipitate. Thermal analysis of the precipitate, its i.r. and p.m.r. spectra and X-ray analysis are under investigation. The main problems are technical difficulties resulting from the easy oxidability of the product.

We have finished measuring the magnetic susceptibility of the green precipitate at room temperature [13]. Its value per gram-atom of uranium equals $(2150 \pm 90) \times 10^{-6}$ CGS units, which is a value somewhat lower than that corresponding to U^{4+}_{aq} ion in solution ($(3785 \pm 10) \times 10^{-6}$ CGS units). The given value decreases linearly with the uranium (VI) content in the precipitate. It is probably one of the reasons for a certain decrease and a considerable scatter of the values for the black hydrolytic precipitate ($(470 - 617) \times 10^{-6}$ or $(261 - 1666) \times 10^{-6}$, respectively [3, 4]).

The concentration of free acid in the solution of U(IV) compounds should be ascertained in some operations (e.g. during electro-reduction of uranyl solutions, extraction of an acid by alifatic amines, etc.). Direct alkalimetric titration does not lead to any result, as the added hydroxide combines with both the hydrogen and the uranium (IV) ions. We tried to solve this problem by means of masking or by precipitation of the ions U^{4+} and UO_2^{2+} [14]. Of all the agents used, the only suitable one was hydrogen peroxide, transforming uranium ions to $UO_4 \cdot xH_2O$. The method may be applied at any U(IV) : U(VI) concentration ratio, excess hydrogen peroxide not reducing the height of the potentiometric jump. Its drawback is the necessity of knowing exactly the concentrations of U(IV) and U(VI), since the reaction of these ions with hydrogen peroxide results in the releasing of stoichiometric amounts of hydrogen ions ($4H^+$ with U(IV) or $2H^+$ with U(VI)) into the solution, for which the direct consumption of hydroxide must be corrected. Even in this case, however, the error in the determination need not, at lower concentrations of U(VI) determined polarographically, exceed 2-3 rel.%. The presence of sulphate ions causes greater systematic error and they must therefore be eliminated from the solution.

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[1] An originally green precipitate adhering to the cathode changes its colour to black after overpoling (anodic oxidation) and becomes similar to that always adhering to the membrane (interelectrode acting as an anode).

The results obtained further indicate that the tetravalent uranium ions in the solution do not have the form of the oxyion UO^{2+}, as has been supposed in some cases [15].

As part of the systematic investigation of the properties of tetravalent uranium we made an attempt to determine the luminescence spectra of the U^{4+}_{aq} ion, because at a sufficient concentration of U(IV) (greater than ~0.3 M/l), with adequate layer thickness, and at a low uranyl ion concentration (below ~3%), the solutions of U^{4+}_{aq} are dark violet in colour (from weak colour shades to intense violet) [16]. This was observed a long time ago [17]. It is usually reported in the literature that U^{4+}_{aq} ion is not luminescent, but this statement is based on indirect data. Our direct experimental results indicate that the ion mentioned cannot really emit luminescent radiation; the unusual violet colour described unquestionably exists but may be explained on the basis of light absorption. In principle, the change in the intensity of individual absorption bands of U^{4+}_{aq} ions is not linearly proportional to the layer thickness or U(IV) concentration (in agreement with the Lambert-Beer law), which results in changes of relative intensity of the individual absorption bands thus determining the resulting colour impression.

(c) Study of the growth and chemical changes of hydroxidic particles

Preliminary experiments on the hydrothermal processing of the green precipitate were carried out in stainless-steel pressure vessels at temperatures up to 250°C and at time exposures up to 5 days.

If the suspension was used, formed by mixing UCl_4 solution with ammonia without removing NH_4Cl electrolyte from the mother liquor, the resulting product was black (not due to oxidation since the ampoules were sealed) and of semi-soft consistency. If the electrolyte was removed by means of repeated washing with water and the precipitate was peptized in HCl (in most cases in the ratio 3 H^+ per U(IV)) so that it contained no neutral electrolyte, after hydrothermal exposure a product was obtained having considerably different granulometric and chemical properties. In extreme cases, brown and very well developed crystals of UO_2 resulted (determined in an optical microscope, by X-ray analysis, and by i.r. spectra).

We intend to carry out these experiments systematically to determine the effect of the preparation conditions on the granulometric properties of the precipitate both after separation from the suspension and after its thermal processing when decomposition to UO_2 results.

(d) Chemistry of various uranium valence states and their interaction

Since the chemistry of uranyl hydroxy complexes was studied in our laboratory [5, 18, 19], and the chemistry of uranium (IV) is the subject of section (b), this step deals mainly with the chemistry of the uranyl ions. We want to determine its tendency towards hydrolysis and some properties of the hydroxidic precipitate (see section (b), first paragraph). The preparatory stage is finished and we are starting with experimental work.

(e) Some aspects of electro-reduction

In the Research and Development Laboratories of the uranium industry the uranium (VI) electrolytic reduction process in carbonate medium was investigated on the basis of Yugoslav experience (K. Štamberg is responsible for this research) [1, 20]. In addition, the problem of reduction and precipitation in relation to the material of the cathode, the composition of the starting solution, stirring the catholyte, the current density, the temperature, etc., was studied. Some interesting observations were made of, for example, the influence of the material of the cathode in connection with current density upon the process of reduction and precipitation which can be performed either merely in the direction of uranium (VI) reduction (amalgamated copper, c.d. about 4 A/cm^2, current efficiency up to 80%) or in the direction of the precipitation of uranium (VI) in the form of uranates (stainless-steel, c.d. more than 4 A/cm^2). The use of the amalgamated copper cathode seems to be distinctly more favourable in comparison with the rotating mercury electrode [20] because of greater simplicity, and hence reliability, of the reduction cell. In addition its stability is sufficient, because when it is kept in carbonate solutions the current efficiency of the reduction of a standard solution is not lowered for about 15 days.

The precipitation process is considerably influenced by temperature in agreement with literature data [1]. The concentration of sulphate ions also plays an important role, e.g. near the value of 100 g SO_4 per litre at room temperature they stabilize the uranium (IV) sols. The stabilizing effects quoted are diminished at elevated temperatures and are completely suppressed at about 80-85°C.

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STATUS REPORT FROM ITALY
Sol-gel research and development

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Abstract

STATUS REPORT FROM ITALY: SOL-GEL RESEARCH AND DEVELOPMENT. Our interest in sol-gel materials for application in nuclear technology largely stems from the following factors:

- the ability of sol-gel processes to produce fissile or fertile materials (or a homogeneous mixture of both), the density of which can be brought close to the theoretical value by sintering at low temperature,
- their unique capacity to produce these materials in the form of microspheres of desired dimensions having superior strength, smoothness and sphericity, these combined properties make them ideally suited for the production of fuel rods by low-energy vibratory compaction.

Sol-gel activities in Italy are therefore primarily intended for high-temperature gas reactor fuels (i.e. fuel kernel dispersed in a graphite matrix) and for the development of fast breeder fuels (i.e. vibratory compacted pins).

Two organizations are active in the sol-gel field in Italy; the 'Comitato Nazionale per l'Energia Nucleare' (CNEN) and the 'SNAM Progetti S.p.A.', a company of the ENI holding. Two different processes have been developed independently. Recently, however, it was decided to explore jointly the application of the SNAM method to the production of mixed urania-plutonia microspheres. This paper reports on these activities, CNEN research and development being described in greater detail. A wealth of information on sol-gel was released in autumn 1967 in connection with the symposium on sol-gel processes held in Turin, this paper is largely based on that material and has been brought up-to-date with some recent results. Research on sol-gel follows parallel lines which include:

- basic chemistry of actinides in colloidal solution, and the mechanism of gelification and sintering,
- process chemistry and establishment of flow-sheets,
- process development and research on specific unit operations,
- product evaluation, irradiation testing, economics.

A description is given of the results so far achieved in these different areas.

1. BASIC CHEMISTRY

Different though they can be with regard to the route to colloid formation and conversion to gel, all sol-gel processes boil down to the following steps:

- preparation of an oxide hydrosol solution;
- conversion of the colloidal hydrosol into a gel (this is normally coupled with an operation aiming at conferring a suitable shape and dimension to the product);
- thermal treatment to promote a sintering to a high density oxide and, in a few cases, to convert chemically the oxide to a different final product.

Each step involves a thorough understanding of the related physical chemistry of the system and an accurate analysis of the complicated phenomena which take place. Besides improving our scientific knowledge this can open the way to a better product.

Undoubtedly there must be a relation between the structure, and hence the properties, of the final products and the structure of the gel; this in turn could also be related to the hydrosol.

Several methods are available for the hydrosol preparation; depending on the mechanism of the colloidal particle formation they fall into two general categories of 'dispersion' and 'condensation'. Peptization of an amorphous hydroxide obtained by precipitation is a typical dispersion method involving the fragmentation of a rather large unit to colloidal size.

Other routes to sol preparation, including dialysis, ion exchange, solvent extraction, and controlled neutralization, are typical condensation methods involving the nucleation and growth of particles to the micelle size.

The size and shape, in other words the morphology, of the micelles in the sol are currently being investigated at CNEN by electron microscopy, low-angle X-ray diffraction and turbidimetry: these techniques were applied to investigate possible morphological differences in sol particles obtained by dispersion or condensation methods and also to obtain information on particle growth due to heating and/or aging.

Preliminary results obtained on thoria and urania sols agree well with previously reported data. In particular, an analysis of sols obtained by long chain amine extraction of nitric acid from nitrate salts gave the following results:

- The size of colloidal particles obtained by dispersion methods, that is, by breaking a precipitate to colloidal size by means of a chemical agent, seems to be smaller than the size of particles obtained by a condensation method.
- The degree of polydispersity shows that in the dispersion methods the particle size is variable as compared with the size of particles obtained by condensation methods.
- Heating and aging promote a growth in the size of the particle as a consequence of the increase of hydrolysis and polynucleation; concurrently a decrease of the degree of polydispersity is noticed, indicating a trend to a more uniform particle size.

More generally we now believe that the choice of a specific method for the preparation of a hydrosol should be dictated more by technical and economic considerations than by basic chemistry requirements; in fact tools are available to control the particle size efficiently and to measure it.

The conversion of a hydrosol into a gel requires the formation of a network which reduces the degree of freedom of the molecules. This can be achieved either by the removal of water from the sol or by the removal of a stabilizing anion, which is probably followed by a condensation reaction. This latter route has been adopted for CNEN processes as a consequence of the relatively high nitrate concentration in the hydrosol. To remove nitrate ions use is made of the anion exchange capacity of long chain aliphatic amines; the gelation takes place through an amine salt formation

$$-\overset{|}{\underset{|}{\mathrm{Th}}}\mathrm{NO_3} + \mathrm{H_2O} + \mathrm{RNH_2} \rightleftharpoons \mathrm{RNH_3NO_3} + -\overset{|}{\underset{|}{\mathrm{Th}}}\mathrm{OH}$$

A tentative scheme of the gelation mechanism under typical CNEN process conditions is given in Fig. 1 and Table I. Nitric acid is transferred through the interphase while the water content in the droplet remains practically unchanged. As a consequence:

- the Z number (i.e. the average hydroxyl number per atom of heavy metal) is increased from 3-3.5 to a value approaching 4;
- since the water content of the droplet is unaffected by the gelation process no shrinkage occurs and the density remains practically unchanged in the conversion from sol to gel.

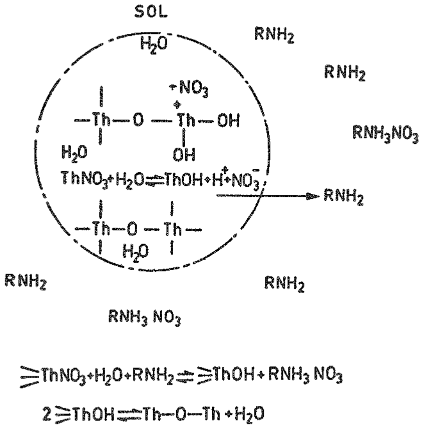

FIG.1. Tentative scheme of gelation mechanism under typical CNEN process conditions.

TABLE I. TYPICAL CHANGE IN COMPOSITION OF A 400 μm (RADIUS) MICROSPHERE DURING GEL FORMATION

	Colloidal (g)	Gel (g)
Th	6.4×10^{-5}	6.4×10^{-5}
NO_3	8.6×10^{-6}	1.7×10^{-6}
OH	1.6×10^{-5}	1.8×10^{-5}
H O	3.27×10^{-4}	3.27×10^{-4}
	4.16×10^{-4}	4.11×10^{-4}
	(sol density 1.5 g/cm^3 NO_3/Th $\simeq$ 0.5)	(gel density 15 g/cm^3, NO_3/Th $\simeq$ 0.1)

This latter aspect has important consequences for the process equipment, since the variation in density occurring during gelation in other processes is normally utilized for collection of the product at the bottom of the gelation column.

In the CNEN process a suitable time must elapse for gelation to be completed and to confer an acceptable mechanical strength to the spheres. The need of this digestion is attributed to a slow reaction rate. Research is under way to identify this rate-determining process; either the nitric acid diffusion across the boundary or the condensation reaction could be responsible for this slow rate of reaction.

We have no information so far on possible variations of the particle size during the gel formation process; if condensation reactions occur, a particle size growth is very likely. The presence of impurities has also to be carefully considered: in fact amines are surface active agents which could interfere with the particle growth rate during gelation and in the succeeding steps.

2. FLOWSHEET DEVELOPMENT

The main effort in sol-gel process development at CNEN is now directed towards the preparation of urania and mixed urania-plutonia oxides for fast reactor fuels. However, extensive research has also been carried out on thoria, thoria-urania, and thorium-uranium carbides. Pilot experiments have shown the suitability of sol-gel techniques for production of uranium nitrides. Future programs include research on uranium carbide and mixed uranium-plutonium carbides and nitrides.

(a) Sol preparation

All the above-mentioned processes have in common, in their first step, the preparation of a hydrous-oxide or oxide hydrosol: the nitrate-to-metal ratio in this sol ranges from 0.4 to 1.5. The sols are normally prepared by contacting aqueous solutions of the nitrate salts of uranium, plutonium and thorium with a water-immiscible solution of a long chain aliphatic amine. By selecting the volume ratios and the concentration of the amine, a controlled extraction of nitric acid takes place across the water-organic interphase, causing the formation of highly hydrolized species in the water phase. In some cases water is subsequently removed by distillation to improve the sol formation and/or to increase the concentration. Small quantities of metal ions are also extracted by the amine phase; these are easily recovered and recycled in the solvent clean-up operation.

In the case of uranium the nitric acid extraction takes place directly on the initial uranyl nitrate solution and the tetravalent uranium sol is obtained by catalytic reduction of the acid-deficient hexavalent uranium solution.

Mixing preformed sols of thoria, urania (IV), and plutonia in the 3-4 M concentration range is a suitable method for preparation of homogeneous binary mixtures of heavy-metal oxides in practically all proportions. That is, sols obtained by amine denitration are fully compatible and no precipitation occurs for a reasonable period.

In the case of mixed uranium-thorium oxides, when the thorium-to-uranium atom ratio is higher than 7, an easier route to sol production is followed by direct amine extraction of nitric acid from a starting solution which contains both thorium and uranyl nitrate. In this way the reduction of hexavalent uranium is avoided and, furthermore, a straightforward process is available to refabricate thorium-uranium fuels without separation of these two elements in the reprocessing step.

A selection of processes is outlined in Figs 2 and 3. They apply, respectively, to the preparation of thoria, thoria-urania, urania and plutonia sols.

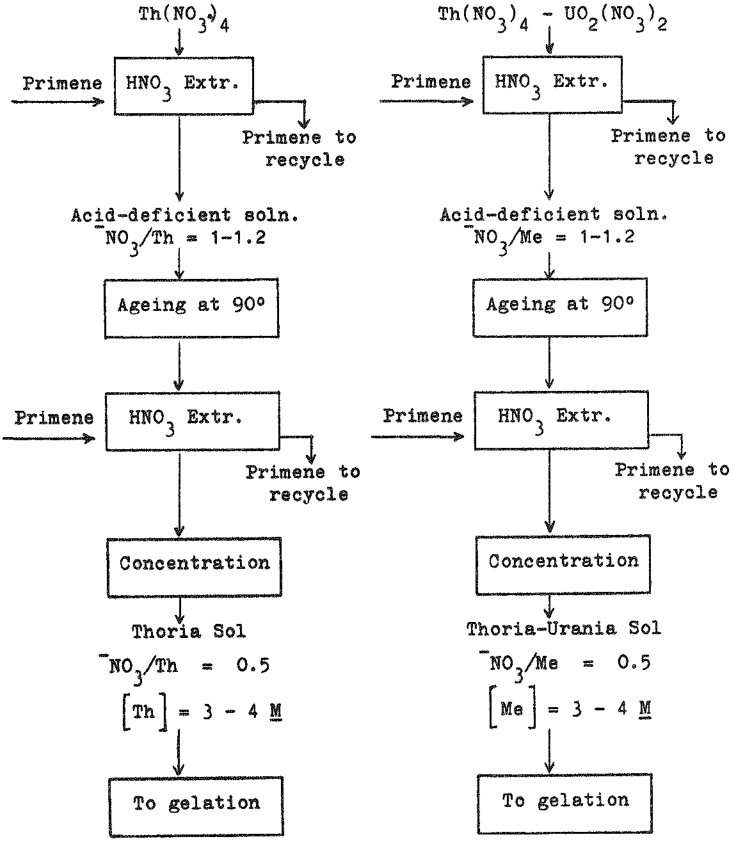

FIG.2. Preparation schemes for thoria and thoria-urania (Th/U > 7) sols.

Primene JMT is a low-cost, commercially available primary aliphatic amine: a 50 vol.% solution in an inert hydrocarbon is used as nitric acid extractant. Solvesso 100, a low-cost, high flash-point aromatic naphta, is used as diluent. The denitrations are usually performed in a single-stage mixer-settler with residence times of about two minutes.

In the case of thoria and mixed urania-thoria sols, nitric acid extraction is performed in two separate steps. In between, an aging of the acid-deficient solution at 90°C is provided to speed up hydrolytic processes. It was found, in fact, that precipitation occurs if one tries to lower the $^-NO_3$-to-metal ratio to less than unity in a single step.

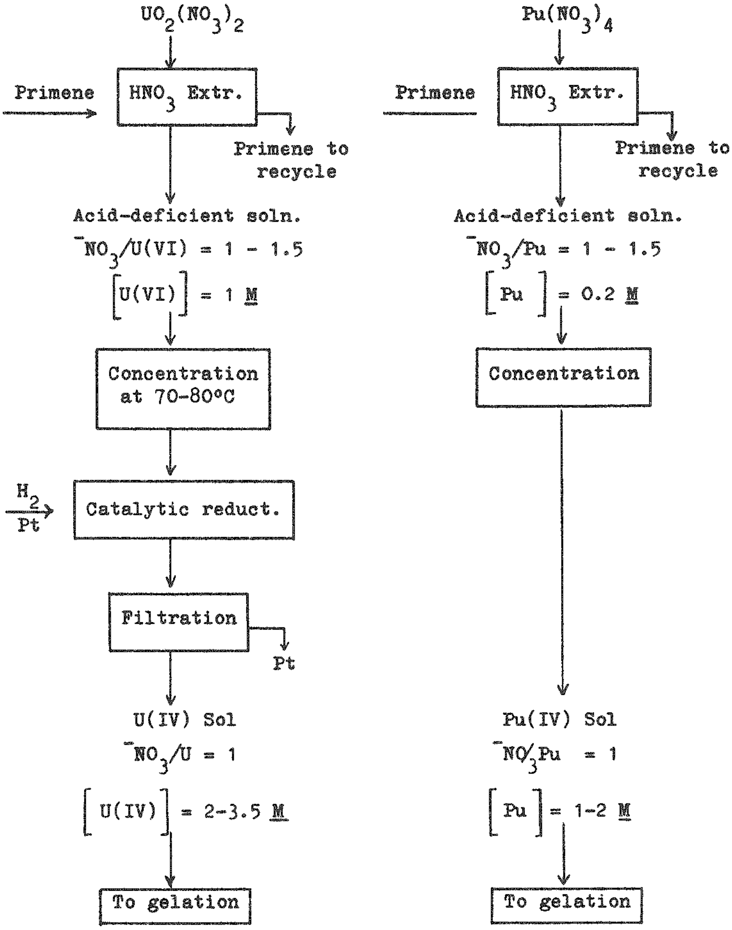

FIG.3. Preparation schemes for urania and plutonia sols.

As already mentioned, when the thorium-to-uranium atom ratio is lower than 7 better results are obtained by mixing preformed thoria and urania sols. This is because, when applying the method of Fig. 3 to higher uranium concentrations, a highly viscous sol is obtained which causes difficulties during dispersion.

In the urania sol flowsheet (Fig. 3), as pointed out previously, the first step is the preparation of an acid-deficient solution of uranyl nitrate; normally an initially 1 M UNH feed is brought into contact with the amine solvent until a final $^-NO_3$-to-U(IV) ratio of 1.5 is obtained. This acid-deficient solution of uranyl nitrate is evaporated to 3 M and then undergoes reduction under closely controlled conditions. Hydrogen under pressure and alumina-supported platinum catalyst are used; this process leads simultaneously to the U(VI)$\longrightarrow$ U(IV) reduction and to the formation of the sol which is then ready for gelation.

Reduction is a delicate process that must be carefully controlled; the penalty for inefficient control can be either the precipitation of U(IV) hydroxide when reduction is still under way or a sudden gelation of the final reaction product. The first type of accident occurs when the reduction rate is low and can be avoided by a proper choice of temperature, pressure and stirring. The second is attributed to a massive reduction of the nitrate ions, yielding nitrogen oxides and, eventually, ammonia, and is favoured by a rise in temperature, by the presence of some impurities (such as copper) and, above all, by pushing the reduction too far.

In selecting a process for plutonia sol production we avoided the peptization of plutonium hydroxide which involves precipitation, filtration washing and, in general, typically discontinuous operations. Again, amine solvent extraction of nitric acid on freshly prepared Pu(IV) nitrate solution was adopted. 0.2 $\underline{M}$ solutions of Pu (NO_3) are solvent extracted until an $^-NO_3/Pu$ value approaching 1 is obtained. Pu(IV) polymer formation readily takes place, as indicated by a sudden change of the colour from brown to dark green. The diluted sol is then concentrated to 2 $\underline{M}$ by evaporation.

Slight variations in the above-mentioned sol preparation procedures are required if the final product is to be carbides or nitrides. In this case appropriate amounts of carbon black must be added to the sol. In this way, after gelation a carbothermal reduction yields dense carbide microspheres; if the reduction is carried out in a nitrogen atmosphere at elevated temperature the final product is a nitride:

$$UO_2 + 2C + \tfrac{1}{2} N_2 \rightleftharpoons UN + CO$$

(b) Gelation

Since the main objective of CNEN is the evaluation of sol-gel products as a fuel suitable for low-energy vibratory compaction, efforts are primarily directed towards the production of microspheres. This implies the choice of a gelation process based on the well-known droplet dispersion technique.

In considering the gelation of the sols described previously one must bear in mind the relatively high nitrate ion content of the sols. The excess nitrate must be removed during gelation to avoid trouble in the thermal treatment. This is achieved in the CNEN method by dispersing sol droplets in a medium in which the presence of small concentrations of a long chain amine causes a slow extraction of the residual nitrate of the sol across the boundaries of the drop. Retrieving the residual nitrate from the sol drop determines, in fact, gelation.

The dispersing medium utilized for gelation is Alphanol 79 (a commercially available mixture of long chain alcohols manufactured by Shell) which has been saturated with water and to which 1 to 2 vol.% Primene and 0.5% surface active agent (Span-85) have been added. Previous water saturation of the solvent helps to prevent dehydration (which would interfere with nitrate extraction); the surface active agent is used to avoid coalescence and sticking phenomena.

Sol dispersion methods vary according to the required final diameters of the microspheres. For a smaller sized product (100 μm or below) a kind of emulsion is formed of the sol in the gelating solution. A baffled cylindrical vessel supplied with a mechanical blade-type stirrer is currently

TABLE II. N/U ATOM RATIO IN SOL AND CORRESPONDING GEL

Sample No.	U(IV) Sol	UO_2 gel
1	1.43	0.158
2	1.37	0.134
3	1.31	0.180
4	1.31	0.07
5	1.31	0.05

used. If a higher fraction of fine product is desired the amine is added to the preformed emulsion. Gelation takes place within a few minutes.

For a final diameter greater than 100 μm a tapered column of the ORNL type is used. Gelation, however, must be performed batchwise, since no variation in density occurs and gelled spheres cannot therefore be collected by gravity. In Table II a comparison is given on the average composition of the product (in this case uranium) before and after gelation.

The product is thoroughly washed with an organic solvent, usually acetone, to remove contaminants of the gelation liquid and, at the same time, to remove most of the water. Drying with a stream of dry air has been found the most effective way to obtain a free-flowing product. The density of the spheres increases from 1.5 to approximately 5 g/cm^3 as a consequence of dehydration. The accompanying volume reduction does not cause cracks and leaves a very smooth surface.

(c) High-temperature treatment

Firing of the gel product to the final high-density oxides is effected in furnaces under an appropriate atmosphere (usually 4 vol.% hydrogen in argon) with a programmed temperature cycle. If good quality spheres have been obtained in the gelation this sintering step is simple and straightforward. Normally a heating rate of 200-300 degC/h is applied until maximum temperatures of 1100°C-1200°C are reached. A couple of hours later the cooling cycle begins. A slow rate of cooling is maintained from the maximum temperature to 900°C, then it increases until at 600°C the furnace is shut off and allowed to reach room temperature. Sintered microspheres display an excellent sphericity (up to approximately 700 μm) and density values in excess of 0.99, the theoretical density. A slight decrease in the density value is observed for urania-plutonia when the plutonium content exceeds 15%. Crushing strength is also very good (6-7 kg).

Carbon is the main impurity introduced in the course of the process. The final content of carbon in the product depends critically on the effectiveness of the gel-washing step. Product specifications indicate that the carbon level can be easily brought down to the 30-50 ppm range.

3. PROCESS DEVELOPMENT

Work in progress on the development of fabrication processes is dealt with in this section, based on hitherto unpublished data. Major stress is laid on a limited number of specific problems to be solved prior to pilot-plant scale operation. These are a high-speed sol feeder, a gelation chamber specially suited to the process and an apparatus to produce, on a continuous basis, small-diameter microspheres to be used as fine fraction in low-energy packing.

To operate prototype equipment of this kind a sizable supply of sol solution is required; it was therefore decided to set up a small pilot unit for the production of a few kilograms per day of 3 M U(IV) sol.

(a) High-speed sol feeder

Several more or less conventional devices have been taken into consideration, such as rotary feeders, two-fluid nozzles and pressurized injectors, but none has given satisfactory results. An ideal sol-feeder should in fact possess the following features:

- high speed, that is, high volume of sol delivered per unit time in the form of drops;
- low dispersion of drop diameter around a preset diameter (range 300 to 1500 μm);
- ability to use multiple units in a single gelation chamber.

Recently a vibrating membrane gravity feeder was successfully tested. The principle of this device is simple: a stainless-steel membrane in contact with the sol is mechanically vibrated at 45 Hz. The combined effect of gravity and vibration accelerates the formation of regular droplets falling from a battery of needles at the bottom of the reservoir. The diameter of the drop is a function of both frequency and width of the vibration and also of the needles' internal diameter. Preliminary results have shown that a feeding rate corresponding to 100 g of U per hour and per needle can easily be obtained. It was also shown that the feeder capacity is a linear function of the number of needles fitted to a single feeder. A very low dispersion in diameter was further observed; yields in excess of 90% of gelled particles were obtained, the dimensions of which were within a single sieve range.

(b) Gelation chamber

As previously mentioned, gelation is effected batchwise in ORNL type tapered columns. The use of columns of this type is not recommended for a pilot production unit because of the low throughput and excessive vertical dimensions. A chamber affording a continuous process is therefore being designed. No details are available so far, but it can be anticipated that sol droplets will be forced to move slowly along a kind of labyrinth in co-current with the gelating medium. At the end of their path the sol to gel conversion will be completed and microspheres will be continuously collected and removed.

(c) Continuous production of the fine fraction

Prototype equipment for the continuous production of small-diameter microspheres (10 to 50 μm) is being tested. In principle it consists of a cascade of communicating small-diameter cyclindrical vessels. Each chamber is provided with a variable-speed blade stirrer. Water-saturated Alphanol and the sol are separately fed to the first chamber. Under continuous stirring the resulting emulsion overflows to the next chamber where a diluted solution of the amine in Alphanol is introduced by a pump. Gelation occurs and the residence time is regulated by a number of similar cells in which the product overflows. After the last chamber the product is collected, washed with acetone, dried and fired. By a suitable choice of the feeding point of the amine and of the stirring conditions, fine fractions centred around preset diameters can be produced. Experiments are in progress but it has already been possible to obtain over 50% by weight of a product with a diameter range from 30 to 50 μm.

4. PRODUCT EVALUATION

A development program to assess the economics of production and the basic irradiation performance of sol-gel fuels was started at the end of 1967.

A preliminary economic evaluation of the fabrication of sol-gel microspheres will not be available before the end of 1968 and will be based on the extrapolation of data from a small-size production unit, now under design, to be installed in a new plutonium-fuel fabrication facility now under final commissioning at the Casaccia Research Centre. This unit will consist of two separate lines. The first, to produce larger spheres (i.e. 500 to 900 μm in diameter), will utilize a process jointly developed by CNEN and SNAM for mixed urania-plutonia and will be based on the SNAM process. The second line will be devoted to the production of the fine fraction (below 40 μm) and will adopt a CNEN flowsheet. Both lines are designed for continuous type operations.

An irradiation program on sol-gel material was established last year involving two different classes of experiment. The first consists of long duration irradiation tests in the Halden reactor on test assemblies and capsule rigs aiming at determining the performance of sol-gel fuels as a function of fabrication variables and in comparison with pelletized fuel. In parallel, at the Studsvik reactor in Sweden short-term irradiation experiments are being carried out to investigate in-pile structural variation of the oxides and in particular to determine the minimum in-pile residence time to achieve a stabilized structure as a function of power density. The program includes a total of seventy irradiations of different samples. So far twenty samples have been irradiated but no information is available pending the results of post-irradiation analyses.

ACKNOWLEDGEMENTS

The work on sol-gel processes reported in this paper was carried out by a team. While it is impractical to mention so many people the author would specifically like to acknowledge the contributions of P.R. Danesi, A. Bazzan, M. Magini and R. Chiarizia for basic chemistry research; G. Cogliati, E. Mezi, R. Lanz, V. Lupparelli, P. Maltzeff and A. Recrosio for flowsheets and process development; G. Testa and

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STATUS REPORT FROM THE NETHERLANDS
Sol-gel fuel studies

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Abstract

STATUS REPORT FROM THE NETHERLANDS: SOL-GEL FUEL STUDIES. In the KEMA laboratories at Arnhem, three sol-gel processes have been developed for the production of uranium-containing thorium oxide·

- the external alkaline gelation process for fuel particles smaller then 25 μm;
- the internal alkaline gelation process applicable to particles up to a few millimetres (an ammonia donor is used in the sol);
- the hot gelation process, which is based on a dehydration by water emulsification at high temperature.

The processes are described in some detail in the paper.

A large number of physico-chemical problems is involved in processes of this type, and studies of a more scientific nature have therefore been performed to understand the underlying chemistry. Some of the most interesting aspects are reported in a separate section.

Industrial interest in the sol-gel processes for nuclear fuel is growing in the Netherlands under the stimulation of the electric power producers, who consider the sol-gel route as a potential source of savings in the fuel cycle costs.

1. INTRODUCTION

At the beginning of 1959 the necessity arose in the KEMA Suspension Test Reactor Project at Arnhem (Netherlands) to have mixed $UO_2.ThO_2$ powders available with particles 5μm in diameter and spherical in form. A process was developed during that year based on the strong tendency towards pseudomorphic behaviour of heavy metal compounds and on the sphericity of a droplet, dispersed in a second liquid. The principle of this technique had been known for years in the production of catalysts, but to our knowledge it had never been applied successfully to nuclear fuel materials.

In this process the gelling of the sol droplets is effected by the action of ammonia diffusing from the surrounding organic medium. This technique of external alkaline gelation limits the application to spheres of a rather small size: 3-25 μm.

The importance of this type of process, which yields a well-defined product of a high thermal reactivity, a controlled, rather narrow size distribution and an attractive range of compositions, had been recognized meanwhile in Oak Ridge National Laboratory. Accordingly, the development of particles of a larger size was started with the intention of applying them as coated fuel in matrix elements or for vibratory compaction.

During this development the principle of alkaline gelation was preserved for most of the work. For reasons which will become evident in a more detailed discussion of the process, this led to the application of the so-called 'internal gelation', where the ammonia is generated from a donor inside the sol droplet. This process was partly developed under a contract with the Dragon Project. It allowed the preparation of oxide spheres of ThO_2, containing up to 15% UO_2, with a size range of 100-700 μm. By incorporating carbon in the sol, carbides could be made. Further studies were performed to increase the U/Th ratio to about unity, to increase the size of the carbide particles to about 3 mm and to clear up a number of more fundamental physico-chemical problems in the process. Furthermore, the achievements in other laboratories (ORNL for dehydration gelation, CNEN for pure uranium oxide and for the application of primary amines for anion extraction) were included in our studies to obtain a simplification of the processes. At present the work is aimed at the production of UO_2 spheres, preferably without a reduction of the U(VI) before the final heat treatment. Such a process would evidently be very attractive for large-scale production. Although encouraging results have been obtained so far, the process is not yet complete.

The production of sol-gel fuel has been on a semi-technical scale only in the Netherlands, to meet the needs of the present project and to demonstrate the feasibility and reproducibility of several variations on a kilogram scale.

The industry in the Netherlands has started to show a profound interest in undertaking production on a technical scale in the near future.

At the Reactor Centrum Nederland, experiments have been started to use sol-gel fuel in vibratory compacted elements for irradiation testing. No irradiations have been performed yet. The programme is supported by the Netherlands electric power producers.

In this paper three processes developed in the Netherlands are described in broad outline. Thereafter a number of interesting physico-chemical studies are reported, which illustrate the significance of a number of process parameters.

2. KEMA SOL-GEL PROCESSES

Each process is divided into a number of steps, such as sol preparation, dispersion, gelation, washing, etc. For each step several techniques can be applied. Consequently, there is a large number of variations, from which a choice has to be made according to the specific requirements of the process or the final product.

The method of gelation seems to be most characteristic, although recent developments have shown that the sol-preparation technique can be of equal importance.

A sol can be gelled in principle by dehydration or by raising its pH. Both methods have been applied for the KEMA processes.

These processes, which are all based on ThO_2 sols and gels, containing uranium and/or carbon as additives, are described here.

2.1. The process of hot dehydration

The sol is prepared in all three processes by precipitation of the respective nitrates with ammonia, followed by washing by means of decantation, and peptization with acid. The sol is then dispersed into an organic phase, which in this case shows no dehydrating properties per se. The dehydration is attained by the emulsification of water from the sol droplets into the organic medium. To this end an emulsifier of the water-in-oil type is applied in the organic liquid. For the non-aqueous phase, kerosene (B.P. 150-170°C) with a combination of 0.2% Atlox 4858 and 0.2% Tegomuls M can be used successfully. The temperature is kept at about 90°C. At this temperature the water-in-oil emulsion is not stable and thus breaks. The water separates from the organic medium. Where a heavy organic liquid such as tetrachloroethylene is used the water can evaporate from the surface of the organic liquid. The gel spheres are withdrawn from the system and treated further. After drying and sintering good spheres are obtained. The advantage of the process is that neither a regeneration of the organic phase nor a washing step is required.

2.2. External alkaline gelation

This process was the first to be developed to produce fuel spheres. The sol is obtained in the way described in section 2.1. After dispersion, gelation is achieved by ammonia which is dissolved in the organic medium and which diffuses into the sol droplets. The gel spheres are dried in the organic phase by distilling off the water, washed to remove the ammonium nitrate, calcined and sintered.

The process has been applied in the preparation of considerable amounts of 5 μm $UO_2.ThO_2$ (U/Th = 1/6) spheres for the KEMA Suspension Test Reactor Project.

Instead of NH_3 gas dissolved in the organic liquid, an ammonia donor can also be used for gelation, for example hexamethylene tetramine and urea, which in this case are dissolved in the organic medium. At an increased temperature the donor produces ammonia at a controllable rate. This method is very convenient for the incidental preparation of small batches of fuel spheres.

It appears that the method cannot be applied to particles with a diameter greater than 25 μm, because osmotic imbalances result, causing severe deformation or cracking in later stages of the process, especially during the drying procedure.

Another process was therefore developed, which is suitable for particles of greater size.

2.3. Internal alkaline gelation

To prevent concentration gradients in the sol droplets, which cause the osmotic interferences mentioned in section 2.2., ammonia is added to the sol in a masked form, e.g. as hexamethylene tetramine and urea, and then gradually set free throughout the sol droplet by increasing the temperature of the organic medium. The medium may be slightly dehydrating, but does not have to be, provided that minor adjustments are made in the process.

For particles up to a size of about 700 μm Alphanol-79 has been used successfully, and the temperature of the process was varied between 50°C and 60°C, depending on the water content of the Alphanol.

A special variation of this process was developed for the production of particles of about 3 mm. In this case some additional problems have to be solved:

- the sol drop size must be extremely large, the shrinkage factor being about 2-2.5 linearly;
- the shape of the drop must be preserved during the solidification.

To reach this goal, an organic medium has first to be chosen with a high density and with a high interfacial tension towards water. The presence of an emulsifier must be carefully avoided. Tetrachloroethylene (density 1.52 g/cm^3, interfacial tension 37 dynes/cm, both at 90°C) proved to be a good choice. Secondly, the solidification of the droplet must be rapid. This could only be attained by again using the internal gelation technique at an increased hexamethylene tetramine concentration and at an increased temperature (90°C).

Particles in the millimetre range have been produced with this method routinely and in sizeable quantities.

3. OTHER PROCESSES

A number of procedures developed in other laboratories were tested and sometimes modified to suit our specific interests. Among the most important are:

- The application of liquid-liquid extraction with Primene J.M.T. for the removal of anions from the salt solution (sol production) or from the sol (gelation). This process, originating from CNEN, appears most promising for production purposes.
- The modification of the process for the production of pure UO_2. On the one hand, the CNEN and ORNL techniques of catalytic reduction of uranyl salts are being studied for this purpose, on the other hand work is being performed to produce UO_3 spheres, because it seems most advantageous to avoid the reduction of U(VI) to U(IV) in the liquid phase.

4. SOME PHYSICO-CHEMICAL ASPECTS OF SOL-GEL PROCESSES

In the course of developing the different sol-gel variations in the Netherlands, some physico-chemical aspects of the processes were encountered which needed further investigation. As the studies are concerned with rather general problems in sol-gel processes, the most interesting have been collected in this separate section of the paper.

It is the strong conviction of the authors that a profound knowledge of the physico-chemical background of the processes is required to optimize the separate steps for production application.

4.1. Sol preparation

4.1.1. Precipitation and peptization

It is felt that a close relationship exists between the method of precipitation and the peptization. Strong indications have been found in a study of the rate of peptization as a function of the NO_3/Th ratio. For this study a precipitate of hydrous thoria was used, obtained by adding a $Th(NO_3)_4$ solution to concentrated ammonia. The precipitate was washed by decantation with dilute ammonia and water, respectively. The resulting solid proved to be X-ray amorphous.

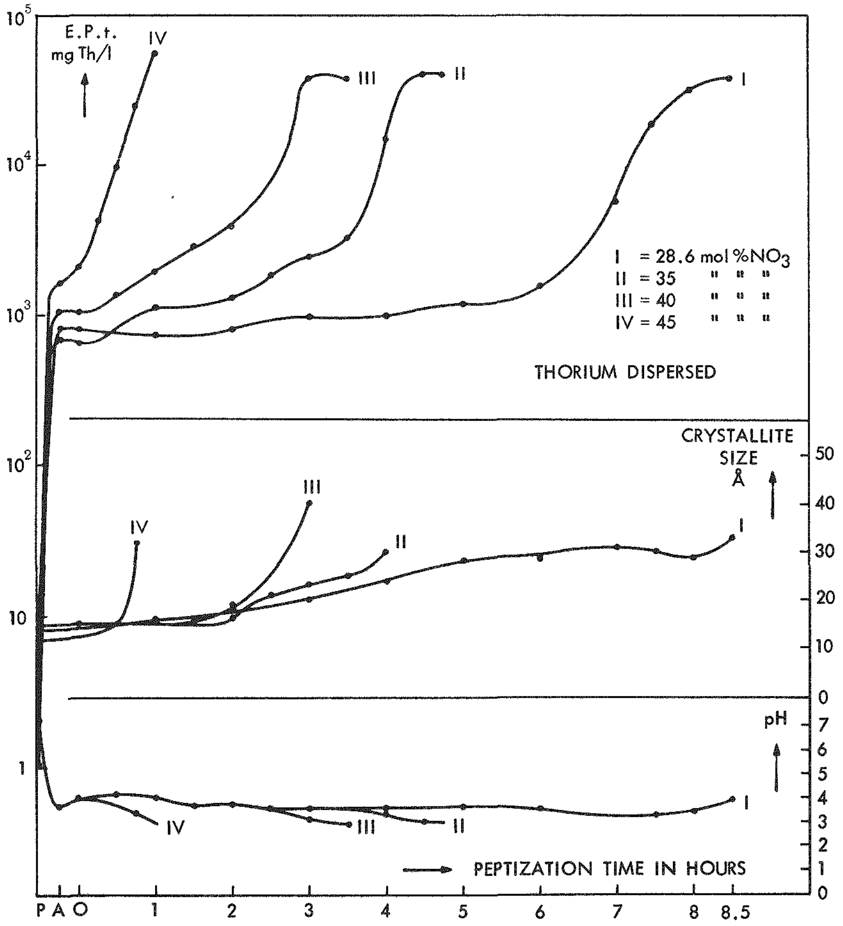

FIG. 1. Results of measurements of mean crystallite size plotted versus time.

By the addition of nitric acid, the NO_3-to-Th ratio was adjusted, and the peptization was carried out by boiling. During this procedure samples were taken from which, after centrifugation, the supernatant was isolated. In this the amount of thorium and the pH were determined. In the sediment the mean crystallite size was measured on the basis of X-ray line broadening. The results are plotted versus time in Fig.1.

Each of the dissolution-peptization curves (Th concentration versus time) shows a fast initial increase of the thorium content of the liquid, but then the rate slows down. After an induction period, however, a steep rise is observed again, which leads to complete peptization. From the rate of crystal growth and the rate of peptization it is evident that a close relationship exists between those phenomena, and that both increase with increasing nitrate-to-thorium ratio.

In our opinion this behaviour has a direct bearing on the maximum sol concentration and on the sol stability, as we hope will be clear from the following.

The significance of the nitrate ion in these oxidic sol systems is indirect and twofold:

(1) Its concentration is a measure - in the present situation - of the acidity, and therefore bears a certain relation to the colloid chemical stability of the sol, which in fact is determined by the hydrogen ion concentration. The hydrogen ion concentration controls the degree of dissociation of water ligands in the surface of the thorium oxide. The amount of acid, and thus the nitrate concentration required for stabilization of a sol, will therefore depend on the total solid surface present.

(2) The acid present - for which the nitrate ion concentration is a measure - determines the amount of dissolved thorium and consequently the rate of crystal growth. In this mechanism, the nitrate groups which are still present on the surface of the crystallites play an important role.

With these two principles in mind and with the knowledge that in a stable sol there is a minimum distance between the sol particles, the graphs can be understood.

Initially the precipitate is X-ray amorphous, consisting of extremely small primary particles. The addition of acid will at once dissolve part of the precipitate and, possibly, peptize another part, but the amount is limited because local flocculation occurs as soon as the distance between the particles becomes too small in a certain part of the system. This means that a dynamic equilibrium is set up between the sol and the residue. The nitrate, however, enhances the growth of the primary particles, which means that with the same inter-particle distance more solid can be accommodated in the sol. At the same time the nitrate ion concentration increases slightly because of a decrease of the total solid surface and the rate of the process increases.

In our opinion the final sol consists of crystallites which are still less crystalline at the surface. This might be responsible for the linking of the crystallites in an alkaline gelation.

From this hypothesis it can be predicted that increasing the nitrate content means faster crystal growth and thus faster peptization, but at the same time a lower stability of the final sol. Furthermore it must be expected that not all anions show this influence to the same extent.

A further conclusion is that there may be a shift of the optimal nitrate ion concentration to lower values towards the end of the process. After the nitrate has served its purpose for crystal growth, it could be removed to some extent if this would be advantageous to further processing. Examples have been encountered.

It is known that some oxides such as PuO_2 do not form crystals readily, and even after they have done so the growth of the crystallites is extremely slow. Unless measures are taken, this will result in sols of low concentration, which, of course, can hardly be concentrated by evaporation. Measures to increase the concentration might be:

- increasing the solubility of the oxide by the addition of a suitable anion in the peptization step;
- precipitating the plutonium under conditions where fewer nuclei are formed, such that the initial crystal size is larger;
- applying an aging step in water, if necessary at a temperature above 100°C.

The success of these measures has been demonstrated.

From the above it will be evident that an optimum has to be found in sol production where fast sol preparation is possible without endangering the stability of the sol during the process and without hindering the subsequent treatments. A sol which, for example, has been acidified too far could not be gelled by an internal alkaline gelation.

4.1.2. Sol preparation by liquid-liquid extraction

The CNEN method of extracting acid anion from a hydrolized salt solution with primary amines is evidently very elegant, because the technique can take care of both the sol formation and the gelation. Experiments to perform both operations in one step have failed so far, probably because of the absence of the above-mentioned crystal growth. On the other hand, it is clear that an intermediate heating step could take care of this, and that is exactly what is being used at present.

If a method could be found to enhance the crystal growth during extraction, an attractive process would result, because the removal of residual electrolyte from the gel sphere would become superfluous.

Extraction work has been performed with both thorium and uranium (IV) nitrate solutions. In the latter case the maximum attainable concentration of the sol was limited to about 2 M. Further concentration by evaporation of water resulted in precipitation. The crystallite size of the sol particles is evidently still too small to allow concentration.

In the experimental work, the effective Primene concentration had to be measured frequently. Analytical procedures reported in the literature are rather elaborate. It appeared that direct titration of the Primene with a 0.1 N nitric acid solution is fast and accurate, provided that a glass electrode is used for the detection of the end point. About 30 ml acetone is added per millilitre of Primene to improve the pH readings, especially at the beginning of the titration. Figure 2 shows two such titration curves, one for virginal, the other for regenerated Primene JMT. The presence of an emulsifier does not interfere with the procedure.

4.2. Sol drop formation

Various methods for emulsification and drop formation of the sol have been studied. For particles in the range of 3 to 25 μm, an emulsion technique is used. The density of the organic medium is adjusted to that of the sol, an emulsifier is added and the water-in-oil emulsion is made with a vibrational stirrer. The drop size is controlled by the amplitude of the stirrer.

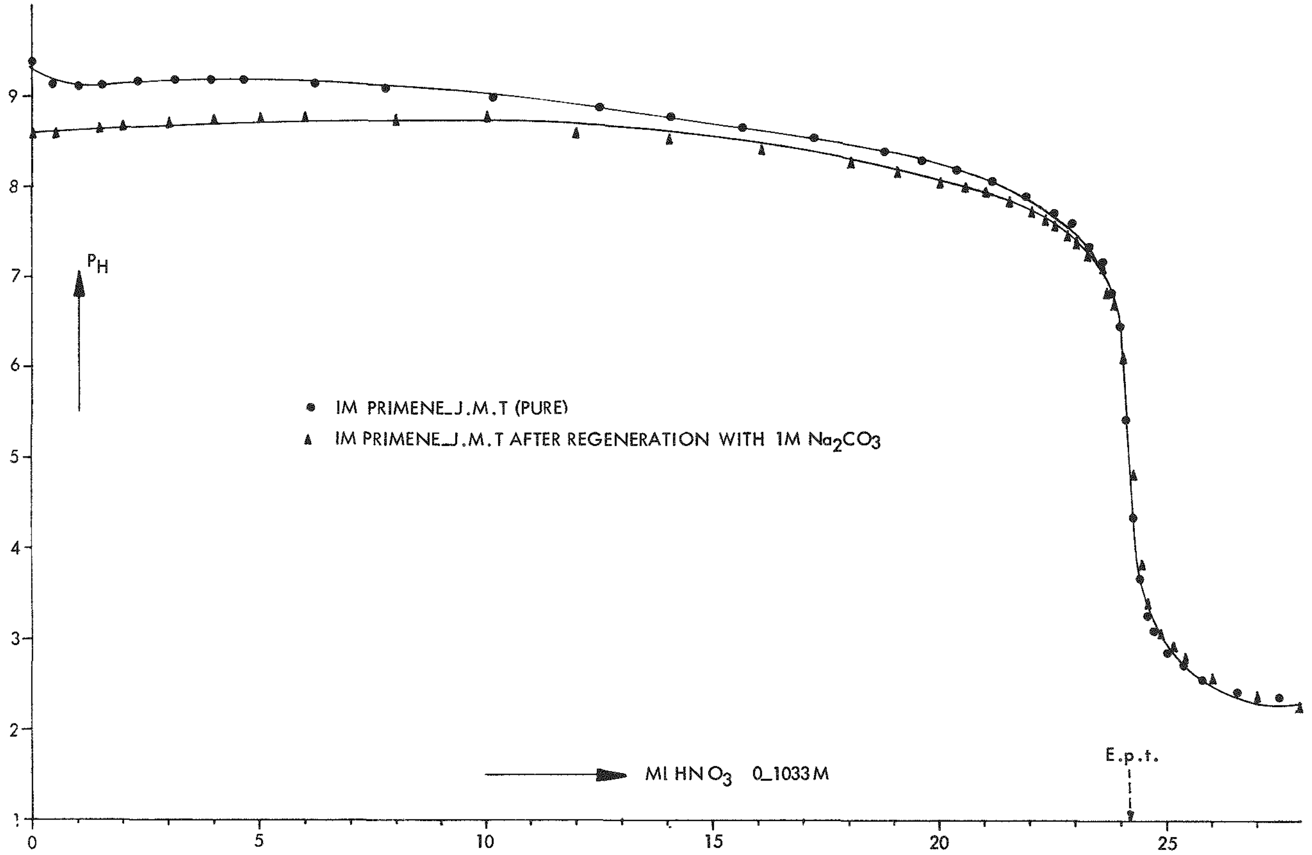

FIG.2. Titration of Primene-JMT (dissolved in Shellsol -A) with nitric acid.

When particles several hundred microns in size have to be prepared, a strip-stream of organic liquid is used around the tip of a capillary from which the sol enters the gelation tower. The drop size here depends on the flow rate of the strip-stream relative to the sol stream. For greater sizes the strip-stream can be omitted, and the droplets are formed at the tip of the capillary by gravity only. In this case the drop size is determined by a number of parameters such as the diameter of the capillary, the difference in density between the liquids, and the interfacial tension.

For particles larger than 0.7-1 mm, special precautions have to be taken to ensure the formation of drops of sufficient size. Further, the drop should be stable enough so that it will not split during gelation.

For example, a high density organic medium is required with a high surface tension against water. Tetrachloroethylene (density 1.52, interfacial tension 36 dynes/cm, both at 90°C) proved to be attractive for the purpose of producing 3-mm fuel spheres, provided that the presence of any surface active agent is rigorously avoided. However, a few additional measures have to be taken: to prevent deformation of the drop in the upstreaming organic liquid during gelation, the gelation must be carried out very rapidly to the extent that the rigidity is sufficient for further gelation without deformation. This is achieved by applying the method of internal alkaline gelation at a rather high temperature (90°C). Hexamethylenetetramine is again used as the ammonia donor. The procedure also prevents the particles sticking either to each other or to the wall.

The process has been applied successfully on a small scale for a very specific purpose.

4.3. Gel formation

In our laboratory several methods of gelation were studied, alkaline gelation being considered the most important method. In this case it is expected that the interlocking of the sol particles takes place more or less through chemical bonding in isolated places of the surface. Dehydration gelation, on the other hand, would tend more towards London-van der Waals forces in the gel structure.

If this were true a careful study of the gels derived from different gelation processes would be most interesting. So far, this specific study could not yet be started in the Netherlands. However, there is an observation which seems to support this view: gels made by dehydration peptize spontaneously, whereas those made by alkaline gelation always need acidification or a very strong dilution with water, even after washing.

In the sol-gel processes an emulsifier is normally added to prevent coalescence of the droplets and sticking to the wall and to stabilize the sol-droplets. From our work it appeared, however, that this emulsifier performs an important second task. It also acts as a dehydrating reagent for the sol, even in a non-dehydrating organic medium, because it disperses water which rises to the surface of the gelling droplet. The small droplets thus formed cause turbidity in the organic medium after it has been used for some time. By using this technique with a non-dehydrating organic liquid of high density (e.g. tetrachloroethylene) and at such a temperature that the water emulsion breaks, the water from the particles collects on top of the organic medium and can easily be removed by evaporation. This is the so called "hot-gelation" variation mentioned in section 2.

Another important phenomenon occurring in gelation is that of osmotic imbalance. An inorganic gel has certain membrane characteristics. This is most evident in our external alkaline gelation, where gelation takes place by the diffusion of ammonia into the sol droplet. On the droplet a gel skin is formed first which acts as a membrane. Concentration gradients of electrolyte across the skin may cause water to flow through the membrane and thus deform or disrupt the skin. Cracked, hollow or wrinkled particles may result. In a less serious, much more common case, stresses are set up in the gel without immediately showing up as defects, because an inorganic gel, weak though it is mechanically, can take some stress without rupture. In a later stage of the process, e.g. in the drying step, cracking is observed because of the additional deformation by shrinkage. Improving the drying technique is useless, because the gelation or the washing has been carried out under unacceptable osmotic conditions.

Although osmotic imbalance does not have to be avoided completely since the gel possesses some elasticity, an aqueous washing liquid must meet the requirement of having a pH such that the gel particle does not peptize (in many cases a buffer has to be used for this purpose) and a total electrolyte concentration near to that of the gel particle. For the buffer and the additional neutral electrolyte a judicious choice has to be made to avoid difficulties in drying and calcination.

The same osmotic phenomena limit the size of spheres which can be made through external alkaline gelation. In fact, the development of the internal alkaline gelation has been a direct consequence of the osmotic difficulties.

Another interesting aspect of gel formation is encountered in the internal alkaline gelation method. Hexamethylene tetramine is used as an ammonia donor. One clear disadvantage of this material is that it decomposes at higher temperature, delivering ammonia to the sol. However, even at room temperature there is so much decomposition that solidification of the sol cannot be prevented during an interruption of the process. A study has been carried out to retard gel formation at room temperature without appreciably affecting the decomposition rate of the ammonia donor at high temperature. It appeared that the addition of some 5 mol.% of urea had a very beneficial effect. The mechanism of this effect is not yet understood.

4.4. Admixtures to the thoria sol

Two admixtures have received attention so far: urania and carbon. The former is for the production of $(U,Th)O_2$ fuel spheres of different composition, the latter for the production of carbides.

The incorporation of uranium is simple up to a U/Th ratio of 0.25-0.20. It is achieved by peptizing the thoria precipitate by the addition of the required amount of uranyl nitrate. It was felt that the amount of uranium which can be taken up depends on the available thoria surface, where it is strongly adsorbed. Increasing the U/Th ratio would then mean that uranium has to be accommodated inside the particles of the ThO_2. This is possible because ThO_2 and UO_3 form a crystalline compound $UThO_5$, which has been found in previous work in the KEMA laboratories. Up to a U/Th ratio of unity, the coprecipitation yields the desired effect. The precipitate can easily be converted into a sol. Above that limit a fast crystal growth prevents peptization, possibly because a separate UO_3 - hydrate phase is formed.

The addition of carbon for the production of carbides is done by simply admixing a suitable type of carbon black into the sol. Initially with some carbons difficulties were encountered in that the hydrophobic carbon particles were transferred from the sol to the organic phase. This can be overcome by changing the surface of the carbon into a hydrophilic one by coating it with the fuel material. The latter can be performed by precipitation of the fuel salt in the presence of carbon, or by finally dispersing a suitable 'oxidized' carbon in the sol.

4.5. The sintering behaviour

Although calcined sol-gel material does not meet in any respect the usual requirements of sinterable powders, it shows a remarkable thermal reactivity due to the extremely small size of the primary particles, the crystallites, and thus to the small size of the pores. A crystallite size of 30-50 Å is normal. During sintering the crystallites grow and the smallest pores disappear first. The shape of the pores is derived from the shape of the adsorption-desorption isotherms. For ThO_2 with minor UO_2 additions, the shape is that of interconnected cavities with a varying diameter between stacked particles. At higher U/Th ratios a more cylindrical form seems to predominate.

The sintering temperature of sol-gel materials is remarkably low as compared with that of the same materials derived from other processes. The addition of uranium to ThO_2 lowers the sintering temperature of the pure ThO_2, as usual, but increases the pore volume at lower temperatures.

5. SOL-GEL APPLICATIONS

In the Netherlands no industrial applications of any of the sol-gel fuel processes have been made yet. For the KEMA Suspension Test Reactor Project a facility has been constructed at Arnhem to prepare the 5-μm $UO_2.ThO_2$ fuels. The facility has a capacity of about 1 kg per day.

The other KEMA variations have only been carried out on a kilogram scale in installations which might be described as small-scale semi-technical ones.

Some of the studies were carried out under contract or on request. Process development was made for the Dragon Project and for the Atomic Energy Board of South Africa.

In the Netherlands there is an increasing interest in vibratory-compacted fuel. The Reactor Centrum Nederland has started a program at Petten to study the possibilities of vibratory compaction.[1] Several fuels have been used for this purpose, some of them being prepared in spherical shape by sol-gel processes.

Furthermore, a provisional program has been formulated for testing elements of this type, first for short runs in the High Flux Reactor at Petten, and then in a power reactor. The program is supported by the Netherlands electric power producers, who consider the development of

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[1] This study is being carried out under the direction of Mr. P.F. Sens (RCN).

this type of fuel to be a potentially important step towards better fuel cycle economy.

The chemical industry in the Netherlands has started to show a serious interest in the production of nuclear sol-gel fuels. A decision was recently taken to construct a facility for the production of sol-gel fuel on a moderate scale and to use the facility for further development.

STATUS REPORT FROM THE UNITED KINGDOM
Sol-gel and gel-precipitation processes

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Abstract

STATUS REPORT FROM THE UNITED KINGDOM: SOL-GEL AND GEL-PRECIPITATION PROCESSES
Sol-gel and gel-precipitation processes are defined and examples are given of the laboratory-scale preparation of ThO_2, UO_2, ThO_2-UO_2, UO_2-ZrO_2 and $(Th,U)C_{2.4}$ particles of controlled composition, size, and shape for nuclear fuels. Processes have also been developed to produce metal powders, and alumina- and zirconia-based metal oxides with applications in the fields of powder metallurgy, refractories and ceramics. Basic physico-chemical studies of the structure and properties of sols and gels and of oxides derived from them are reviewed. Progress on the scale-up of the processes and equipment is described, and the potential technical and economic advantages of these processes are assessed in comparison with conventional processes for the fabrication of pelleted, granular and spherical nuclear fuels for a number of types of reactor.

1. INTRODUCTION

The development and physico-chemical aspects of processes that use sols and gels for the preparation of nuclear fuel materials and also for materials of use in the fields of refractories and ceramics have been studied in the United Kingdom over the last five years. Two main types of process called sol-gel and gel-precipitation are defined. Materials of controlled composition, shape, size and properties have been prepared on the gram to kilogram scale and further scale-up of equipment is being studied. An assessment is being made of the potential technical and economic advantages of these processes in comparison with conventional processes which use ceramic powders for the fabrication of pelleted and granular nuclear fuels for a range of reactors.

2. DEFINITION OF TERMS

A sol-gel process is one in which a sol, i.e. a dispersion of particles of the metal-containing compound usually in an aqueous phase, is first prepared and then converted into solid gel particles of controlled shape and size; the gel particles are then calcined to dense or porous particles of metal oxide or carbide in a suitable atmosphere at a temperature in the range 1000-1800°C. Mixtures of sols, or solutions and sols, can be used to prepare mixed oxides or carbides.

A gel-precipitation process is one in which the solid gel particles of controlled shape and size are prepared directly from a solution of one or more metals which usually contains an organic additive; the main advantage of this type of process is that a sol does not have to be prepared.

% T. D. is used to denote the percentage of theoretical crystal density measured at room temperature by the method stated.

3. PROCESSES FOR NUCLEAR FUELS

3.1. Sol-gel processes for thoria and thoria-urania

Two types of process were developed [1] at AERE, Harwell, to prepare concentrated (3-5 M) sols of thoria and thoria-urania.

(1) Thermal denitration of hydrated thorium nitrate in air at 490°C for 30 min, to a residual nitrate/thoria mole ratio of 0.05, followed by dispersion in boiling 0.1 M nitric acid to give an opaque sol containing 4-5 M thoria and a nitrate/thoria ratio of 0.08. Up to about 5 wt% of uranium was added to this type of sol as uranyl nitrate at the dispersion stage, and the mixed sol was cooled and adjusted to pH ~ 3.4 with ammonium hydroxide before evaporation to a final concentration of U + Th = 3 M and nitrate/total metal = 0.15. Mixtures containing 10 wt% uranium were prepared by adding the uranium (VI) as a solution which had been partially denitrated to a nitrate/uranium ratio of 1 with a 1 M solution of long-chain amine, Primene JMT, in xylene.

(2) Ammonia precipitation of a thorium nitrate solution. The solution was partially denitrated to a nitrate/thorium mole ratio of 1.5-2.0 by treatment at 95°C for 1 h with formaldehyde, and then precipitated by adding the boiling thorium nitrate solution with rapid stirring to a dilute ammonia solution at 100°C. The precipitate was filtered and washed with water until the conductivity of the filtrate was < 150 μmho, the nitrate/thorium ratio then being ~ 0.1. The filter cake was dispersed to a clear sol by heating it with dilute nitric acid or thorium nitrate at 100°C for 1 h, the final nitrate/thorium ratio being adjusted to ~ 0.3 and the thoria concentration to ~ 4 M. Transparent red-brown thoria-uranium oxide sols were prepared by dispersing the filter cake in a dilute solution of uranyl nitrate. The initial step of formaldehyde denitration gave in the following stage a precipitate which had improved filtration characteristics.

The pure and mixed sols from both of these processes were converted to gel aggregate by tray-drying, and to spheres by dewatering in a tapered glass column containing a long-chain alcohol, Alphanol-79 (Shell), to which 0.5 wt% Span 80 (Geigy) was added as a surfactant. The gel aggregate and spheres were dried and calcined to dense (95-99% T. D.) oxides after two hours at 1150°C in air for thoria or in hydrogen for thoria-urania.

A process for preparing porous ThO_2-UO_2 spheres for use, coated with pyrolytic carbon, in high-temperature reactors was developed in the Dragon Fuel Element Laboratories at Winfrith [2]. Thorium hydroxide was precipitated from 1 M thorium nitrate solution with an excess of 18 M ammonia, washed with ammonia and then with water and peptized with uranyl nitrate and free nitric acid at 90-100°C to give a final nitrate/

metal ratio of ~0.3, Th/U ratios of 9-15 and a total metal concentration of 4-5 M. Carbon black (United 15, surface area 370 m^2/g) was added to the mixed sol at a mole ratio of carbon to total metal in the range 1-5. The sols were formed into gel spheres (350-500 μm) either by internal gelation with hexa-methylene tetramine at 45°C in a column of 2-ethylhexanol partially saturated with water, or by dewatering in a column of dry 2-ethylhexanol. The gel spheres were heated:

(a) for 2 h at 1600°C under 1 atm. of carbon monoxide to prevent the carbon reacting with the oxides, and

(b) at 800-1000°C in oxygen to burn out the carbon to give a final porosity in the range 20-60%; the amount of porosity was controlled by the amount of carbon filler added, or by a final heat treatment at 1600°C in CO, longer times giving lower porosities.

3.2. Sol-gel processes for urania

The initial work on the preparation of sols and dense aggregate and spheres of urania was described in 1966 [3] and later work on the 500-g scale in 1967 [4]. The basic process consisted of four stages: reduction of uranyl nitrate to U(IV) nitrate, precipitation and peptization to give a UO_2 sol, formation of aggregate and spheres of gel of controlled size, and calcination to aggregate and spheres of dense UO_2.

The catalytic hydrogenation of uranyl nitrate solution at atmospheric pressure was rapid (1 h) and efficient, provided that vigorous mixing of the catalyst, solution and hydrogen was achieved. Hydrous uranous oxide was precipitated to a pH of 7.8 in the presence of formic acid with an ammonia-hydrazine mixture and the precipitate filtered in a basket centrifuge.

The precipitate was washed with water to a filtrate conductivity of < 200 μmho, and peptized by heating it at 60°C for 3-4 h. The properties of a typical sol produced by this process are:

pH	2.2
U(IV) concentration	1.8 M
nitrate/U ratio	0.1
conductivity	8×10^3 μmho
total U concentration	2.0 M
viscosity	1.5 cp at 25°C.

Gel aggregate and spheres of 50-500 μm diameter were prepared initially in 25-g batches, the aggregate by drying sol in boats in a vacuum oven, and the spheres by dewatering sol droplets with Alphanol in a tapered column and vacuum drying. The aggregate and spheres were calcined in CO_2 at 900°C and hydrogen at 1150°C for 4 h to particles of 95-97% T.D. (Hg method), an O/U ratio of 2.005 ± 0.005 and a carbon content of 0.02 ± 0.01 wt%. The spheres had a grain-size of ~1 μm and a high crushing strength, e.g. 4-6 kg for 250-350 μm diameter.

Routine operation of this reduction-precipitation-peptization flow sheet on batches of 540 g UO_2 gave reproducible sols, and these were converted into gel spheres in 100-g batches in an Alphanol column, with a time per batch of about one hour. The drying of the gel spheres on the 300-to 400-g scale gave rise to several problems and the initial vacuum drying stage was replaced with drying in a slow stream of air at room temperature for about a day. The air-dried spheres contained about 15 wt% of volatile material and were dried further in a tube furnace at 80°C for 3 h before calcination in CO_2 to 900°C, and in hydrogen to 1150°C. The spheres had a more reproducible density of 95-96% T.D. with this method, compared with 75-90% T.D. when they were initially vacuum-dried.

Fuels required for high burn-up systems may require built-in porosity to accommodate fission products, and methods were therefore examined to produce spheres with controlled porosity. Porous UO_2 spheres were prepared [4] by the addition of carbon, and various carbon compounds, to the UO_2 sols and calcining to burn out the carbon. The addition of sucrose or polyvinylalcohol at a carbon-to-uranium mole ratio of 1 followed by calcination at 1150°C gave approximately 75% T.D. (Hg method), a residual carbon content of 0.025-0.05 wt%, and a crushing strength of about 1 kg for 350-μm diameter spheres. Calcination of the spheres to 1450°C increased the density by about 5%. The addition of finely dispersed carbon black at C/U mole ratios of 1, 0.9 and 0.75 gave spheres with densities of 70, 75 and 90% T.D. respectively, O/U ratios of 2.00-2.02, and a residual carbon content of less than 50 ppm.

3.3. Sol-gel processes for urania-zirconia

Zirconia sols have been made by several methods and their compatibility with UO_2 sols studied with the object of preparing UO_2-ZrO_2 spheres over the range of Zr/U mole ratios of 1-3 for future advanced reactor fuels. Commercially available zirconyl nitrate ($NO_3/Zr = 1.2-2.2$) was formed into sols [1]

(a) by direct dissolution in water of material containing a low (1.2-1.4) ratio of NO_3/Zr up to a zirconium concentration of about 4 $\underline{M}$;

(b) precipitation of hydrous zirconium oxide with ammonia and dispersion of the well-washed precipitate in hot solution of zirconyl nitrate to give final sols containing 2 $\underline{M}$ Zr and $NO_3/Zr = 1$;

(c) denitration of the solid in air at 200°C to give a water-soluble product containing 55 wt% ZrO_2 and $NO_3/Zr = 1$;

(d) denitration of a solution of zirconyl nitrate with a long-chain amine, Primene JMT, to give sols with $NO_3/Zr = 0.7-1$.

These sols were not compatible with UO_2 sols which had a low nitrate content ($NO_3/U \sim 0.1$), but ZrO_2 sols with a much lower $NO_3/Zr = 0.03-0.07$ prepared at a concentration of 1-2 $\underline{M}$ Zr by a hydrothermal treatment (4 h, 200°C) of high-nitrate ZrO_2 sols and subsequent removal of residual nitrate by mixed-bed ion exchange were compatible [5]. Mixed 2 $\underline{M}$ sols of UO_2 and ZrO_2 were formed into gel spheres by dewatering in Alphanol columns. The best combination of surfactants to produce spheres with good surface finish and minimum clustering was 0.5 vol.% Span 80 and 0.5 vol.% Amine-O. The density of spheres ranged from 60% T.D. after calcination in hydrogen at 1150°C to 97% at 1450°C, and X-ray crystallography showed the main phase to be cubic $(U,Zr)O_2$ with some monoclinic $(Zr,U)O_2$ also present.

3.4. Sol-gel processes for carbides

The preparation of thorium/uranium carbide spheres suitable for coating with pyrolytic carbon and for use in high-temperature reactors was studied at Winfrith [2]. The basic process for forming the mixed sols containing carbon is described in section 3.1. Most of the work was done with 4.4 mole of carbon added per mole of total metal present in 4-5 M sols, and spheres were formed by the internal gelation method.

The gel spheres were converted to carbide by heating them in 100-g batches as follows: 2 h in air at 80°C, 2 h 120°C, 2 h 180°C, and then in vacuo from 25 to 900°C in 2 h, 900-1450°C in 1 h, 1450-1700°C in $\frac{1}{2}$ h, 1700-2000°C in $\frac{1}{2}$ h, at 2000°C for 1 h, and cooling to room temperature in 2 h. Larger batches (kg) were heated and cooled more slowly. The products were spheres 0.25-0.8 mm in diameter with 70-80% T.D. and the composition $(Th, U)C_{2.4}$. Higher or lower density was obtained by increasing or decreasing the final soaking temperature. Spheres with Th/U ratios of ∞ to 7 were coated with pyrolytic carbon and silicon carbide without difficulty.

3.5. Gel-precipitation processes for thoria and urania

A gel-precipitation process was developed [6] at AWRE, Aldermaston, in which a polymeric organic compound was added to a solution of a soluble salt of one or more metals to make a viscous solution and form a complex with the metal ions. The solution was then formed into the required shape, e.g. spheres by adding it dropwise into a solution which precipitated the metals as insoluble compounds, or rods by extruding the solution through an orifice. Oxide spheres were made by precipitating solutions with ammonium or sodium hydroxide.

Dextran was widely used in this work as the polymeric organic compound and is a polysaccharide having a molecular weight up to about 5×10^6, good stability in acid solution, and can be easily dispersed. Other suitable materials were natural gums and polyvinylalcohol.

The solid gel spheres or rods were washed with water, dried and heated to remove the organic additive, e.g. dextran in vacuo at 250°C, and finally sintered to metal oxides at a higher temperature, e.g. 800-1200°C. The gel spheres were generally transparent, rubbery, and easily handled both wet and dry. Carbide spheres were made by dispersing finely-divided carbon in the solution of metal salts prior to spheroidization, and carbothermic reduction of the dried gel spheres.

In a typical preparation of ThO_2-UO_2 spheres, 2 g dextran was added to 10 ml of 2 M nitric acid containing 100 g U(VI)/l and 100 g Th/l as metal nitrates; precipitation of drops through a 1-mm diameter jet with ammonium hydroxide gave 3-4 mm diameter transparent amber gel spheres, which were washed, dried and calcined.

4. PROCESSES FOR NON-NUCLEAR MATERIALS

4.1. Sol-gel processes for metal oxides

In parallel with work in the nuclear field, sol-gel processes have been developed [7, 8] at AERE, Harwell, to produce particles of metal oxides of controlled composition, shape, size, and properties for various industrial applications, e.g. in refractories and special ceramics.

Alumina- and zirconia-based mixed oxides were prepared from concentrated (1-5 M) sols made by two main types of process:

(1) precipitation of a hydroxide or hydrous oxide, washing, and peptization with acid; precipitation was effected by ammonia or other base, or by a hydrothermal method followed by ion exchange to remove residual ions;

(2) preparation of a high surface area oxide from a thermally unstable salt, e.g. nitrate, followed by peptization with acid.

Sols containing mixtures of metals were prepared by mixing:

(a) solutions of salts followed by one of the methods given above;
(b) pre-formed sols; or
(c) sols and solutions of suitable salts.

The sols were converted into gel particles of controlled shape and size by a variety of methods (Table I).

Photomicrographs of typical alumina- and zirconia-based products prepared by methods 1, 2, 4 and 6 have been published [8]. The gels were calcined to oxides by heating them to a temperature usually in the range 500-1500°C depending upon the particular form of metal oxide required.

TABLE I. METHODS OF FORMATION OF GELS FROM SOLS

	Method	Shape of product	Size of product
1.	Removal of water by tray drying	Irregularly-shaped fragments (aggregate)	mm-cm
2.	Removal of water by solvent extraction	Spheres	5-1000 μm diameter
3.	Removal of water by spray-drying in air	Spheres (usually hollow)	1-100 μm diameter
4.	Partial removal of stabilizing anion with ammonia or organic solvent	Spheres	5-200 μm diameter
5.	Internal gelation with ammonia-donating reagent	Spheres	5-500 μm diameter
6.	Removal of water during or after extrusion of concentrated viscous sol, or sol + solid particles	Fibres, rods	10 μm-1 cm diameter

4.2. Gel-precipitation processes for metals and metal oxides

The gel-precipitation process described for thoria and urania in section 3.5 has also been used [6] to prepare particles of metals and compounds of other metals, e.g. oxides of Fe, Cu, Ni, Cr and Al. Spheres of pure and mixed metals were made by heating dextran-bonded gel spheres containing reducible-metal compounds in hydrogen or carbon monoxide e.g. to give Fe or Ni. These particles have applications in the expanding field of powder metallurgy.

5. BASIC PHYSICO-CHEMICAL STUDIES

Information on the composition and structure of polynuclear complexes of heavy metal ions, e.g. uranium [9], zirconium [10], or ruthenium [11], which occur in nuclear systems, has been accumulated over several years at AERE. More recently the larger polymers which exist in sols and gels of hydrated oxides and hydroxides have been studied with the techniques of spectrophotometry in the ultra-violet and visible regions, infra-red spectroscopy, pH, conductivity and molecular weight determinations [12]. The solid oxides derived from the gels have been examined by X-ray crystallography, by scanning electron microscopy [13], and by the measurement of adsorption isotherms [14]. In addition, detailed studies of sols and gels of urania [15] and rare-earth oxides [16] were made in collaboration with the Oak Ridge National Laboratory. The published work on the preparation and structure of sols and gels of metal oxides of interest in the nuclear field was reviewed at the Turin Symposium in 1967 [17].

6. EQUIPMENT DEVELOPMENT

Sol-gel processes have been operated on the laboratory scale, e.g. 10 to 500 g per batch, for the preparation of thoria, urania, alumina and zirconia spheres and aggregate. Typical equipment was described [4] for the preparation of 500-g batches of urania sol and 100-g batches of gel spheres in a tapered column containing Alphanol-79 (Shell) as the dewatering solvent. Standard furnaces with controlled atmospheres were used to calcine oxides to 1150°C [4] and carbides in up to kilogram amounts to 2000°C [2].

Equipment to produce multi-kg/day of gel spheres of controlled size over the range 50-600 μm diameter and to calcine them is being developed in the Chemical Engineering-Process Technology Division at AERE [18]. Theoretical and experimental studies are in good agreement for the rate of mass transfer of water from drops of concentrated sols falling through columns of Alphanol. Vibrating jets for the production of streams of uniformly-sized sol drops are considered to have a greater potential for scale-up than the dual concentric jets used in small laboratory columns, and the effects of the various parameters on the drop size and production rate are being studied.

A vertical tube evaporator 7 mm in diameter and 3 m high was developed for the continuous distillation and drying of Alphanol at 10 l/h at 160-180°C. This was designed to operate in the slug-flow regime and to provide data that could not be predicted because of the lack of data on the vapour-liquid equilibria of Alphanol. The water content of Alphanol cannot be reduced below 0.5 wt% in a single-stage apparatus of this type without a large recycle organic stream. Gas chromatography of Alphanol that had been redistilled ten times showed that small quantities of lower alcohols were removed in the aqueous distillate but that no significant decomposition occurred.

7. COMPARISON OF SOL-GEL AND CONVENTIONAL PROCESSES FOR NUCLEAR FUELS

In the United Kingdom a large program of research, development and commercial operation of Advanced Gas-Cooled (AGR) and Fast Breeder Reactors has begun [19]. There is also work on a High Temperature Reactor (Dragon type) and a Steam Generating Heavy Water Reactor (SGHWR). The potential savings to be made by improvements in the fuel cycles are large, but the introduction of sol-gel processes into large-scale production will depend upon their showing significant technical or cost advantages over conventional processes. It is only possible at the present time to indicate the potential technical advantages, but some of these may have a large impact upon the economics of a fabrication process or on an integrated fabrication-reprocessing-refabrication cycle:

(a) spheres can be produced over the size range 10-1000 μm with close size control at the gel stage; out-of-size spheres can be recycled at an early stage before sintering, thus simplifying any recycle stages;

(b) pure and mixed oxide spheres can be sintered to high (> 95%) density at moderate temperatures, i.e. at least 200°C lower than in conventional processes, and can also be produced with controlled porosity, e.g. 70-90% T.D.;

(c) a small grain size and high strength can be achieved even in porous spheres;

(d) the basic processes can be scaled up as unit operations and are suitable for fully remote operation;

(e) there is no appreciable dusting in the preparation of spheres in various size-ranges, compared with grinding or powder aggregation processes; this may be particularly important where losses of plutonium or enriched uranium must be minimized;

(f) the basic processes and equipment for oxide spheres can be used to prepare carbide and nitride spheres by carbothermic reduction of oxide spheres containing carbon.

Sol-gel processes therefore appear to be particularly attractive for the production of spheres for vibrocompaction into narrow fuel tubes, for kernels for coated particles, or for incorporation into cermets. The conventional processes which are being operated or which are proposed for pelleted or spherical particle fuels involve many stages of handling of fine active powders, but these processes were the best available at an advanced state of development at the various times at which plant designs had to be selected to meet target dates for reactor operation.

The possible compositions of fuel, methods of fabrication, and types of reactor in which sol-gel derived fuel could be used in the future in the

TABLE II. POSSIBLE COMPOSITIONS OF FUEL, METHODS OF FABRICATION, AND TYPES OF REACTOR

Composition	Size and density	Method of fabrication	Possible reactor
UO_2, UC or UC_2	500-1000 μm, dense 50-100 μm, dense	2-size vipac or coated particles	Advanced AGR
UO_2-PuO_2 or UC-PuC	500-750 μm, dense 50-75 μm, dense	2-size vipac in narrow tube	Civil fast reactor
UO_2-ThO_2 or (Th, U) carbide	700-1000 μm, dense or porous	Coated particles in wide tube	Dragon or HTR
UO_2 or UO_2-ZrO_2	100-350 μm, porous	Incorporation into cermet	Ship reactor
UO_2	500-1000 μm, dense 50-100 μm, dense	2-size vipac in narrow or wide tube	SGHWR

United Kingdom are given in Table II. The next stage will be to estimate the plant and operating costs of sol-gel processes for particular specifications of fuel and throughput for selected reactors.

8. CONCLUSIONS AND FUTURE PROGRAM

Sol-gel and gel-precipitation processes have been developed to produce a wide range of pure and mixed metal oxides and carbides on the laboratory scale. The processes appear to have technical advantages over conventional processes used in both the nuclear and non-nuclear industries, particularly for the production of spheres of closely-controlled composition, size and density. The development of equipment to the multi-kg/day scale, and estimates of costs and the most appropriate fuel cycles are in progress.

There has been only limited irradiation testing of sol-gel fuels so far and further experiments are planned. Pyrocarbon-coated ThO_2-UO_2 sol-gel particles irradiated in a loosely packed bed in a loop in the PLUTO reactor at AERE gave the best circuit cleanliness ever achieved with an experimental gas-cooled reactor fuel element, and no deterioration was observed even though the estimated temperature was 1450°C [19].

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STATUS REPORT FROM
THE UNITED STATES OF AMERICA
Sol-gel work on ceramic fuel production

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Abstract

STATUS REPORT FROM THE UNITED STATES OF AMERICA: SOL-GEL WORK ON CERAMIC FUEL PRODUCTION. The paper is a brief survey of the work on sol-gel methods performed by six firms in the United States of America and by Oak Ridge National Laboratory.

INTRODUCTION

Representatives of seven organizations in the United States of America were contacted to obtain information. In general, response was quite limited, either because of small effort or proprietary interest. Each organization is discussed separately below.

GULF GENERAL ATOMIC (GGA), SAN DIEGO, CALIF.

At present GGA is performing no active work in the sol-gel process area but has a representative working on assignment at ORNL directly in sol-gel process development. This assignment may last two years. GGA has had a sol-gel development program on ThO_2 and ThO_2-UO_2 materials and has a long-term interest in sol-gel processes for remote recycle of fuels, especially HTGR fuels. (The Thorium Utilization and Sol-Gel Process programs at ORNL are in many ways directly related to GGA's needs and interests.)

NUMEC, APOLLO, Pa.

There is a modest interest in sol-gel processes at NUMEC. Their interest is in both mixed UO_2-PuO_2 for fast reactors and UO_2. So far NUMEC has patterned its processes after those used by ORNL. Process development work has been privately funded and limited. Work is continuing. Interest is in pellets, sphere compaction and shard compaction as fuel forms. Irradiation tests on sol-gel material are planned.

GENERAL ELECTRIC (GE), SUNNYDALE AND SAN JOSE, CALIF.

Sol-gel processes are used only in speciality applications. ORNL processes are used. Materials of most interest are ThO_2 and PuO_2, although there is a little interest in making UO_2 by sol-gel methods. Sol-gel processes are used mostly for making microspheres. Of special interest is the effect of non-homogeneity of PuO_2 distribution in fast and thermal reactor fuels. The question being asked is "how large can a piece of PuO_2 fuel (e.g. a PuO_2 microsphere) be before it results in excessive fuel non-homogeneity?". Irradiation tests are just beginning. No fuel fabrication development work based on sol-gel methods is being carried out.

WESTINGHOUSE (W), PENN CENTER, PITTSBURGH, Pa.

A modest development program on sol-gel processes for use in Pu recycle has been decided upon by W. The interest is in both fast reactors and light water reactors. Work should already be underway.

BABCOCK & WILCOX (B&W), LYNCHBURY, Va.

B & W is developing urania-plutonia sol-gel fuels for use in fast reactors under a USAEC contract. The program includes laboratory development, engineering demonstration and finally a 1 kg/week pilot plant. The work is now at the engineering development stage. Mixed (U, 20% Pu)O_2 spheres are being made in less-than-kilogram amounts with the ORNL mixed-sol-flow sheet (wherein a PuO_2 sol prepared by the ORNL method is mixed with a UO_2 sol prepared by precipitation-peptization). The work on UO_2 sol preparation by solvent extraction by ORNL is being followed closely, and work on it will begin shortly.

At present 20 people are assigned to the contract work. An irradiation program on these methods has been started. The first exposure of vibratory compacted mixed-oxide spheres is scheduled for June, 1968. At least 20, and perhaps 28 capsules, will be exposed in the B & W test reactor (BAWTR), and up to 96 pins will be exposed in EBR-II. All thermal reactor capsules will contain pellets, packed spheres and packed shards to provide intercomparison. The specific objectives of the irradiation program are: (1) to determine irradiation time required to restructure fuel, (2) gas evolution, and (3) performance in the EBR-II fast-neutron spectrum. Additional tests on thermal conductivity, fuel compatibility with sodium, and transient behaviour are under discussion.

In addition to the above AEC-sponsored program, B & W itself also has a substantial effort under way. In May 1968 over 17 000 square feet of new laboratory space became available for plutonium work at a capital cost to B & W of $980 000. Space has been provided for future expansion, and B & W expects to install hot cells for studying irradiated plutonium fuels in the next few years.

W.R. GRACE (GRACE), CLARKSVILLE, Md.

The work being performed by Grace was discussed by L. V. Triggiani at the Sol-Gel Symposium in Turin, Italy, in October 1967. Mr. Triggiani provided the following additional information.

Grace has worked with all methods that appear to them to have relevance to present or future fuel cycles. Their work includes not only oxides, but carbides and nitrides as well. In all cases their interests include multicomponent systems. Grace's effort is substantial and development is privately funded. They have carried out work from the laboratory bench to full-scale production. Much of their production is directed to classified US Government uses.

Grace has examined the full range of fuel fabrication techniques for their materials. They have completed very extensive irradiation tests, but the data cannot be released.

Grace has about 40 patents in the general sol-gel area, dating back to 28 May, 1963.

OAK RIDGE NATIONAL LABORATORY (ORNL), OAK RIDGE, TENN.

A broad range of ceramic materials is being studied at ORNL. ThO_2, UO_2, PuO_2, and ZrO_2 and several of their admixtures are the ones most studied, and in the order given. Some work on the carbides, nitrides and carbonitrides has also been done, but much more has been carried out on carbides than on the other two. Steam denitration (for ThO_2O, precipitation-peptization (for UO_2, UO_2-Tho_2, PuO_2 and ZrO_2) and solvent extraction are the processes most used. Present efforts are devoted to solvent extraction processes.

About 25 scientists and technicians are working directly on sol-gel process development work. The emphasis is on fast reactor fuels. Another 14 are engaged in fabrication and irradiation tests. The average cost per man-year on these programs is $40 000. This cost is all-inclusive, i.e. services by other groups, operating equipment, wages and overhead are included.

All aspects of the work are directed toward eventual pilot-plant demonstration. Pilot plants for ThO_2-UO_2 and UO_2 sol preparation and microsphere formation are in operation on the kg/hour scale. A pilot plant demonstration of ThO_2-UO_2 shard preparation and compaction into fuel rods has been completed (the Kilorod Program).

Fabrication processes for sphere compaction, pelletization, and extrusion are being developed. Sphere compaction is receiving most emphasis with pelletization next.

Work with PuO_2 is growing at ORNL. Existing facilities have been enlarged and new ones added. Irradiation tests on UO_2-PuO_2 carried out so far on compacted tests of spheres show that such fuels behave the same way in thermal reactor tests as comparable pellets. Additional thermal and fast reactor (EBR-II) tests are planned, as are tests during reactor power transients.

STATUS REPORT FROM YUGOSLAVIA
Research on sol-gel processes

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Abstract

STATUS REPORT FROM YUGOSLAVIA: RESEARCH ON SOL-GEL PROCESSES. A brief survey describes the background of nuclear power research in Yugoslavia, together with the economic considerations. Yugoslav experience with sol-gel processes is outlined.

In Yugoslavia research is being conducted under a medium-term research and development program in nuclear power, which envisages a gradual introduction of nuclear power into the country's economy and, in the long run, the construction and exploitation of nuclear power plants. As a basis for selecting research problems and concrete fields of research, we have taken the assessment of our own research and production capabilities, and ultimately the economic justification with regard to the future utilization of the results obtained. Technical co-operation with non-Yugoslav partners, which has been foreseen for all stages of the development of the program, also assumes co-operation in research. In that respect a number of arrangements has been planned on the distribution of activities, development of joint team-work, industrial co-operation, etc. At the present stage, when no concrete forms of co-operation with a definite non-Yugoslav partner have yet been established and no reactor type has been selected, the program is arranged on a broader basis, to the extent that it is to be increasingly more concentrated on the solution of particular problems associated with a certain type of reactor and the associated fuel elements.

Analyses conducted so far indicate that the first generation of power stations to be built in Yugoslavia will probably use water-cooled and water-moderated reactors. The whole program will therefore rely on this type of reactor. The main technological problems are common to all water reactors, so that later it will be possible to concentrate further efforts around the key tasks of one type of water reactor. In recent years our laboratory investigations have been concentrated on heavy-water reactors.

Since research on heavy-water reactors has never been the only purpose of our flexible program, it has been possible to develop other techniques for the production of ceramic fuel elements, such as vibratory compaction and rotary swagging.

Laboratory-scale research into vibratory compacting achieved interesting results. In working with UO_2 a clear advantage in using fuel of uniform shape and density was shown. Particular attention was paid to fuel element types attractive for reactor application. This, in particular, implies annular and inverted (tube-in-shell) fuel element types.

There are technical advantages in using spherical fuel particles produced by sol-gel processes in the production of ceramic fuel elements by vibratory compaction. This refers particularly to the production of fuel elements with enriched fuel, in which the problem of homogeneous distribution of fine fraction (usually the carrier of 'enrichment') becomes fully evident. Our experience in the production of UO_2 and ThO_2 spherical particles by sol-gel methods enables pilot-plant-scale production to be introduced relatively soon, if necessary. Current work is being directed toward solving problems in the preparation of enriched UO_2 spherical particles, as well as toward the production of mixed UO_2-ThO_2 fuel by the sol-gel process. The preparation of UO_2-PuO_2 fuel by the same process is also envisaged.

All three Yugoslav nuclear institutes are conducting research in this field. The Jožef Stefan Institute at Ljubljana has already commenced preparation of individual and mixed oxide fuels by the sol-gel process, while the Ruder Bošković Institute in Zagreb and the Boris Kidrič Institute in Belgrade (Vinča) also have the equipment and trained personnel to cope successfully with the task. Only the Vinča Institute is working on vibratory compaction.

BASIC RESEARCH

SOL-GEL PROCESSES AT TOKAI

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Abstract

SOL-GEL PROCESSES AT TOKAI. The development of sol-gel processes in Japan has mainly been concentrated on the preparation of dense UO_2 and UO_2-PuO_2 spheres which can be used for vibratory compaction. Preparation of the dense UO_2 spheres on the gram-to-kilogram scale has been carried out to improve the processes. Preliminary experiments applying the sol-gel process have also been performed on UO_2 pellets and uranium monocarbide spheres.

1. INTRODUCTION

Sol-gel processes have been studied and developed by the Power Reactor and Nuclear Fuel Development Corporation (P.N.C., Government Establishment), Japan, since 1962, when the corporation was called the Atomic Fuel Corporation. Although some basic work on thoria microspheres with diameters ranging from 4 to 20 μm was carried out at the Japan Atomic Energy Research Institute [1], most of the work in Japan on sol-gel processes with a view to practical application to nuclear fuels is performed by the P.N.C..

Development efforts have been concentrated mainly on the preparation of dense UO_2 and UO_2-PuO_2 sherds which can be used for vibratory compaction. Dense UO_2 sherds on the gram-to-kilogram scale were prepared to improve the process, and present efforts are being concentrated on the preparation of PuO_2-UO_2 mixed oxide sherds. Preliminary experiments with the sol-gel process, however, were also performed on UO_2 pellets and uranium monocarbide sherds. The preparation of UO_2 microspheres by means of an ORNL type column is now being tried.

2. OUTLINE OF THE P.N.C. SOL-GEL PROCESS

2.1. Preparation of sol-gel UO_2 sherds

The P.N.C. has been producing metallic uranium for about ten years by the so-called "excer process", which is characterized by a completely wet method of uranous tetrafluoride preparation. This process gives uranous chloride solution as an intermediate product by the electrolytic reduction of uranyl chloride solution. This uranous chloride solution is used as the base material for the sol-gel process.

The schematic flow sheet of the P.N.C. sol-gel process for the preparation of dense uranium dioxide sherds is shown in Fig. 1. The first step of the process is the precipitation of hydrated uranous oxide from the uranous chloride solution by the addition of aqueous ammonia. The uranium concentration of the solution is 100 g/l and the U(VI)/U total ratio has been adjusted in the range from 0.05 to 0.10. The precipitate is easily suspended into a sol state by simple mixing. The sol is diluted five times and stirred well again.

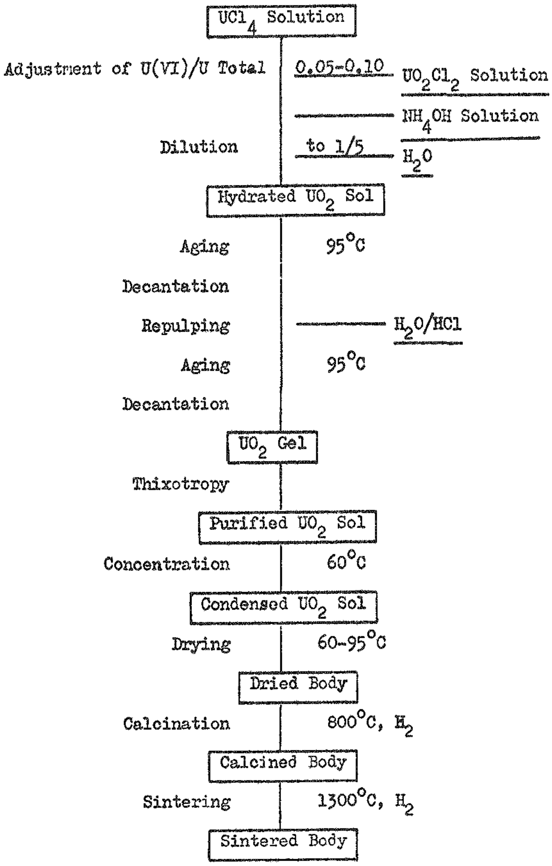

FIG.1. Schematic flow sheet for preparing UO_2 sherds.

The precipitate gives a diffuse X-ray diffraction pattern of UO_2 structure even with the as-precipitated sample in wet condition. This implies that an atomic arrangement of UO_2 is formed instead of uranous hydroxide as the result of the polymerization of uranous ions to a three-dimensional lattice. The pH, the rate of ammonia addition and the method of stirring were examined, and a comparatively low pH of the sol (1-2), a slow rate of ammonia addition and vigorous stirring were found to be suitable to give a higher sintered density.

The original method for washing the precipitate or purifying the sol was centrifugation, but this was replaced later by warm aging and decantation because of its inconsistent reproducibility. Preparation of sol based on dechlorination by dialysis or by electrodialysis or with anion exchange resin was also tried, but discarded because of the time-consuming operation and some difficulty in employing the techniques.

After the sol has been aged at 95°C for one night, the colloidal particles settle on the bottom of the container in the form of a gel, and the supernatant solution is decanted. The gel is then repulped with water back into a sol state. After the second aging and decantation, purified gel is transformed to sol by simple shaking, utilizing thixotropy. The sol is condensed to 2 to 3 mole U/1 by heating at 60°C with mild stirring, and then dried at 95°C in air. The dried substance is calcined at 800°C for 2 hours, and sintered at 1300°C for 2 hours under hydrogen or N_2-5%H_2 atmosphere. The heating rate is 50 degC/h for the calcination and 100 degC/h for the sintering.

The fired products have densities of 96 to 97% T.D. by the mercury immersion method (100 mmHg) and a grain size of about 15 μm. It is noticeable that the impurity content is very low compared with other UO_2 products, such as pellets and fused UO_2.

2.2. Preparation of PuO_2-UO_2 sherds

Experimental work has been performed on the preparation of PuO_2-UO_2 mixed oxide sherds by the sol-gel process at the Plutonium Fuel Development Laboratory, Tokai Works, P.N.C., since October 1966. The process for mixed oxide sherds is similar to that for uranium dioxide sherds except that the former has a blending step whereas the purified UO_2 sol is mixed with a suitable plutonium compound.

Five kinds of plutonium compound have been examined for the preparation of 2% PuO_2-UO_2 sherds [2]: plutonia sol, plutonium hydroxide precipitate, plutonia powders (peroxide and oxalate derived) and plutonium peroxide. Plutonia sol was made from $Pu(NO_3)_4$ solution by a process similar to that for UO_2 sol. Plutonium hydroxide precipitate was prepared at pH 9.6 to 9.8 by adding ammonia water. Plutonia powders were obtained by heating either the peroxide at 450°C or the oxalate at 800°C. The blending of UO_2 sol and one of the plutonium compounds was done by vigorous stirring for one to four hours.

The blended sols were condensed at 60°C to 45 wt% metal, dried at 60°C, dehydrated at 800°C for 2 hours at a heating rate of 50 degC/h, and then sintered at 1400°C for 3 hours at a rate of 100 degC/h under a N_2-5%H_2 atmosphere. The sintered products were examined for density, plutonium distribution, chemical compositions and micro-texture. The densities measured by the mercury immersion method (100 mmHg) ranged from 95 to 96% T.D. except where the plutonia powders were used, when the densities were about 94% T.D.. Homogeneity of plutonium distribution was examined by means of micro-autoradiography, and excellent homogeneity was obtained with plutonia sol for blending, although all of the results were satisfactory. The best quality of sintered substance was obtained by using plutonia sol blending in all aspects, although this is the most elaborate process. The other processes were somewhat inferior with respect to homogeneity and micro-texture, but can be used for the preparation of sherds with a lower plutonium concentration (less than 20%).

2.3. Vibratory compaction

Vibratory compaction of the sol-gel UO_2 products in 12.6-mm diameter cladding for thermal reactor use was examined with binary and ternary size components [3]. The highest density (88.8% T.D.) was obtained with ternary components with the ratio of 4-8 mesh : 20-65 mesh : -200 mesh = 60:20:20, but similarly high density (88.6% T.D.) was also obtained with binary components with the ratio of 4-8 mesh : -200 mesh = 75:25. The economical preparation of these particle size distributions of both the binary and ternary systems, which enables almost 100% utilization of the as-fired sol-gel UO_2 for fuel rods, was achieved by a proper combination of crushing methods with crusher, hammer mill and ball mill. The application of the sol-gel products to vibratory compaction of narrow tubes for fast breeder use has also been carried out successfully.

3. BASIC RESEARCH

Some basic research work has been performed on each step of the above-mentioned sol-gel process. The essential results were reported at the CNEN Sol-Gel Symposium, Turin, Italy [4]. Some properties of the intermediate and final products of the process are shown in Table I. Correlation between the properties was analysed by a statistical method. The properties which were found to have positive correlation with the bulk density of the final product in 99 or 95% confidence are crystallite size of the dried substance and crystallite size and lattice strain of the calcined substance. The larger crystallite of the dried substance enables a high and constant density of the sintered substance to be obtained. The dried substance with a crystallite size of less than 200 Å usually gave a product with a bulk density less than 90% T.D., and very fine microcracks were generally observed with a microscope in this sintered material.

3.1. Properties of the sol

The crystallite growth rate in the aging step is affected by the concentration of hexavalent uranium and chloride ion, pH, etc. The effects of the hexavalent uranium were reported at the CNEN symposium at Turin [4], and the addition of a small amount of U(VI) ion was recommended for better crystallite growth. It seems worthwhile mentioning that the peculiar effect of the uranyl ion may be concerned with its adsorption on the UO_2 crystallite surface.

Sulphate ion was found to retard the crystallite growth rate very markedly, since the crystallite size of a dried substance made from a uranous chloride solution containing sulphate ion of 10 wt% of uranium grows only up to 70 Å, while the average size of the common dried substances is about 300 Å. The sintered material prepared from sulphate-containing uranous chloride solution was low in density, and a peculiar Widmanstätten structure was observed in the UO_2 crystal grains under a microscope.

The effect on the resultant sol properties of the amount of ammonia added to the uranous chloride solution was examined. A definite amount of ammonia was added with vigorous stirring after the uranous chloride

TABLE I. SOME PROPERTIES OF INTERMEDIATE AND FINAL PRODUCTS OF THE P.N.C. SOL-GEL PROCESS

Product	Bulk density (%T.D.)	BET (m^2/g)	Crystallite size	Lattice strain (radian)	Lattice constant (a)	Cl content	O/U ratio
Hydrated UO_2 sol	-	-	30 Å	-	5.49	5 %	2.05
Purified UO_2 sol	-	-	200 Å	0	5.46	1.5 %	2.05
Dried substance	53	9	300 Å	0.003	5.44	1 %	2.35
Calcined substance	58	13	500 Å	0.006	5.45	0.2 %	2.2
Sintered substance	96	0.03	15 μm	0	5.47	< 5 ppm	2.00

solution (100 g/l) had been adjusted for a U(VI)/U total ratio of 0.1. The ratio x of the ammonia added to the uranium is calculated by the following equation:

$$(NH_4OH) = x(U(IV)) + \tfrac{1}{2}(U(VI)) + (HCl_{free})$$

( ) : mole

Aging and decantation were repeated twice in the manner of the flow sheet shown in Fig. 1.

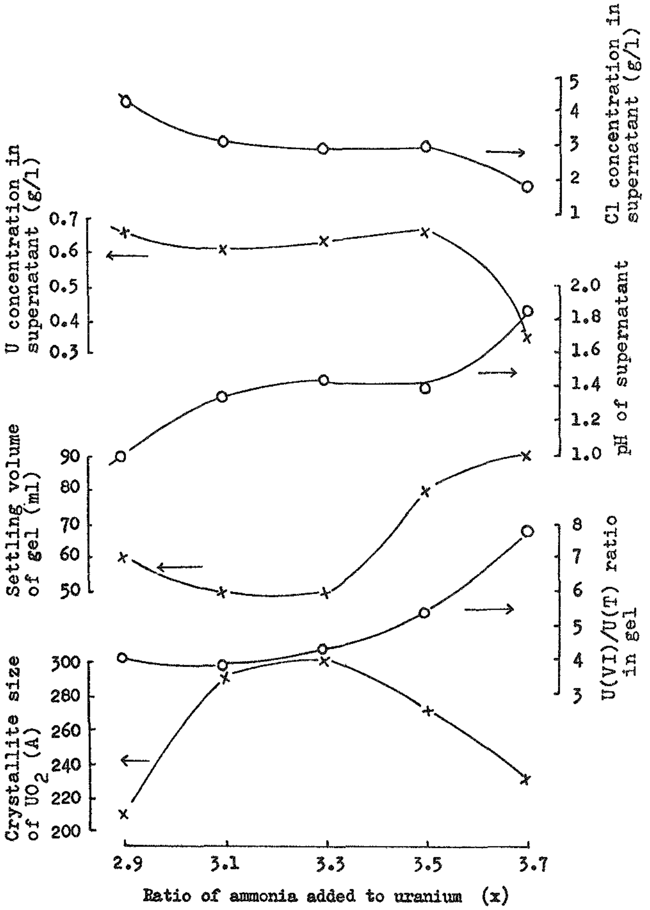

FIG. 2. Changes of properties of the UO_2 sol after the second aging with varying ratio of ammonium added to uranium.

Changes in the properties of the supernatant solution and the gel precipitate with different x after the second aging are shown in Fig. 2. Crystallite grows most rapidly and the settling volume is smallest at an x of 3.3, where pH is buffered to about 1.4. A similar tendency was also observed after the first aging.

Zeta potentials of the sol particles were measured by means of electrophoresis. The potentials measured were from 25 to 45 mV in the pH range from 2.5 to 5.0 and were fairly constant although the U(VI) concentration was varied.

3.2. Properties of intermediate products during firing

The dried materials obtained from purified sol have a very fine texture which could be distinguished by means of electron micrographs of their cracked surfaces. By means of a mercury porosimeter, it was found that open pores of radius larger than 100 Å contribute only 10% of the total porosity, which is 47% of the total volume on the average.

There is a crystallographical indication that the UO_2 crystals of the dried materials have some chloride ions substituted for oxygen ions in the lattice, the amount of which was estimated at about 0.8 mole% of the total oxygen or about 0.2 wt% of the total UO_2. This chloride ion is not released easily on heating, and its complete release below the analytical detection limit (5 ppm) requires heating at a temperature as high as 1200°C. The release was found to proceed slowly with the growth of the UO_2 crystals. The chloride ion contributes greatly to the low temperature sinterability of the material, since the lattice is somewhat activated by the chlorine of large ionic radius and, furthermore, it is especially activated along the diffusion paths of the chlorine during its release. Details of the behaviour of the chlorine were discussed in the paper presented at the CNEN Symposium [4].

The UO_2 crystal growth was found to obey the well-known third power equation of crystal growth in sintering, $r^3 - r_0^3 = kt$. The activation energy of the growth of the sol-gel UO_2 was estimated at 152 kcal/mole at temperatures above 1000°C, and the growth rate is formulated

$$r^3 - r_0^3 = 10^{22.6} t \exp(-152\,000/RT) \ (\mu m\ 3/h)$$

It is noticed that the activation energy coincides with the largest value among reported values of the common UO_2, and the frequency factor is at least three orders of magnitude higher than that of the common UO_2.

The densification mechanism of the sol-gel UO_2 was studied with a dilatometer, and it was found that the sol-gel UO_2 is densified during firing by a kind of plastic flow caused by the movement of dislocations in the crystals as reported in another paper submitted to this Panel.

4. APPLICATION OF THE SOL-GEL PROCESS

4.1. Pellets

Low-temperature sintering of UO_2 pellets was studied with UO_2 powder prepared by the sol-gel process. As mentioned above, UO_2 crystallites of the sol-gel dried substance must be properly stabilized by increasing their size and decreasing their chlorine content by means of aging and decantation to obtain high density UO_2 sherds. Powder for the pellets should be even less active than that for the sherds, as the green pellets suffer from more stress and the arrangement of the UO_2 crystals in them is not homogeneous. Stabilization of the UO_2 crystals for the pellets was accomplished either by calcining at moderately high temperatures or by aging at a higher temperature (200°C). The former method was found to be preferable because with the latter it was difficult to obtain constant reproducibility. The established conditions of the process are as follows.

Uranous chloride solution was hydrolized by adding ammonia water at about pH 5 and mixing well. The precipitate was centrifuged, washed with water twice, and then dried at 95°C. The dried material was pulverized with a vibration mill and calcined at 900°C. The calcined powder was pulverized well again, and then cold pressed at 5 tons/cm^2 into pellets. The green pellets were sintered at 1400°C under a N_2-5%H_2 atmosphere.

The mean bulk density was 96.12% T.D. with a standard deviation σ of 0.18 % T.D.; the mean pellet diameter was 5.841 mm with σ of 0.0048 mm. These σ values were found to be much smaller than those for the common UO_2 pellets from A.D.U.. This seems to be the result of the higher green density (about 66 % T.D.) which may be obtained with the round crystal shape of the sol-gel UO_2.

Similar procedures were also applied to the uranous nitrate solution. The bulk densities fired at 1400 and 1600°C were 92.2 and 95.0% T.D., respectively, which are less than those from the uranous chloride solution. The superior sinterability of the chloride process can be ascribed to the effect of the chloride ions incorporated in the UO_2 crystal lattice.

4.2. Preparation of sol from UO_2 powder

Methods of preparing sol from UO_2 powder were investigated. Since preliminary experiments indicated that ceramic grade UO_2 powder with a crystallite size of about 1000 Å could not be dispersed even by hot hydrochloric acid treatment, partial chlorination by carbon tetrachloride vapour was tried for the sol preparation.

Nitrogen gas containing a constant partial pressure of carbon tetrachloride vapour was obtained by flowing nitrogen through liquid carbon tetrachloride held at a constant temperature (30-50°C). The nitrogen saturated with carbon-tetrachloride vapour was then introduced into a furnace heated at 450 to 500°C, where the surface of the UO_2 powder on a boat was chlorinated for 15 to 60 minutes. The resultant sample, which was composed of UO_2, $UOCl_2$ and UCl_4, in that order, from the centre to the surface of the particle, was easily suspended in water. The sol was adjusted for pH in the range from 1.6 to 2.0 by adding dilute ammonia water, aged at 95°C for 17 hours, and then decanted to separate the supernatant from the settled, gel-like precipitate. Exactly the same conditions of drying, calcination and sintering were applied for the sample. Sintered densities of more than 95% T.D. were obtained where the extent of chlorination was sufficient or the Cl/U molecular ratio was larger than 1.

4.3. Uranium monocarbide sherds

Uranium monocarbide sherds were made from mixtures of carbon black and UO_2 sol prepared either by the common method from uranous chloride solution or by the chlorination of UO_2 powder described above.

A variety of factors such as the kind of carbon black, the type of UO_2 sol and the firing conditions were studied for the preparation. The best result, with bulk densities higher than 95% T.D., was obtained by using furnace carbon with a particle size of 350 Å and UO_2 sol obtained by chlorination, treated with supersonic oscillator for mixing, and by firing up to 1900°C with a heating rate as high as 1200 degC/h after holding at 1000°C for 2 hours. Ball milling for a comparatively long time was also an effective way of blending carbon homogeneously, but the use of surfactants, although it improved the suspension of carbon fairly well, resulted in low sintered density.

It should be mentioned that low sintered densities (around 80% T.D.) were also obtained either by a lower heating rate for sintering or by holding for 2 hours at a temperature higher than 1200°C where extensive carbothermic reduction reaction occurred. This suggests that a sort of reaction sintering mechanism contributes greatly to densifying the material, even when there is extensive gas evolution.

5. EVALUATION

Evaluation of the sol-gel vipac fuel has been made mainly in comparison with the pellets. It was found that the thermal conductivity of the former, measured by the radial heat flow method, was similar to that of pellets of the same density. The impurity contents, including gas components, were found to be much lower in the former than in the latter.

Preliminary irradiation testing of the sol-gel vipac fuel of natural UO_2 was carried out in JRR-2 (CP-5). A central void of 3.2-mm diameter was observed, together with surrounding columnar grains having many lenticular voids. It was suggested that the central void was formed by microvoid migration, but not by central melting.

Irradiation testing of 2.6% enriched UO_2 vipac capsules was carried out in JRR-2 and GETR. The rod power was estimated as being 400-500 W/cm and the burnup of the sample by GETR was 5000 MWd/t. Post-irradiation testing of these capsules is now being performed.

Two vipac fuels of 2% PuO_2-UO_2 were also irradiated in GETR. The designed rod power is about 400 W/cm, and the blending techniques of UO_2 sol with plutonia powder and plutonia sol are compared for their irradiation behaviour. They are now under cooling. Many irradiation tests of the sol-gel mixed oxide vipac fuels are planned with varying Pu enrichment from 2 to 40% for thermal and fast reactor uses in GETR, JMTR, HALDEN and the E. Fermi reactor.

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EXAMINATION OF SOL-GEL UO_2 SURFACES BY SCANNING ELECTRON MICROSCOPY

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Abstract

EXAMINATION OF SOL-GEL UO_2 SURFACES BY SCANNING ELECTRON MICROSCOPY. Scanning electron microscopy has many advantages over optical microscopy and transmission electron microscopy for the study of bulk samples. The external and fracture surfaces of 500-μm diameter spheres of dense and porous sol-gel UO_2 have been examined with this new technique at magnifications up to 9200 without the need for lengthy sample preparation. The results are compared with those from optical micrographs of polished and etched sections.

Spheres of UO_2 of 89 and 96% density calcined for 4 h at 1150°C in hydrogen had a smaller grain-size (0.2 - 0.4 μm) in the surface layers than in the bulk (0.6 μm); closed pores of the order of 0.1 μm diameter were present on the grain boundaries. Spheres of UO_2 of 500 μm diameter and greater than 98% density calcined for 4 h at 1400°C in hydrogen had a surface layer of 30 μm depth containing grains of about 1 μm mean size, with larger grains (3 μm) in the bulk.

A possible explanation of these observations is grain growth inhibition in the surface layers by impurities, which may be metallic oxides or particles of carbon arising from the decomposition of organic material used in the preparation of the gel spheres or gaseous impurities trapped in small closed pores.

1. INTRODUCTION

The microtopography of the surface and internal structure of solids has been examined up to now by optical microscopy and by electron microscopy using conventional replication techniques. These methods usually require lengthy sample preparation and suffer from many disadvantages, particularly when rough or fragile surfaces are to be examined at high magnification.

The scanning electron microscope [1] eliminates many of the disadvantages of the above-mentioned methods and allows surfaces to be examined with little or no sample preparation at magnifications from 20:1 to 100 000:1 and a resolution of 200 A.U. We have used this technique to examine the internal and external structure of dense porous UO_2 spheres made by a sol-gel process, and have compared the results with conventional optical microscopy of polished and etched surfaces.

2. EXPERIMENTAL

2.1. The scanning electron microscope and its advantages

The instrument is made by the Cambridge Instrument Co., London, and uses a focused electronbeam, accelerated by a voltage which can be varied continuously between 1 and 20 kV, and focused to small size on the specimen surface. The low-energy secondary electrons emitted from the specimen are collected on a scintillator which is coupled to a photomultiplier. The primary electron beam is made to scan the specimen in a square raster, and the secondary electron current is used to modulate the beam intensity of two CR tubes which are scanned in synchronism with the primary electron beam. A magnified image of the surface of the specimen is built up on the screens of the CR tubes, one of which can be observed visually and the other photographed.

The specimen chamber will accept specimens up to 12 mm in diameter and 3 mm thick, and the stage can be moved and rotated to enable the specimen to be viewed from different angles and to allow stereo-pair photographs to be obtained. Most specimens require little or no preparation; normally it is necessary only to stick or clamp the specimen onto a small removable metal stub in the stage. There need be no polishing or etching of surfaces, and since large samples can be accepted, there is no need to cut thin sections. Insulating specimens should be given a thin conducting layer of evaporated material to prevent charging. However, with some sacrifice of resolution it is possible to observe uncoated specimens if the accelerating voltage is kept below the secondary emission crossover voltage (1-3 kV) for the particular surface. This may be useful for biological specimens. The energy of the electron beam is small so that fragile specimens can be examined with little risk of damage.

The instrument is ideally suited to the direct examination of the topography of solid bulk specimens which have rough surfaces or which have other characteristics, e.g. fine whiskers, which make them difficult or impossible to replicate and to study by transmission electron microscopy. The depth of focus of the scanning electron microscope is at least 300 times that of an optical microscope at the same magnification, and yet gives an image on a screen which appears very much like that seen with an optical microscope. A maximum magnification of about 200 000 can be obtained, but about 20 000 is the practically useful maximum. A resolution down to about 200 A.U., mainly limited by the size of the scanning spot, is possible. This is not as good as the transmission electron microscope for thin sections, but not unreasonable in comparison with the resolution that can be obtained on replicas of rough or fragile surfaces.

2.2. Preparation of UO_2 spheres

The UO_2 gel spheres were prepared by the standard method described in detail elsewhere [2] from a UO_2 sol dewatered in a column of Alphanol-79 (Shell) containing 0.5 vol.% Span 80 (non-ionic) and 0.5 vol.% Amine-O (anionic) surfactants. The spheres were dried and calcined in the three ways outlined in Table I to give final oxide spheres of 400-600 μm diameter, densities of 89, 96 and 98% theoretical density (T. D.), an O/U ratio of 2.005 and a carbon content of about 0.02 wt%.

2.3. Preparation of samples for optical microscopy

Spheres were mounted in acrylic resin and polished with SiC grit, and finally with 1 μm diamond. They were examined by reflected light in a Zeiss Ultraphot II microscope at 160-240 magnification and photographed on 5 in × 4 in cut film. Polished sections were etched with sul-

TABLE I. METHODS OF DRYING AND CALCINING THE UO_2 SPHERES

Sample	Drying schedule	Calcination schedule	Final density (%T.D. Hg method)
A	Vacuo, 25°C, 24 h	CO_2, 850°C, 4 h, H_2, 1150°C, 4 h	89
B	Air, 25°C, 24 h	As above	96
C	Air, 25°C, 24 h	Steam, 450°C, 3 h; CO_2, 850°C, 4 h, H_2, 1400°C, 4 h	98

phuric acid-hydrogen peroxide at 25°C for 30 seconds. Whole spheres were photographed at 30 times magnification in thin layers by transmitted and reflected light.

2.4. Preparation of samples for scanning electron microscopy

Specimens of spheres were fractured with a mortar and pestle and placed on the surface of an aluminium specimen stub which had been coated with DAG colloidal graphite. The sample was allowed to dry for 5-10 minutes and placed in the scanning electron microscope, the magnification having been selected in the range 1-9000, using an accelerating voltage of 20 kV and fields of fractured surfaces or unbroken external surfaces photographed on 5 in × 4 in cut film.

3. RESULTS

Optical micrographs of the 98% dense UO_2 spheres as received and then polished and etched are given in Fig. 1. Little detail, apart from micron-sized pores, could be seen on the polished spheres, but etching showed up the UO_2 grains. The apparent mean grain-size in the centre of the majority of the spheres was about 12 μm, whereas there was a band of much smaller (1 μm) grains extending about 30 μm below the surface on 460-μm diameter spheres (etched, Fig. 1.). Pores were visible as black spots on grain-boundaries and, less often, within grains. There were indications of very faint boundaries within the clearly defined 12-μm grains in the centres of the spheres, and it has been reported before [3] that this etching technique does not show up grain boundaries clearly as dark lines unless they contain significant impurities. A few spheres were observed which did not contain the larger grains, but these spheres usually had a few small cracks or imperfections in them.

The scanning electron micrographs (Fig. 2) of a fractured sphere of nominally 98% density shows the outer edge, a band of small grains (mean size 1.5 μm) extending 20 μm into the sphere, and a mean grain size of 3 μm over the next 20-μm deep section. Small pores of about 0.3 μm diameter show as black holes on the grain boundaries The small white areas are due to charging effects on the surface or on small particles on top of the surface.

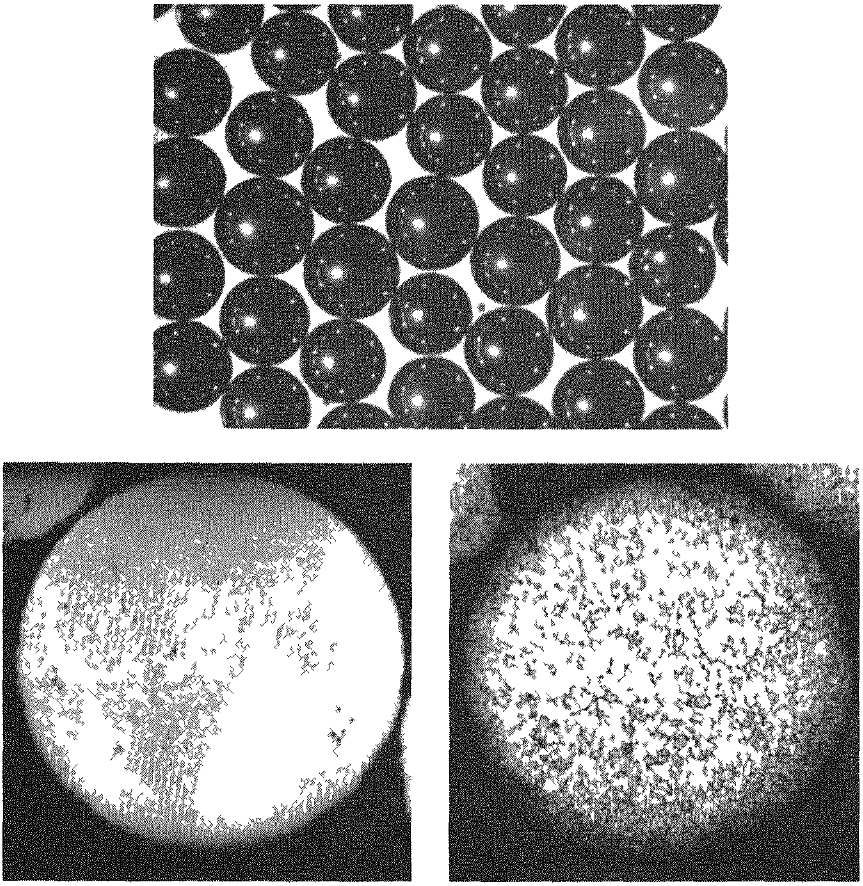


FIG.1. Optical micrographs of 98% dense UO_2 spheres, top, as received, × 21, bottom left, polished section before etching, × 168, bottom right, polished section after sulphuric acid etch, × 112.

The external as-received and internal fractured surfaces of a 98% dense UO_2 sphere are shown at higher magnification in Fig 3 The mean grain-size in the external surface is 0 5 μm, whereas grains of 2-6 μm width are seen near the centre in this photograph with a few 0 1-0 5 μm diameter pores on the boundaries

Optical micrographs of polished sections and scanning electron micrographs of external surfaces and fractured surfaces of 96% and 89% dense UO_2 spheres are shown in Figs 4 and 5, respectively There is the same general effect of smaller grains in a 20 30 μm deep surface layer compared with the centre, as in the 98% dense specimen calcined at 1400°C The mean grain sizes in the external surfaces were 0 25 μm and 0 4 μm for the 96% and 89% dense spheres, respectively In both samples the mean grain size at about the centre of the sphere was 0 6 μm, but the grains appeared to be tightly connected into sheets in the 96% dense sample whereas they were more loosely and randomly connected in the 89% dense sample

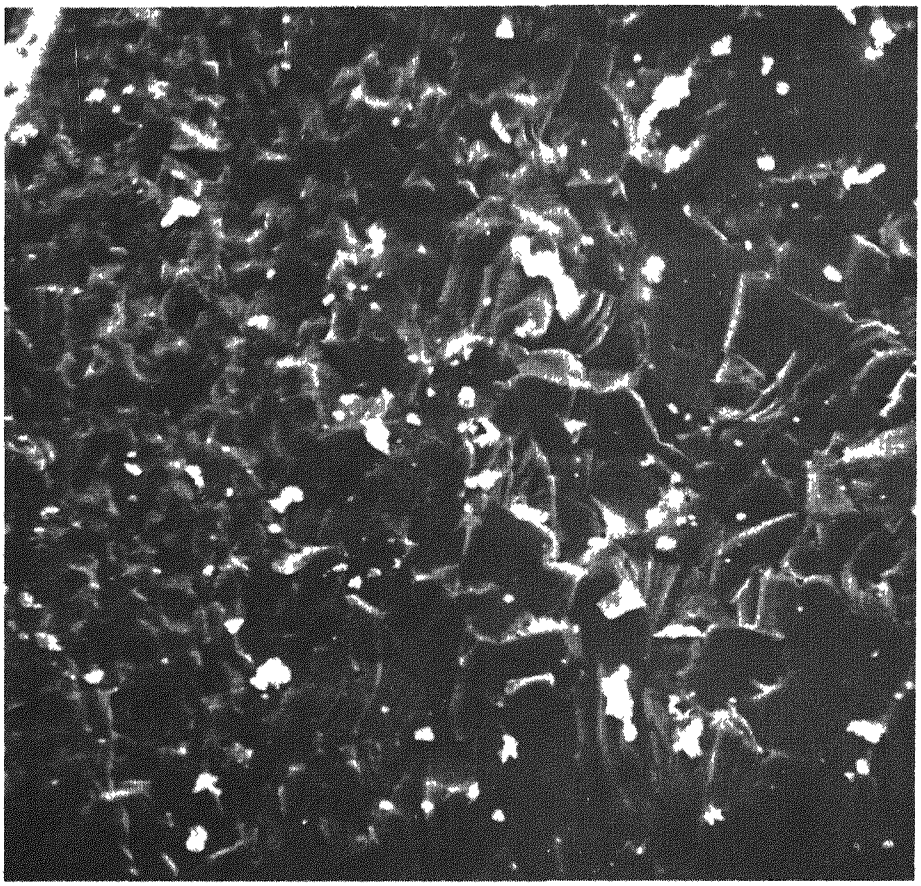


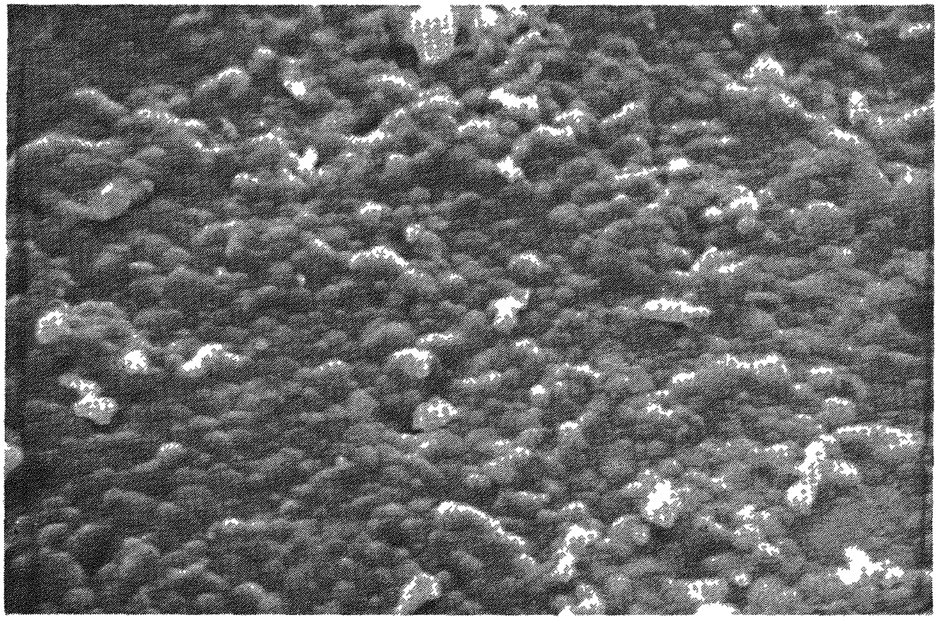
FIG. 2. Scanning electron micrograph of fractured surface of 98% dense UO_2 sphere showing small grains in outer surface (top left) and large grains in centre, × 2800.

Intergranular polygonal pores of 0.1-0.3 μm width were present inside the spheres in both samples, but the pores visible on the surface appeared to be smaller (< 0.1 μm).

4. DISCUSSION

The three batches of UO_2 spheres all contained a 20-30 μm thick shell of finer grain material (0.25-0.5 μm) around a core of about 450-μm diameter of fairly uniform grains (0.6 μm for 89 and 96% dense, about 3 μm for 98% dense). The thickness of the shell was not markedly dependent on the final sintering temperature (1150 or 1400°C) or on the atmosphere (vacuo or air) during the initial drying stage.

Willmarth [4] observed a band of about 6-μm thickness at the surface of dense ThO_2 spheres of about 500-μm diameter prepared by dewatering



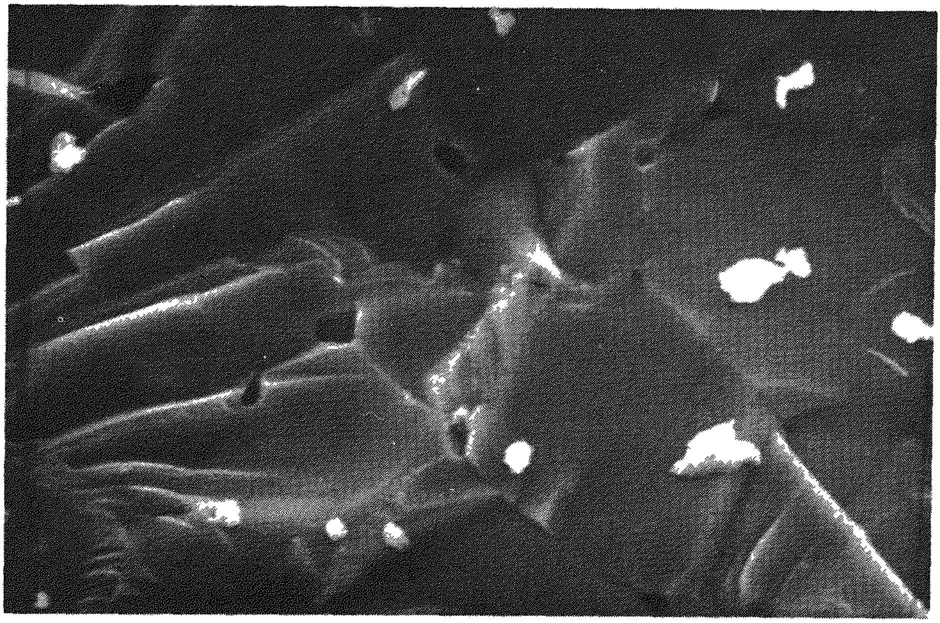


FIG.3. Scanning electron micrographs of 98% dense UO_2 sphere: top, external surface, X 7350; bottom, centre of fractured sphere, X 7040.

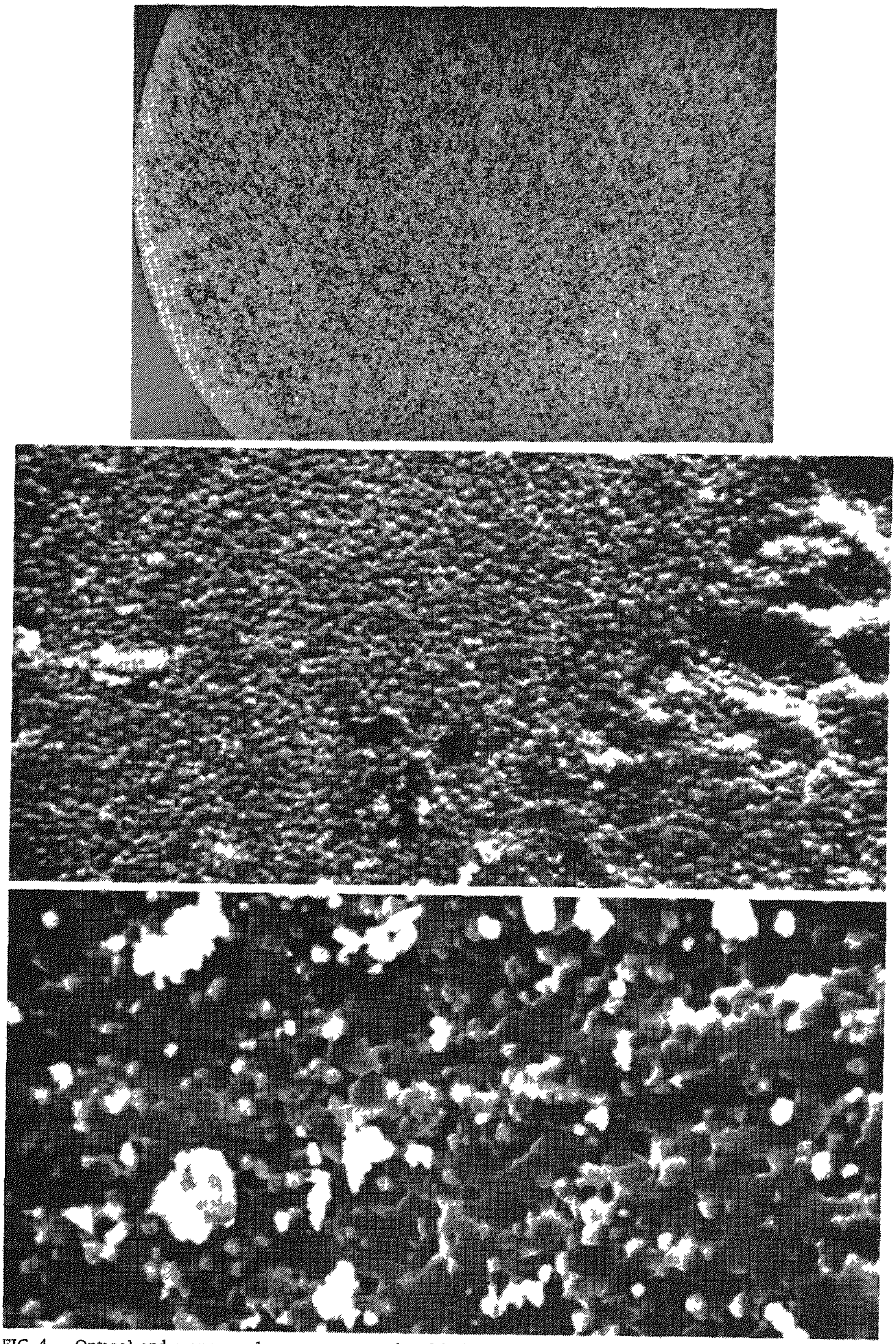


FIG.4. Optical and scanning electron micrographs of 96% dense UO_2 spheres: top, optical, polished section, X 192; centre, SEM, external surface, X 6950, bottom, SEM, centre of fractured sphere, X 6720.

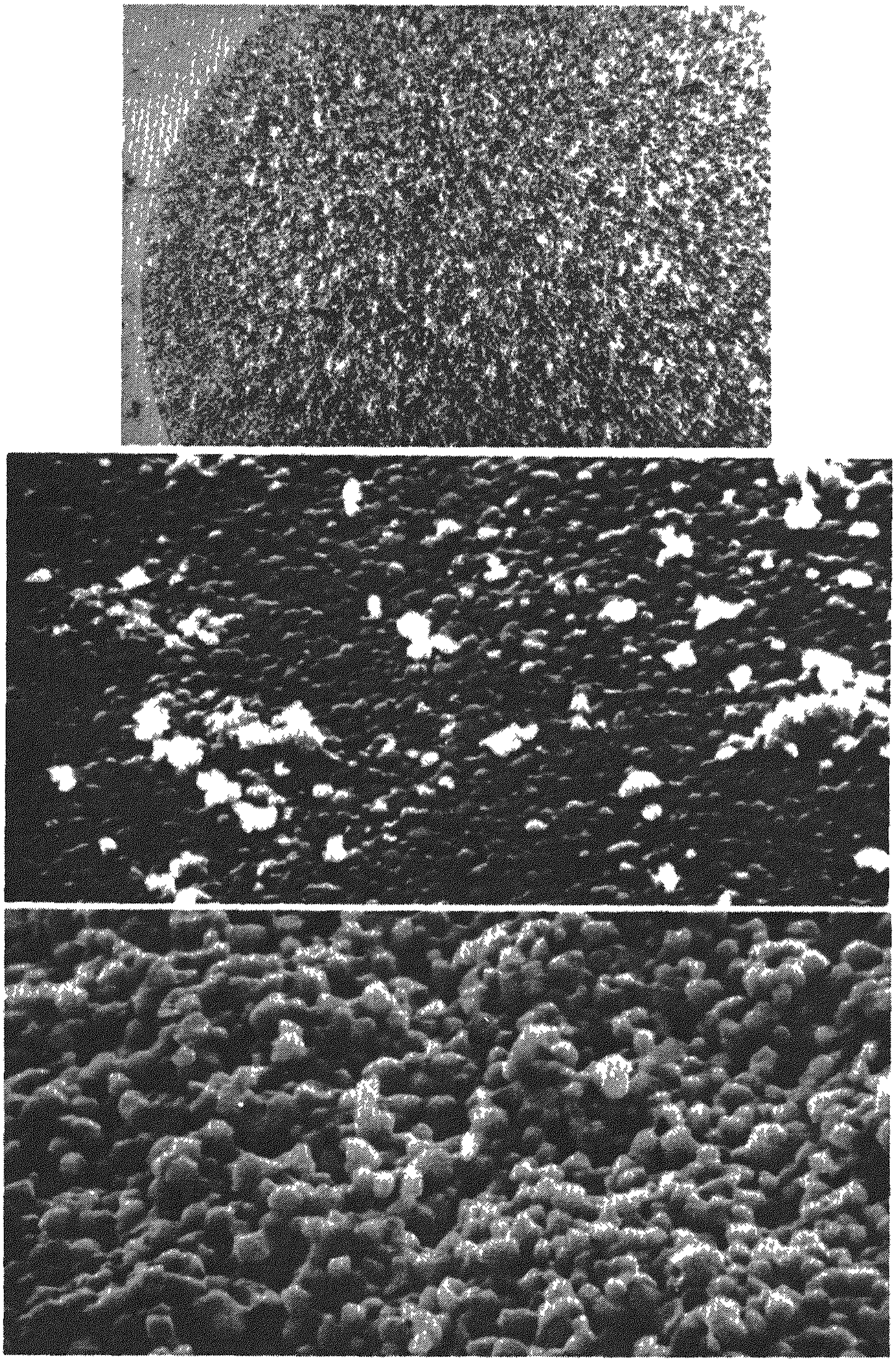


FIG. 5. Optical and scanning electron micrographs of 89% dense UO_2 spheres: top, optical, polished section, × 192; centre, SEM, external surface, × 6800; bottom, SEM, centre of fractured sphere, × 6720.

a ThO_2 sol in 2-ethylhexanol containing a non-ionic surfactant and then calcined in air. He reported that the outer shell had no observable structure when examined as a polished section in the optical microscope or as a replica in the electron microscope. He suggested that the principal constituent was amorphous carbon derived from the non-ionic surfactant, and claimed that the shell was not obtained when cationic surfactants were used. The ratio of the thickness of the shell to the diameter of the ThO_2 sphere was a factor of 4-5 less than we observed for the UO_2 spheres, and the shell in the UO_2 spheres had a definite grain structure compared to the structureless shell in the ThO_2 spheres. We used a mixture of non-ionic and anionic surfactants.

It seems probable that the finer grain material in the UO_2 shell is due to grain growth inhibition by impurities rather than exaggerated grain growth in the centre, such as has been reported by Amato [5] for UO_2 pellets sintered with organic additives. Grain growth inhibition could be caused by·

(a) Small amounts of inorganic impurities, particularly metal salts soluble in water, which may have migrated towards the outer surface of the spheres during the slow removal of water from the gel spheres.

(b) Small particles of carbon derived from the surfactants and Alphanol remaining in the spheres after the initial drying stage, and only slowly removed in the following calcination stages The final carbon content of the bulk of the spheres was only of the order of 0.02 wt%, and if most of this was in the outer shell it would amount to 0.12 wt%. This is not high, but could have been much higher in the early stages of sintering at 850°C and at the beginning of the final sintering stage at 1150 or 1400°C.

(c) Gases, derived from the decomposition of organic compounds, trapped in pores which are thus prevented from shrinking, as suggested by Amato [5] The observation of a more uniform grain size across the diameter of a few spheres which had imperfections and cracks fits in with this explanation, because there may be a higher proportion of open porosity in these spheres which allows gases to escape more easily

Further experiments are planned to examine the method of formation of the outer shell of finer grain material and to study the effects of various types of surfactant. However, this preliminary work has demonstrated the advantages of the scanning electron microscope in the investigation of the topography of solid surfaces, compared with optical microscopy and conventional electron microscopy using replicas, both of which techniques require lengthy sample preparation and give results which are often criticized as not being representative of the as-received surfaces.

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✓ INFRA-RED SPECTRA OF THORIA GELS

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Abstract

INFRA-RED SPECTRA OF THORIA GELS. The infra-red spectra of thin films of thorium nitrate and thoria gels derived from thorium nitrate by precipitation and by thermal denitration were measured on silver chloride plates. This technique gave good quality spectra and avoided the use of mulling agents with interfering absorption bands in the 2-15 μm region, or alkali halide discs in which rearrangement reactions with nitrate groups are known to occur. The nitrate was present as co-ordinated nitrate groups in the gels prepared by both methods and containing a range of nitrate-to-thorium mole ratios of 0.02-0.3. Small amounts of residual nitrate, and the solid state reaction of this with potassium bromide, have been overlooked in previous interpretations of the spectra and structure of thorium hydroxide precipitates derived from thorium nitrate.

1. INTRODUCTION

The preparation and structure of sols and gels of thorium oxide and uranium oxide and their conversion into solid particles of controlled composition, shape and size for use in nuclear fuels have been reported from many laboratories and were reviewed recently [1]. Infra-red spectroscopy has been used very little as a technique to study the structure of these sols and gels or the nature of the residual anions, e.g. nitrate, present in them. Infra-red spectra of thorium hydroxide precipitates prepared from thorium nitrate solution have been reported [2] as part of a study of hydrated thorium oxide as a cation-exchanger. However, in the latter work and in some previous work [3, 4], the presence of residual nitrate in the precipitate and its reaction with the potassium bromide used to prepare sample discs was overlooked, and the principal absorption bands appear to have been wrongly assigned.

Infra-red spectra of thoria gels prepared by two methods have been examined by a technique which avoids interfering absorption bands from mulling agents, or from reactions with potassium bromide. The absorption bands are compared with those in hydrated thorium nitrate and interpreted in terms of the bonding of water molecules and nitrate groups to the thorium atoms.

2. EXPERIMENTAL

2.1. Preparation of thoria gels and hydrated thorium nitrate

Dispersible thoria gel, prepared by denitration of hydrated thorium nitrate crystals at 475°C for 3 h in steam, was obtained from the Oak Ridge National Laboratory, Oak Ridge, Tennessee. It contained 0.028 mole residual nitrate per mole of thorium. A sample was peptized with dilute nitric acid to form a 2 M ThO_2 sol containing a total of 0.08 mole nitrate per mole of thorium. Samples of B.D.H. Analar $Th(NO_3)_4 \cdot 6H_2O$ were used (a) as received, (b) dried at 100°C for 1 h, and (c) dried at 140°C for 18 h. The weight loss of a sample of the as-received $Th(NO_3)_4 \cdot 6H_2O$ ignited to 1000°C for 1 h corresponded to that expected for the hexahydrate. The weight loss after 1 h at 100°C corresponded to 0.7 H_2O, assuming that no nitrate was lost under these conditions.

Thorium hydroxide was precipitated from 0.25 M thorium nitrate solution with a slight excess of ammonium hydroxide at 20°C, the precipitate washed with water, and peptized with dilute nitric acid to give a 3 M Th sol containing 0.3 mole of nitrate per mole of thorium. When dried at room temperature, or at 80°C for 1 h, this sol gave a transparent glassy gel.

2.2. Measurement of infra-red spectra

Samples of the above materials were ground to fine powders with an agate mortar and pestle and pressed by hand with a spatula as thin films on silver chloride plates (3 cm × 1 cm × 1 mm thick) which are inert towards metal nitrates and water. A few drops of the sols were dried as thin films on the plates at 80°C for a few minutes. Infra-red spectra over the range 2-15 μm were measured with a Hilger and Watts Infrascan spectrometer. Samples of solids were also incorporated into thin discs of paraffin wax pressed between 25-μm thick films of polythene at 2 tons/in^2 [5], and spectra measured over the 15-45 μm range (against a blank wax/polythene disc in the reference beam) in a Hilger and Watts DM4 spectrometer purged with dry nitrogen.

3. RESULTS

The absorption bands in the 2-15 μm region are given in Table I and the band-shapes for four of the samples are shown in Fig.1. The spectra of the hydrated thorium nitrate as-received and also dried was measured for comparison of the nitrate absorption bands with those for the gels. The frequencies of the bands are in general agreement with those reported by previous workers [6-8] who used KBr discs or nujol mulls, both of which techniques can give interferences because of a solid-state reaction with KBr, or overlapping bands with nujol.

Preliminary measurements in the 15-45 μm region indicated bands (cm^{-1}) at 485s, 405m, 320s, 235w for the ORNL thermally denitrated thoria powder and at 465w, 322s, 233w for the transparent gel dried from a 3 M ThO_2 sol made from precipitated thorium hydroxide.

4. DISCUSSION

4.1. The structure of hydrated thorium nitrate

The crystal structure of $Th(NO_3)_4 \cdot 5H_2O$ was determined recently by X-ray diffraction [9] and neutron diffraction [10] and it was shown that there are eleven oxygen atoms bound to the thorium atom, eight being

TABLE I. INFRA-RED ABSORPTION BANDS (cm^{-1}) OF THORIUM NITRATE AND THORIA GELS
(s = strong, m = medium, w = weak, sh = shoulder, v = very, b = broad)

	Form on AgCl plate	H_2O st.	H_2O bend	NO^{II} st.	NO^{I} antisym. st.	NO^{I} sym. st.	ONO bending bands
$Th(NO_3)_4 \cdot 6H_2O$	powder	3460m 3100m	1640m 1615sh	1540sh 1500vs	1312m 1280s	1034sh 1028s	811m 758w 725w 805w 745m 705w
as above, 1hr, 100°C	powder	3500m	1612m	1535sh 1500vs 1470sh	1308s 1284s	1032s	810m 760w 748w
as above, 18hr, 140°C	powder	3500s	1620m	1510vs	1285vs,b	1030s,b	809m 758w 749m
ThO_2, thermally denitrated, NO_3/Th = 0.028.	powder	3300vb	1670b	1430s	1345s	1035m	very weak.
Gel from 2M ThO_2 sol, denitrated, NO_3/Th = 0.08	dried as thin film	3500s,b	1615m	1515sh 1485s,b	1300s,b	1030m,b	814w 740w
Gel from 3M ThO_2 sol, precipitated, NO_3/Th = 0.3	dried as thin film	3500s,b	1633m	1500s,b	1307s,b	1036m	810w 736w

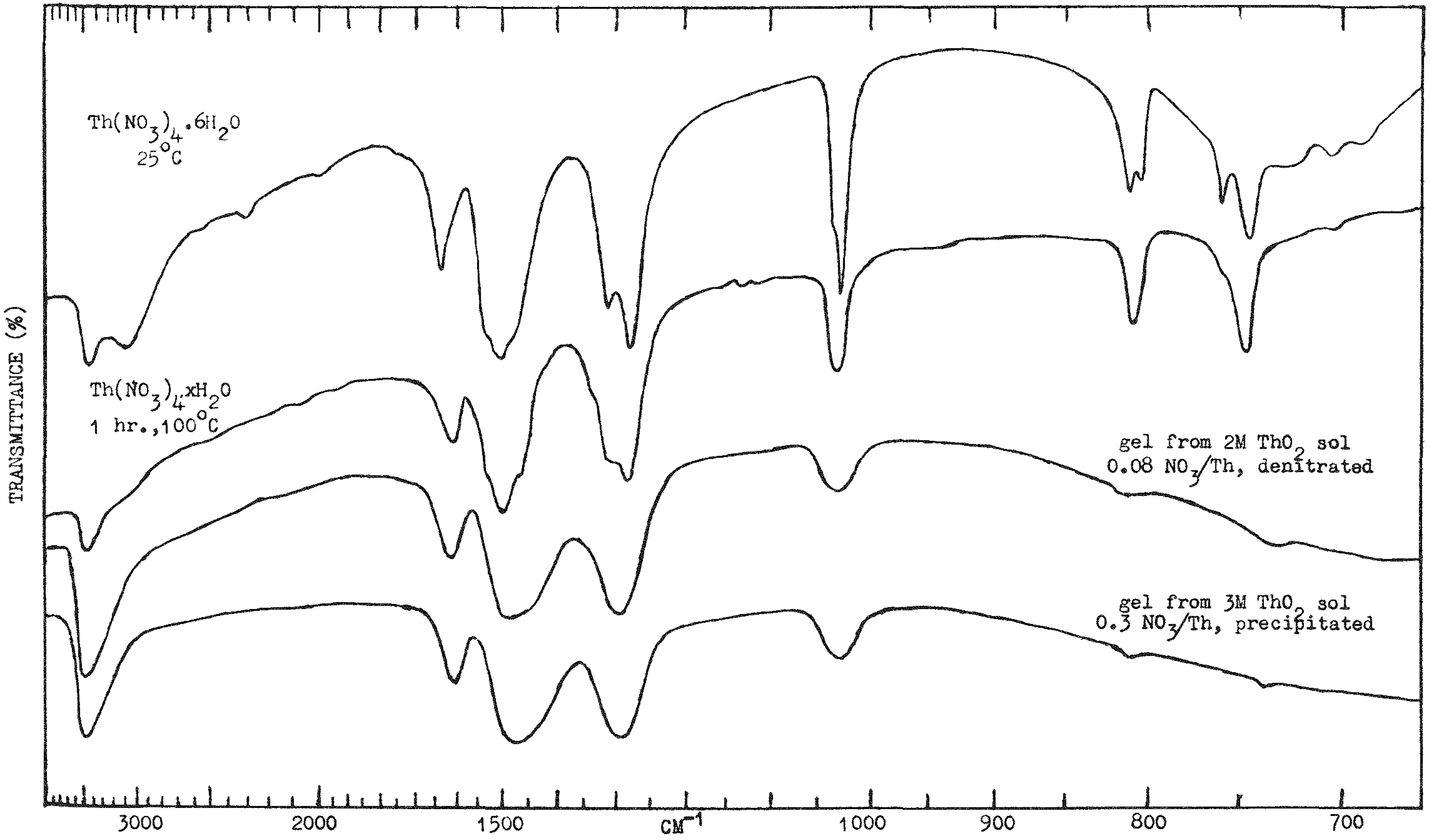


FIG.1. Infra-red spectra of thorium nitrate and ThO_2 gels.

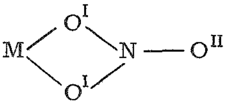
from four bidentate nitrate groups and three from water molecules. These nitrate groups and water molecules together with the other water molecules, are bound in a hydrogen-bonded network in which the hydrogen-bonds are either 'strong' water-water hydrogen-bonds, or 'weak' water-nitrate oxygen bonds. Each pair of the bidentate nitrate groups have somewhat different Th-O bond distances (2.62, 2.50 A.U.) than the other pair (2.59, 2.58 A.U.); all are planar groups but the N-O bond distances are significantly different for the two pairs.

The two groups of authors [9, 10] did not prove that 5 H_2O was present in the crystals by any analytical method, but referred to a recent study [11] of the thorium nitrate-nitric acid-water system which claimed that the stable hydrates at 25°C were the penta- and the tetra-hydrate (the latter only at high nitric acid concentration). Commercial samples are often labelled $6H_2O$ or $4H_2O$, and gravimetric analysis of the sample used in this work indicated $6H_2O$, of which $0.7H_2O$ was readily removed on drying at 100°C for 1 h.

4.2. Absorption spectra of thoria gels

The absorption spectra of the gels derived from thorium nitrate are qualitatively similar to those found for thorium nitrate hydrates and the bands arising from nitrogen-oxygen vibrations have therefore been tabulated under the assignments [12] for bidentate nitrate groups co-ordinated to a metal atom, i.e. structure I.

Structure I



The splitting of the nitrate absorption bands in thorium nitrate hydrate, due to the two types of nitrate bonding environments about the Th atom, is not observed with the gel samples.

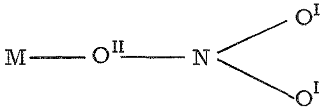
Absorption bands which can be assigned to stretching and bending vibrations of water molecules are observed in the gels. There are two clearly separated bands in the 3 μm region for the thorium nitrate hydrate at 25°C, reflecting the two types of water molecules in the structure. The band at 3100 cm^{-1} is considerably reduced in intensity when the sample is heated to 100°C, and is not present in the spectra of the gels which have been dried out from sols. There is no sharp band in the spectra of the gels in the region of 3600-3700 cm^{-1} which could be assigned to non-hydrogen bonded OH groups bonded to Th atoms, as have been observed for gels of rare-earth hydroxides [13].

A water bending vibration at 1615-1630 cm^{-1} is observed in the gels corresponding to the stretching vibration at 3500 cm^{-1}. The observed bands in these two regions are broad and asymmetric and appear to be the envelopes of several bands. In hydrated thorium nitrate as-received, the band maximum is at 1640 cm^{-1} with a shoulder at 1615 cm^{-1}; when a part of the water is removed at 100°C the maximum of the band shifts to 1612 cm^{-1} (and the intensity of the stretching band at 3100 cm^{-1} decreases). Hence it appears that the 1640 cm^{-1} band and the 3100 cm^{-1} band arise from water molecules strongly hydrogen bonded and the 1612-1615 cm^{-1} band and 3500 cm^{-1} band arise from weakly hydrogen bonded molecules.

4.3. Absorption spectra of thermally denitrated thorium nitrate

The absorption bands observed for the sample of thoria from ORNL (and containing a NO_3/Th mole ratio of 0.028) are at significantly different frequencies to those for gels prepared by adding nitrate to the powder or to precipitated thorium hydroxide, and to those for hydrated thorium nitrate. The water bending band is at the relatively high frequency of 1670 cm^{-1}, the NO^{II} stretching band at the relatively low frequency of 1430 cm^{-1}, and the NO^{I} stretching band at the relatively high frequency of 1345 cm^{-1}. It is possible that the small amount of residual nitrate is bonded to thorium in a unidentate (structure II) rather than in a bidentate configuration; the two highest frequency N-O stretching bands would then be expected to be closer together. The separation of these two bands is only 85 cm^{-1} compared with a mean separation of 220 cm^{-1} for the hydrated thorium nitrate samples, and 189 cm^{-1} for the two gels derived from sols containing 0.08-0.3 NO_3/Th. It is likely that in the gels there are nitrate groups bonded in both unidentate and bidentate configurations to the thorium atoms. This would account for the marked asymmetric shape of the absorption bands at 1500 and 1300 cm^{-1}, since they would represent the envelopes of overlapping bands of different intensities and frequencies.

Structure II



4.4. Absorption spectra of thorium hydroxide precipitates

The infra-red spectra of thorium hydroxide precipitates prepared from thorium nitrate solution have been measured [2-4] in KBr discs and paraffin mulls and the bands interpreted as arising from the basic thorium hydroxide or hydrated ThO_2 matrix. The bands reported by these authors at about 1530-1550, 1400, 1300, 1045-1060 and 840 cm^{-1} correspond closely in frequency and shape to those for residual co-ordinated nitrate groups, or nitrate ions formed by reaction of the co-ordinated groups with KBr, and have obviously been assigned incorrectly by these authors. Only the stretching band at about 3300 cm^{-1} and the bending band at 1615-1650 cm^{-1} for co-ordinated and interstitial water can be unambiguously associated with the aquated thoria matrix from their published results. Further measurements are required over the range 2-50 μm on freshly prepared thorium hydroxide which has been thoroughly washed to remove impurities, and then analysed to determine the residual nitrate content, before the characteristic vibrations of the matrix can be obtained and interpreted correctly.

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DEVELOPMENT OF PROCESSES AND EQUIPMENT

SOL-GEL PROCESSES FOR THE FABRICATION OF CERAMIC FUEL PARTICLES FOR HIGH-TEMPERATURE REACTORS

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Abstract

SOL-GEL PROCESSES FOR THE FABRICATION OF CERAMIC FUEL PARTICLES FOR HIGH-TEMPERATURE REACTORS. In co-operation with organizations and firms working in the field of high temperature reactors and their fuel, the Departments of Chemistry and Metallurgy at the Reactor Centre Seibersdorf of the Österreichische Studiengesellschaft für Atomenergie have been actively engaged in developing and evaluating ceramic fuel particles for this type of reactor. Irradiation tests of the fuel have also been carried out. Although the work was originally concentrated on development, experimental fabrication and testing of fuel particles based on refractory carbides coated with PyC and SiC, in recent years oxide particles have also been studied extensively with respect to their manufacture and application in nuclear reactors. Following the concept of coated fuel particles, three types of product and procedure for oxide-containing particles and processes for oxide-containing kernels have been developed.

Fuel particles from resin bonded metal-salt solutions: The utilization of resin components for the stabilization of droplets of solutions is an aid for the manufacture of ceramic particles based on both real solutions and sols. This process is extremely valuable if carbon diluted oxide kernels for ultra-high temperature applications are required. By variation of the production procedure kernels of melted carbides, carbon-diluted carbides and carbon-diluted oxides can be obtained.

Thorium oxide particles from a combined sol-gel resin bonding process: By utilizing a process similar to that described in the preceding paragraph but with thorium oxide sols instead of metal-salt solutions, thorium oxide particles with high density have been obtained.

Uranium oxide fuel particles from uranium peroxide sols: To avoid the necessity of reducing the uranium to the tetravalent state for production of a stable sol, a sol-gel process based on uranyl nitrate solutions, which are first converted to hydrated uranium peroxide, has been developed. This peroxide is transformed to a stable sol with tetraethyl ammonium hydroxide, which can be concentrated by evaporation under vacuum. Gelation is accomplished by the addition of diethylester of malonic acid. The particles are obtained by spraying, dried by ethylhexanol and converted to the desired final product by suitable heat treatment.

1. INTRODUCTION

In co-operation with international organizations and firms engaged in the design, construction and operation of high-temperature gas-cooled reactors (HTGR), the Departments of Chemistry and Metallurgy of the Österreichische Studiengesellschaft für Atomenergie (SGAE) have been working since 1961 on the development of fabrication methods, experimental manufacture, evaluation and testing of fuel particles. Various methods for the production of different types of fuel kernel have been developed, as well as coating equipment and methods for the deposition of pyrocarbon, carbides (SiC, ZrC), oxides (Al_2O_3, ZrO_2) and metals (W, Mo, Ta).

Although refractory melted carbides were originally preferred as kernels, experimental evidence and theoretical considerations aroused interest in porous kernels as well as in kernels where the fissile or fertile compound is diluted with an 'inert' material such as carbon. The development of processes for the manufacture of microspheres of uranium and thorium oxides in the laboratories of KEMA, ORNL and CNEN introduced further prospects for the arrangement of fuel kernels in the HTGR.

The methods for the preparation of spherical kernels, irrespective of composition, may be broadly classified into powder agglomeration and surface tension methods. Whereas the former is the method used for the fabrication of the fuel for the high-temperature reactors at present in operation, the latter, in which real solutions or sols are transformed into spherical droplets and solidified, presents the advantages of increased uniformity in shape, size and composition of the kernels and the use of recycled fissile or fertile material.

2. SOLUTION PROCESSES FOR FUEL KERNEL PREPARATION

2.1. Fuel kernels from resin bonded metal-salt solutions

Resin components to stabilize droplets can be used in the manufacture of ceramic particles based on both real solutions and sols. As a final product, high density melted dicarbides, carbon-diluted carbides, carbon-diluted porous oxides or pure porous oxides may be obtained.

This precipitation method is based on the condensation reaction of phenols, or phenol-urea mixtures with aldehydes, particularly the reaction of resorcinol and formaldehyde. The two components are mixed in a nozzle system and sprayed through Teflon needles into a paraffin-oil bath at 70-90°C. The pot-life of the mixture is adjusted by organic inhibitant to about 1.2-1.5 min. By the addition of surfactants coalescence is avoided; other additives can be used, for example to adjust the carbon-metal ratio of the final product to the desired value.

Condensation at this temperature leads to rather large particles, which are first washed to remove the paraffin oil and then carefully dried by slow heating up to 160°C. These green kernels are mainly transformed into one of the three varieties of final product:

(a) Melted or sintered carbide kernels

The green kernels are fired in air at 850°C. The resulting porous oxide kernel is coated with carbon black, and in a carbothermic reaction converted to carbide. By increasing the temperature in the graphite crucible to 2420°C (in the case of uranium and thorium) melted carbide spheres with a dense graphite skin of 5-8 μm are obtained.

(b) Carbon-diluted porous carbide kernels

The green kernels with the adjusted carbon/metal ratio are heat treated in the fluidized bed in an inert atmosphere. By this heat treatment the organic resin is thermally cracked and the metal oxides converted to carbides After this heat treatment the porous kernels are coated in the same bed with the first layers of pyrocarbon.

(c) Carbon-diluted porous oxide kernels

To avoid the transformation of the metal oxides to carbides the thermal cracking of the resin as in (b) above is performed in a CO atmosphere The resulting kernels are characterized by an extremely fine dispersion of oxide in carbon which induces stability against fuel migration through pyrocarbon coatings, even at temperatures of 2500°C if during the initial stages of coating a sufficient pressure of CO is maintained to avoid the transformation of oxides to carbides.

2.2. Porous thoria kernels from a combined sol-gel resin process

The basic principles of the procedure are the same as those described in section 2.1. To obtain thoria kernels with 80-90% theoretical density, required for experiments with our 5-7 kg batch coating unit the metal content or molarity of real salt solutions is too small.

By peptization of thorium hydroxide in HNO_3, followed by denitration with formaldehyde, a sol is obtained which is added to the two-component resin just before spraying. The solidification is therefore accomplished, not by real gelation, but by gel-condensation. After the microspheres have been cleaned to remove oil traces, they are first dried at 60°C. A further treatment with either dilute ammonia solution or in a stream of nitrogen saturated with H_2O vapour reduces the residual salt and nitrate content. The particles are then calcined in CO to convert the thorium hydroxide into ThO_2. The cracked carbon residue is finally combusted in O_2, leading to a porous ThO_2 kernel which is finally sintered at 1600°C in argon to give strong kernels with densities between 80 and 85% T D

2.3. Porous UO_2 kernels from sols of uranium peroxides

To avoid the reduction of uranium to the tetravalent state prior to the formation of a sprayable sol, we studied the conditions for the preparation of a sol based on uranium peroxihydrates and its gelation to spherical UO_4 particles The process consists of the following main steps

- Formation of a uranium peroxi-dihydrate by precipitation of uranyl nitrate with H_2O_2

- Formation of the sol of uranium peroxide. The dried, fine grained $UO_4\ 2H_2O$ is added to an aqueous solution (24%) of tetraalkyl ammonium hydroxide under agitation. The resulting sol can be concentrated by evaporation at reduced pressure (20 mmHg) at 55°C to a concentration of 2-2 5 M The existence of a colloidal solution could be demonstrated by X-ray and by rheometric measurements.

- Gelation of the sol by internal gelation with diethylester of malonic acid. After the pH in the sol is changed from 14 to 5 gelation occurs. This shift in pH is best obtained by adding the ester to the sol. The total gelation time is 7-8 min. During this pot-life the mixture can be sprayed through the usual Teflon needle nozzle system with a pressure of 5-7 atm. into a column filled with a mixture of 1, 1, 1 trichloroethane and trichloroethylene to obtain the gelled microspheres.

- Drying, calcination and reduction. Dehydration is performed by contacting the gelled particles with dry 2-ethyl-hexanol and drying at 160°C. Calcination of the particles in argon or nitrogen at temperatures up to 1300°C, followed by a reduction in hydrogen or hydrogen-nitrogen mixtures at 1100°C, produces stoichiometric UO_2 particles with the desired densities of 80-85% T.D. Optimization of the various steps of heat treatment by use of thermogravimetric (DTG and DTA) methods is still continuing, and the scheme given above is therefore only tentative.

3. INVESTIGATION OF THE PRODUCTS

Since interest is mainly centred on the production of fuel particles for high-temperature reactors, most of the investigations are concerned with:

- pre-irradiation evaluation such as stability of kernels and coatings at high temperature (fuel migration and contamination), mechanical properties (crushing strength), internal and surface structure (Stereoscan, X-ray);

- irradiation experiments in purged capsules at temperatures between 1250 and 1650°C to burn-up values of 9% fima;[1] and

- post-irradiation examination, particularly with respect to gross particle failure, microcrack formation and release of solid fission products.

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[1] Fima = Fissions per initial metal atom.

PRODUCTION OF THORIUM- AND PLUTONIUM-DILUTED SOL-GEL PARTICLES

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Abstract

PRODUCTION OF THORIUM- AND PLUTONIUM-DILUTED SOL-GEL PARTICLES. The sol-gel process tested by the OECD Dragon Project was utilized by the Joint CEN-BelgoNucléaire Plutonium Group at Mol in 1964-1965 to determine the feasibility of producing spherical particles containing ThO_2, PuO_2 and C in the proportion necessary to fabricate thorium-plutonium carbide kernels for coated particles. The process was extended successfully to the preparation of thorium and plutonium gels having a significant excess of carbon. Other experiments were performed to test the feasibility of incorporating UO_2 powder into the gel spheres. With this technique U-to-Th ratios of up to 9/1 were obtained.

1. INTRODUCTION

The work described in this paper was performed by the Plutonium Project BelgoNucléaire-CEN, under Dragon Contract No. CON/WIN/57020 'Research and Development of High Temperature Reactor Plutonium Containing Fuels Involving the Sol-Gel Process'.

The aim of the commitment was to assess the feasibility of preparing Th-Pu-bearing coated particles employing the sol-gel process and to ascertain which dilution material could be incorporated into the kernel and in what amount.

The preparation of various sols and the production of gel spheres in a development-scale apparatus are described in this paper.

2. EXPERIMENTAL TECHNIQUE

The flow sheet of the sol-gel process envisaged is indicated in Fig.1. Details of the successive steps are described below.

2.1. Preparation of the sol

Hydroxide precipitate is obtained by pouring an aliquot of 1.5 M (Th or Pu) $(NO_3)_4$ solution into an equal volume of concentrated NH_4OH. The precipitation is quantitative and results in very good filterability. The residual nitrate is removed by stirring (vibromixer) the precipitate repeatedly with very diluted NH_4OH and with water. No losses of thorium or plutonium were observed during these washings. Precipitation and subsequent washings are carried out at room temperature.

The precipitate is then mixed with a quantity of 1.5 M thorium, uranium or plutonium nitrate to reach $NO_3/Pu + U + Th = 0.4$. Peptization of this mixture is then carried out. In several cases it was necessary to add a small quantity of concentrated HNO_3 to reduce the viscosity of the mixture which resulted in a final NO_3/heavy metal ratio of 0.5 to 0.6.

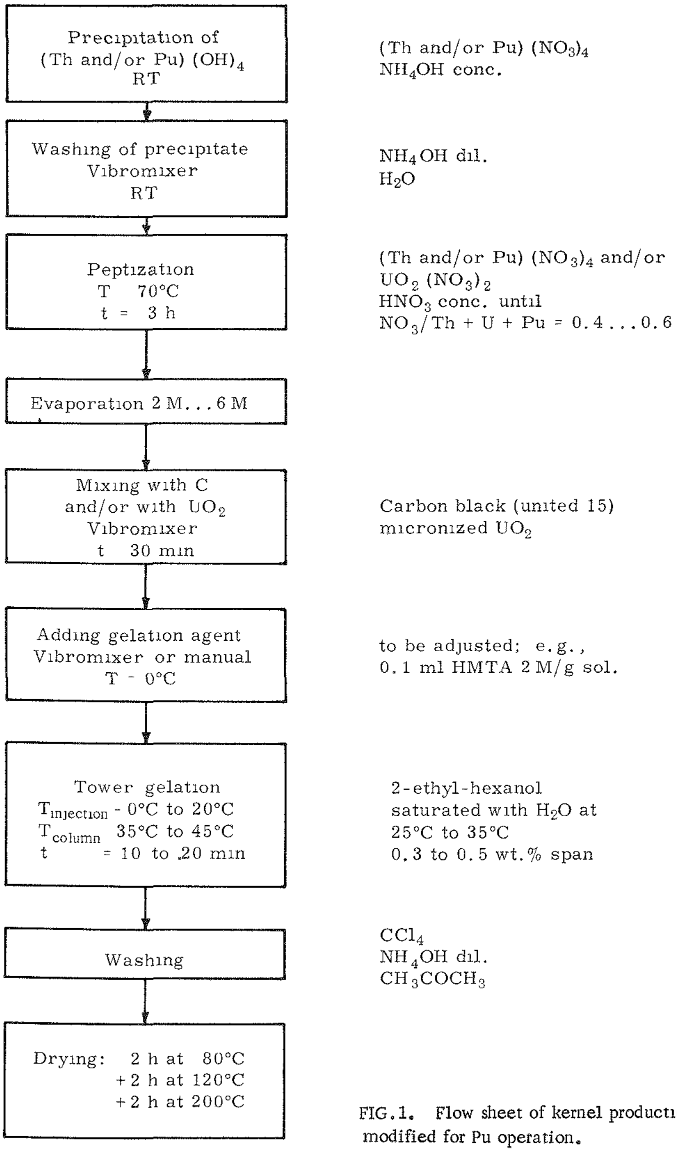

FIG.1. Flow sheet of kernel production by the sol-gel processes, modified for Pu operation.

Transition of the suspension into the sol phase can be observed easily: after heating at 70°C for about three hours the milky suspension turns into a transparent 'oily' sol in the course of a few minutes. This transition is characterized by spot-tests on a droplet of the mixture: before the transition into the sol, the sample dries into a non-coherent powder, whereas after the transition a smooth film is obtained.

Several sols were prepared with molarities ranging from 3 M to 6 M of heavy metal. The desired molarity is obtained by condensing the sol by evaporation to a given volume. Undiluted sols remain stable for at least two months in a closed container.

2.2. Mixing with carbon

To facilitate the control of heavy metal concentration and to reduce the operations with carbon, the carbon is mixed with the previously prepared sol. Very homogeneous carbon-containing sols are achieved by stirring the mixture vigorously with a vibromixer for about 30 min. Visual control of the homogeneity is made by a paint test.

In the case of 12 C/heavy metal ratio sols, a maximum concentration of 3 M heavy metal can be achieved at higher concentrations, the mixture becomes too viscous for further manipulation.

2 3. Preparation of uranium-containing sols

For U/U + Th ratios up to 0.3, the sols were prepared by peptizing the $Th(OH)_4$ precipitate with $UO_2(NO_3)_2$ To obtain sols with higher uranium concentration, UO_2 powder (1 to 2 μm) is mixed with the sols described above in the same manner as the carbon. This addition of uranium can be made parallel with the addition of carbon. For instance, sols of U/U + Th ratios up to 0 9 and C/U + Th ratios of 4 have been prepared to obtain carbide kernels

2.4. Addition of the gelling agent

The gelation of the sol is achieved by an internal gelation technique with hexamethylene-tetramine (HMTA) The sol is mixed with the required amount of HMTA at 0°C and maintained at that temperature to prevent it gelling before and during the injection of the sol into the gelation column. The exact amount of HMTA has to be determined for each sol, it is of the order of 0 12 ml 2 M HMTA/g of sol for mixtures having a carbon to metal ratio of 4/1.

No HMTA was necessary to obtain perfect gelation of the spheres in the case of the 12 C/metal sols.

2.5. Gelation

2 5.1. Apparatus

The principle of the apparatus is shown in Fig.2. The gelling liquid is pumped in a closed circuit through a tapered column, the temperatures of the liquid inside the column (35-45°C) and at the injection point of the sol (0-20°C) are regulated automatically to ±0.5°C by means of contact thermometers, controlling heating and cooling units

2 5 2. Procedure

The sol is introduced, at a selected temperature between 0°C and 20°C, into the column through an injection needle

Gelation of the sol is achieved partly by thermal decomposition of the HMTA inside the spherical particles and partly by extraction of water. This dehydration is carried out with 2-ethyl-hexanol, which is not completely saturated with water, the temperature of the operation being about 10 degC above saturation temperature.

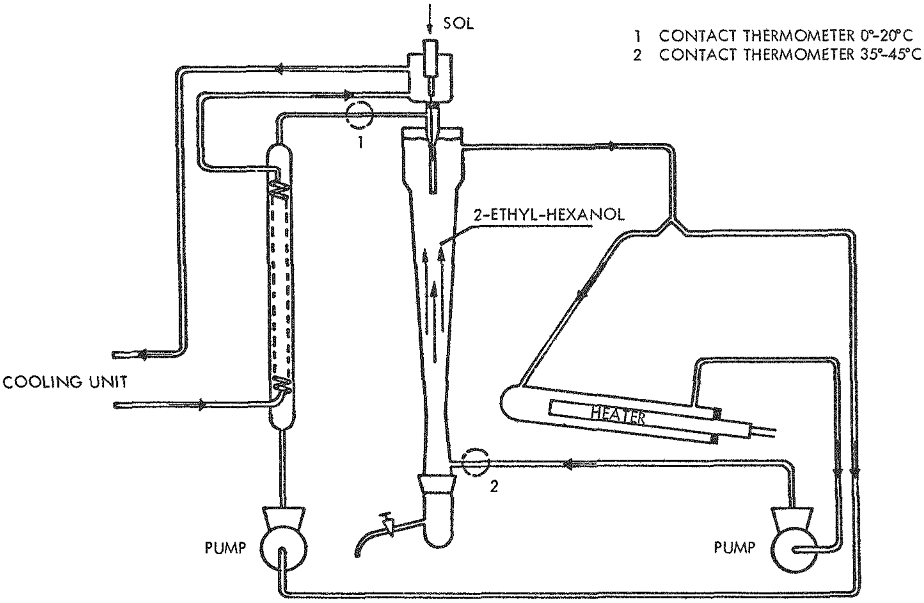

FIG.2. Tower gelation apparatus.

The 2-ethyl-hexanol contains up to 0.5 vol.% of a surfactant (Span) to avoid adhesion of the particles to each other and to the tapered column.

The diameter of the particles so produced depends on the diameter of the injection needle and on the relative flow velocities of the sol and the 2-ethyl-hexanol stream around the injection point.

The spheres are fluidized inside the column until gelation is complete, which takes 10 to 20 min.

2.6. Washing and drying

The particles are taken out of the column with a small basket and washed successively with CCl_4, diluted (2 M)NH_4OH, and acetone.

Drying of the spheres is performed in an oven for 2 h at 80°C, 2 h at 120°C and 2 h at 200°C. No particle disintegration occurred during these treatments.

With very diluted kernels (C/Pu ratios of 20) no special heating schedule is necessary for the drying, which can occur during the normal power raise of the heat treatment furnace.

3. EXPERIMENTAL RESULTS

3.1. (Th, U) kernels with a C/Th+U ratio of 4

The optimum quantity of HMTA and the optimum gelling conditions have to be determined for each sol.

For instance, the best results for a sol with a C/U+Th ratio of 4 and a density of 2.4 g/cm^3 are obtained, in partially saturated 2-ethyl-hexanol containing 0.5% Span, for a molarity of the sol of 1.5, a HMTA addition of 0.27 ml/ml sol and a gelling temperature of 35°C.

3.2. Thorium kernels with a C/Th ratio of 12

With 2-ethyl-hexanol saturated with water at 30°C and containing 0.5% span, the gelling can be performed at 35°C with no addition of HMTA.

Various diameters were obtained by changing the diameter of the injection needle and the relative velocities of the sol and the 2-ethyl-hexanol streams. Under the conditions tested, gelled particles with diameters between 500 μm and 1.3 mm can be obtained, producing by the heat treatment kernels of any specified diameter between 300 μm and 1.2 mm.

3.3. Thorium kernels containing C and U powder

Carbon-containing thorium sols prepared as described above were mixed with UO_2 powder and formed sols that could be injected into the column.

However, the stability of the sol was restricted to short periods (5 min) and this limitation was imposed on the sol immediately before injection into the gelling column.

3.4. Plutonium kernels with a C/Pu ratio of 12

The preparation of 3 $\underline{M}$ sols can easily be performed and the gelation requires operating conditions similar to those used for the thorium sol, except for the HMTA content which needs to be 0.4 ml/ml sol.

3.5. Plutonium kernels with a C/Pu ratio of 20

To obtain a sol which can be gelled by dehydration without the use of a gelling agent was impossible with a NO_3/Pu ratio of 0.3. The ratio needed to be raised to 0.6 with a plutonium content above 1 $\underline{M}$/l. The carbon was added under vibromixer stirring in the form of 'United-15' carbon black.

The high viscosity of the mixture prevents it from being injected in conditions necessary to give small-size kernels. The lowest diameter of heat-treated kernels that could be reached was 500 μm.

The gelled green kernels can be submitted immediately to the heat treatment cycle without any previous washing, drying or other conditioning steps. The following heating program was utilized for the preparation of kernels of a perfectly glossy appearance:

20 - 400°C : 100 degC/h.
400 - 1100°C : 700 degC/h.
above 1100°C : depends on the required characteristics of the kernels.

4. CONCLUSIONS

The sol-gel work performed at Mol for the preparation of kernels for coated particles has been only of an exploratory nature. However, the following has been achieved:

(1) A gelling unit with an injection device operating down to 0°C was designed and operated successfully.

(2) A new technique for incorporating major amounts of carbon and UO_2 powder into the kernels was demonstrated.

(3) The process was applied to various compositions of thorium and plutonium sols containing additions of uranium and carbon and of carbon.

(4) The conditions for preparation of plutonium sols were found to differ from those for thorium. The preparation of the sols (NO_3/Pu, Pu concentration, pH, etc...) and the gelation behaviour (viscosity, Span concentration, water content in the 2-ethyl-hexanol, temperature and gelation time) are conditioned by the presence of plutonium.

(5) With high concentrations of inert material in the sol, the conditioning of the gel particles may be reduced and even abandoned completely without impairing the quality of the product.

ACKNOWLEDGEMENTS

The excellent co-operation between the Dragon staff of Winfrith, the Plutonium Project staff BelgoNucléaire/CEN-SCK and the Metallurgy Department of the CEN-SCK at Mol must be recorded here.

We are especially indebted to R.A.U. Huddle, G. Horsley and J.J. Huet for their valuable advice and enthusiastic support and to I. LaFontaine for his co-operation from the safety point of view.

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Last but not least, R.Ingels and his group are acknowledged for the ceramographic work on the Pu spherical particles at the various stages of production.

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HEAT TREATMENT OF SURFACE TENSION KERNELS FOR THE MANUFACTURE OF COATED PARTICLES

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Abstract

HEAT TREATMENT OF SURFACE TENSION KERNELS FOR THE MANUFACTURE OF COATED PARTICLES. Various heat treatments were carried out to study the range of porosities obtained with normal gelled uranium-oxide particles. The paper describes the purpose of the study and the experimental results.

1. INTRODUCTION

The advantageous behaviour of coated particles under irradiation has advanced the development of high-temperature gas-cooled reactors. A common design for coated particles is a carbide or oxide spherical kernel consisting of fertile, fissile and/or inert material coated with successive layers of pyrolitic carbon and, in some cases, a SiC layer. The main requirement is for the coating to act as a pressure vessel to contain the fission gases and as a barrier against contamination of the primary circuit with fuel material or solid fission products.

From the mechanical standpoint, this pressure vessel is most efficient when the particle is ideally spherical in shape. The coated particle fuel therefore offers a perfect field of utilization for surface tension type kernels.

2. KERNEL REQUIREMENTS

The kernels are usually made of ceramic fuel compounds, mainly oxide or carbide. The nominal dimension is selected between 200 and 1500 μm and a narrow size range is desirable. The specifications call for porosities ranging between 0 and 30% within close reproducibility limits.

The present paper treats, as an example, an exploratory investigation of heat treatments to be applied to surface tension oxide particles to cover the required range of porosities.

3. THE PROBLEM

The aim was to produce particles of uranium oxide from green kernels manufactured by a surface tension process (SNAM process). It was necessary to obtain porosities up to 20% with good reproducibility within a batch and from batch to batch, and which had to be stable up to 1500°C. The approach to the problem was to work only on the heat treatment cycle to try to define what porosity ranges could be covered.

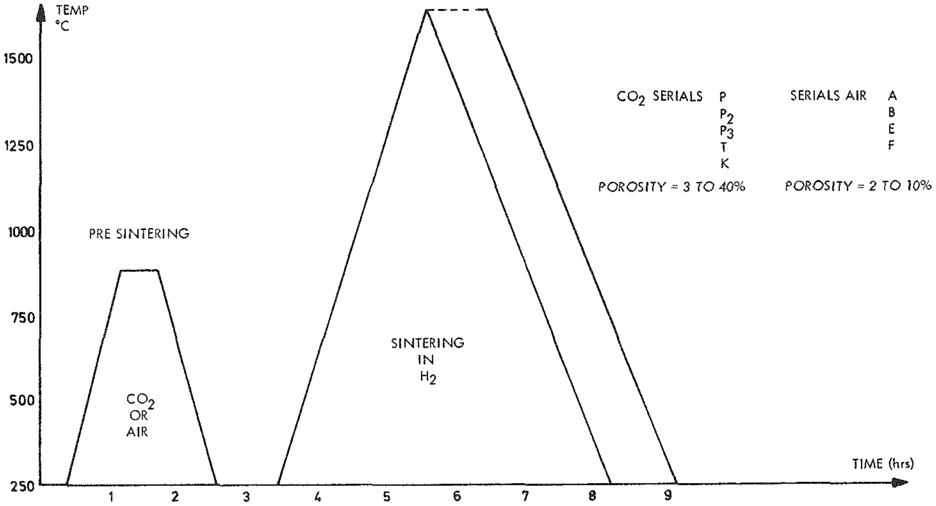

FIG. 1. Presintering and sintering treatment.

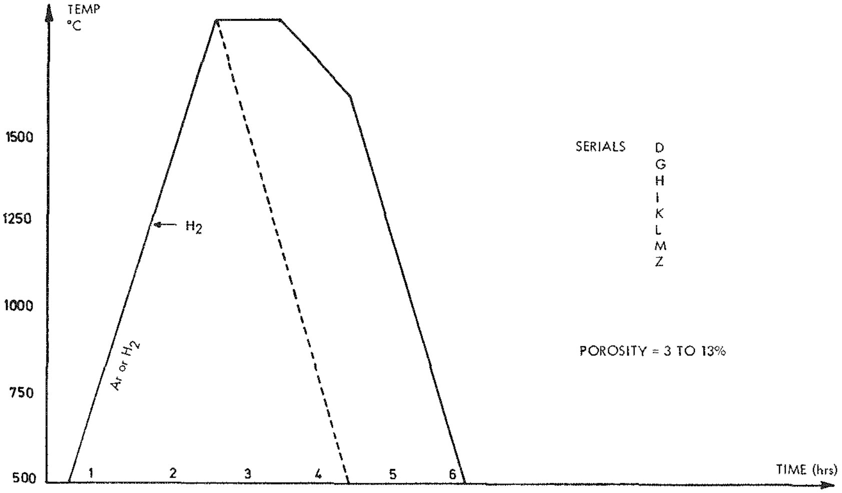

FIG. 2. Flash sintering.

4. EXPERIMENTAL PROCEDURE

The experimental procedures were selected on the basis of good applicability in commercial type equipment. This means that it was necessary to limit treatment to a dual or single atmosphere process which could, for instance, be applicable in dewaxing and sintering furnaces.

The presence of volatile material inside the gelled spheres produced considerable gas evolution in the 300-700°C range. Examples of the sintering operations investigated are given in Figs 1 and 2.

5. RESULTS (TABLE I)

5.1. Conditioning

Heating the particles in an oxidizing atmosphere required a slow evolution rate of the volatile organic materials (step of 4 h at 450°C or low heating rates). The utilization of hydrogen enabled a fast heating schedule to be applied.

To ensure reproducibility throughout the larger batches, a treatment in vacuo is more advisable; the optimum parameters are still under investigation. The vacuum treatment yields a density of 2 to 3% lower than the treatment in air for identical sintering conditions.

5.2. Sintering treatment

5.2.1. The oxidization-reduction sintering

Treatment in air at different heating rates and up to various temperatures, followed by a sintering step in H_2, led to the following conclusions:

- the heating rate has to be lower than 800°C/h to avoid disintegration of the particles, unless a conditioning step is used;
- a maximum porosity of 10% can be achieved.

The following conclusions were drawn from the trials of treatment in CO_2 followed by sintering in hydrogen:

- the heating rate and the treatment temperature in the 700-900°C range influence neither the quality of the particles nor the density, even if no conditioning step is applied;
- the dispersion of densities within a batch seems to be related mainly to the heating rate during the pre-sintering period and the duration of the treatment;
- the density depends strongly on the sintering temperature (densities of 65 to 85% T.D. can be obtained in the 1500-1600°C range);
- the length of the sintering period at a temperature of 1600°C does not influence the density.

5.2.2. Flash sintering or fast H_2 sintering

A porosity range from 3 to 13% can be obtained. The dispersion of diameters within a batch is, however, larger than for the previous method.

TABLE I. RESULTS OF THE HEAT TREATMENT EXPERIMENTS

Series	Conditioning			Pre-sintering				Sintering in H_2				Density	Diameter(μm)		Quality
	Atm.	degC	h	Atm.	degC/h	degC	h	(a)	degC/h	degC/h	h	% T.D.	average	variance	
Green	-	-	-	-	-	-	-	-	-	-	-	2.2g /cm³	1250	20	Cherry red
A	-	-	-	air	500	750	1	t	700	1600	1	97	725	5	Glossy
B, E, F	-	-	-	air	300 to 900	900	1	t	700	1600	1	96 to 90	730 to 760	10 to 14	Dull redish, well shaped to heavily cracked
U 1	-	-	-	CO_2	125	700	4	t	900	1600	0	85	800	40	Dull brown, good shape
X	-	-	-	CO_2	125	900	4	t	1000	1500	0	65	880	25	Yellow brown, good shape
U, T	-	-	-	CO_2	125	900	4	t	900	1600	0 to 2	(93) to 86	(740) to 775	10	Glossy black, good shape to some particles cracked
P	-	-	-	CO_2	900	900	4	t	1000	1500	0	69	870	32	Dark grey, good shape
P2 P3 }	-	-	-	CO_2	900	900	4	t	900	1600	1 to 4	86 to 84	780 to 790	20 to 25	Brown to black, good shape to some particles cracked.
R	-	-	-	-	-	-	-	t	1000	1500	0	93	740	nd	Glossy black
M	air	450	4	Ar	800	900	0	-	-	-	-	88	770	nd	Glossy black
O	air	450	4	-	-	-	-	t	1000	1500	0	92	750	nd	Glossy black
N	vacuum	450	4	-	-	-	-	t	1000	1500	0	90	760	15	Glossy black
Z	vacuum	450	4	-	-	-	-	p	1000	1500	0	88	770	nd	Glossy black
H, I, L	vacuum	450	4	-	-	-	-	t	800	1550 to 1600	0	88 to 93	770 to 740	10 to 20	Glossy black
K	vacuum	450	4	-	-	-	-	p	800	1600	0	89	760	20	Glossy black
D, G	vacuum	450	4	-	-	-	-	t	670 to 650	1600	1	91 to 96	750 to 730	25 to 20	Glossy black

(a) p = pure
t = technical.

6. COMMENTS

It may be seen that only the utilization of dual heat treatment processes enables the porosity range from 3 to 30% to be covered. The danger is that such a process yields large, unevenly distributed porosities, which may lead the particle to crack the coating either during the manufacturing process or during irradiation; development is proceeding on this particular aspect.

On the basis of the present results, it seems that no difficulty is encountered in covering the range of porosities between 3 and 10% and there is no major problem between 15 and 25%.

SOL-GEL PROCESS ON PLUTONIUM OXIDE AT THE EUROPEAN INSTITUTE FOR TRANSURANIUM ELEMENTS

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Abstract

SOL-GEL PROCESS ON PLUTONIUM OXIDE AT THE EUROPEAN INSTITUTE FOR TRANSURANIUM ELEMENTS. Several methods were investigated to produce a plutonium-oxide sol that could be converted into microspheres. A critical factor appeared to be the NO_3/Pu ratio of the sol. All sols were made by peptization of a plutonium-oxyhydrate with an appropriate amount of HNO_3. The following methods were tested to produce sols with a low nitrate content:

(a) Dialysis of plutonium oxide sol with a high nitrate-to-plutonium ratio of 0.8 - 1.0.
(b) Baking a plutonium oxide gel with a high nitrate-to-plutonium ratio of 0.8 - 1.0 at 120° - 160°C for several hours and redispersing the final product.
(c) Precipitation of plutonium-oxyhydrate under such conditions that direct dispersion into dilute HNO_3 produced a sol with a nitrate-to-plutonium ratio of 0.2 - 0.3. This method appeared to be the most reliable and efficient one.

The feasibility of producing microspheres from different sols was tested with the method of water extraction through 2-ethylhexanol. A nitrate-to-plutonium ratio under 0.35 was found to be essential for the formation of sound microspheres. The properties of the PuO_2 were investigated by electron microscopy. It seems that the sol is polydispersed and consists of amorphous particles. Sols aged far more than a year reveal no crystalline structure by electron diffraction. Drying and calcination of the microspheres coming from the ethylhexanol column are discussed. 100 g of PuO_2 microspheres were produced with methods discussed under (c). An outline of the sol-gel program in the European Institute for Transuranium Elements is presented.

1. INTRODUCTION

Dense nuclear fuel of oxides and oxide mixtures can be produced with the sol-gel method. Powder, microspheres and shards can be produced at temperatures far below the generally accepted sintering temperatures. Much experience has been acquired with Th, U and Th-U fuel, but experience with Pu is rare. The two methods reported are:

(1) The method developed at 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 by solvent extraction and a sol with a NO_3/Pu ratio of 1 is obtained.

The aim of the sol-gel work performed in the European Institute for Transuranium Elements is the production of microspheres of PuO_{2-x} of controlled density and diameter and a study of the parameters affecting this process, in particular the colloidal solution.

2. FORMATION OF COLLOIDAL SOLUTION

All the methods we used to produce PuO_2 sols were based on the peptization of a plutonium oxyhydrate with HNO_3. It appears to be essential to have a low NO_3/Pu ratio in the sol to produce sound microspheres The primary aim of our work was therefore the reduction of nitrate in the PuO_2 sol.

The methods we compared were:

(a) Dialysis of plutonium oxide sol with a high nitrate-to-plutonium ratio of 0.8 - 1.0.

(b) Baking a plutonium oxide gel with a high nitrate-to-plutonium ratio of 0.8 - 1.0 at 120 - 230°C for several hours and redispersing the final product.

(c) Precipitation of plutonium oxyhydrate under such conditions that direct dispersion into dilute HNO_3 produced a sol with a nitrate-to-plutonium ratio of 0.2 - 0.3.

A colloidal solution with a nitrate-to-plutonium ratio of 0 5 - 1.0 was produced in the following way. A solution containing about 30 g Pu/l and a free acidity of 1.5 $\underline{M}$ HNO_3 was poured into $12\frac{1}{2}\%$ NH_4OH solution. The precipitate was filtered, washed and dispersed into a 10-fold excess of water (based on a final concentration of 2 $\underline{M}$ Pu). Enough HNO_3 was added to form a NO_3/Pu ratio of desired value The mixture was evaporated in six hours to form a sol of 2 $\underline{M}$. This is a clear green transparent solution with a low viscosity. It was thus possible to achieve a nitrate-to-plutonium ratio as low as 0.5. This seems to be the limit and frequently an insoluble heel is left. Higher values of 0.6 - 0.7 are easily obtained.

2.1. Dialysis of the sol

The sol described above was dialysed. This was performed in a PVC 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 was constantly measured.

The pH changed from 1.3 to 3.0 during 16 hours of dialysis and the resulting liquid was so viscous that it had to be diluted to get a more fluid 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. It gelled at 90°C and a small portion of Pu(IV) precipitated irreversibly. This precipitation also occurred after the sol had stood for two weeks at room temperature. It was practically impossible to obtain a NO_3-to-Pu ratio lower than 0.35 with this method, and at this ratio the sol was already rather diluted (0.36 $\underline{M}$). The colour of the sol was unchanged. It was still a dark green transparent solution.

2.2. Decreasing the NO_3-to-Pu ratio

It is possible to produce microspheres from this solution, but since it is so diluted drying in the column is very time consuming and the spheres are small. Several experiments were performed with the aim of decreasing the NO_3-to-Pu ratio by heating the gel.

The gel was heated for different periods at temperatures ranging from 120 - 230°C under normal and reduced pressures. 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.

Plutonium ions in aqueous solution are already considerably hydrolysed at a pH of 1 - 2 [3 - 5]. 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 oxyhydrate was dispersed in HNO_3 and the possibility of forming 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 to 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 ammonia. At this point the colour of the mixture was greenish and the solution became cloudy. The next step was precipitation at a pH of 7. This precipitate was washed with water and with diluted ammonia. 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 was again 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 to 2 M Pu sol resulted. After 8 hours of heating the resulting product was a coarse 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 of particles that were considerably larger than those mentioned before. The HNO_3 content in the initial solution seems important. If this is too high, nitrate ions may complex plutonium ions and prevent the formation of relatively large primary particles.

3. PRODUCTION OF MICROSPHERES

The methods for the production of microspheres were based on that developed at Oak Ridge National Laboratory, which involves the 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 about 50 μm in size were obtained by pouring the sol into a beaker filled with 2-ethylhexanol stirred at constant speed. With this method the size dispersion is considerable. Beads up to 500 μm were produced in the tapered column.

The sol was dispersed through a double-nozzle system into a counter current of ethylhexanol in the column. The water content of the ethylhexanol was kept at about 1% by constantly distilling a water-ethylhexanol mixture at approximately 150°C in a side loop. The temperature of the ethylhexanol was kept around 20°C. At higher temperatures the viscosity is too low and the counter current should be strong. We added different surfactants such as sarkesyl-O, Primene and oil BX 5 to the ethylhexanol. The last-mentioned was considered the best, since we could use it at a very low concentration, depending on the sol used, e.g. 0.1%. (The oil is a lauryl (poly- 1-oxapropene), oxaethane carboxylic acid made by Chemy, Bodegraven, Holland).

The ethylhexanol should countain about 1% water. If it is too dry, the beads gel too fast and will fracture. During the production of microspheres we occasionally added surfactant when the beads showed a tendency to stick together. To prevent the beads from sticking to the glass wall of the column the glass was treated with dimethyl dichlorsilan. Beads made of sol with a NO_3/Pu ratio of 0.5 also showed a strong tendency to agglomerate. Higher surfactant concentrations should be used in this case. The sol was dispersed into the ethylhexanol and after about 20 minutes the beads were collected and washed with petroleumether. Washing with acetone resulted in the breaking of the spheres.

Carbon tetrachloride was not used so that Cl contamination could be avoided. The spheres were kept in air at room temperature for 8 hours.

3.1. Drying the microspheres

Drying the beads has been a problem for a long time. It was time consuming and the risk that the beads would be destroyed was considerable Microspheres produced from a sol with a nitrate-to-plutonium ratio of about 0.2 dried more easily provided that they were washed with petroleumether. It is possible to dry these beads by heating them in an oven up to 270°C within 30 minutes and keeping them at this temperature for two hours Experiments in which the microspheres were heated in hot air containing a large amount of water resulted in considerable loss due to breakage.

3.2. Production of 100 g of microspheres

One hundred grams of PuO_2 beads were reduced in an H_2 atmosphere at 1600 - 1700°C resulting in microspheres with an average diameter of 285 μm. The structure of the beads did not change much in this step. Porous

TABLE I. PHYSICAL CHARACTERISTICS OF Pu_2O_3 MICROSPHERES

Specimens	Weight of Pu (g)	X-ray analysis		O/M gravimetric	Picnometer *density* (g/cm³)	Temperature *of reduction* (°C)	Time of *reduction* (h)
		O/Pu	Density (g/cm³)				
PuSO 17	23.575	1.74	10.90	1.759	10.38	1600	4
PuSO 18	11.478	1.67	10.74	1.679	10.05	1720	4
PuSO 19	26.679	1.76	10.94	1.772	10.69	1700	4
PuSO 20	18.641	1.73	10.87	1.721	10.50	1600	4

beads developed reduced porosity. The beads are to be covered with different layers of pyrolytic carbon and a layer of silicon 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 characteristics. 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, when the crystallographic O/Pu ratio was also obtained [6]. The beads will be irradiated to a burn-up of 30% and higher at a temperature of about 1350°C. This is part of the irradiation program of the Institute.

4. PARTICLE SIZE IN PuO_2 SOLS

The colour and visible aspect of the different sols gave the impression that the particle size in the colloid varies. Sols with a high nitrate-to-plutonium ratio are transparent green and those with a low ratio are not transparent and are lighter green.

Some electron microscope photographs were made of different sols. An electromicroscope Elmiscop IA of Siemens was adapted for work with plutonium. The sol was diluted to a molarity of 10^{-4} and sprayed on a film that was placed on a supporting framework.

Diluting the sol presents a problem. It can be diluted at constant pH by adding HNO_3 or it can be diluted with water. Both methods were compared. An additional uncertainty is the behaviour of the particles during evaporation of the solution on the film and in the electron beam. Figs 1 - 8 show the different photographs made.

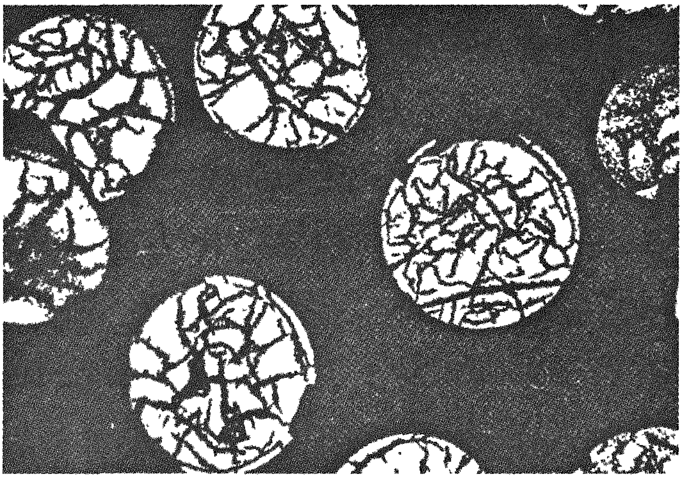

FIG.1. Microspheres from a sol with a Pu/UO_3 ratio of approximately 0.5 (diam. = ~250 μm).

Diluting at constant pH results always in a conglomeration to larger particles. Aging the sol that was diluted with water also resulted in larger particles. No striking difference between the nitrate-to-plutonium ratios was observed.

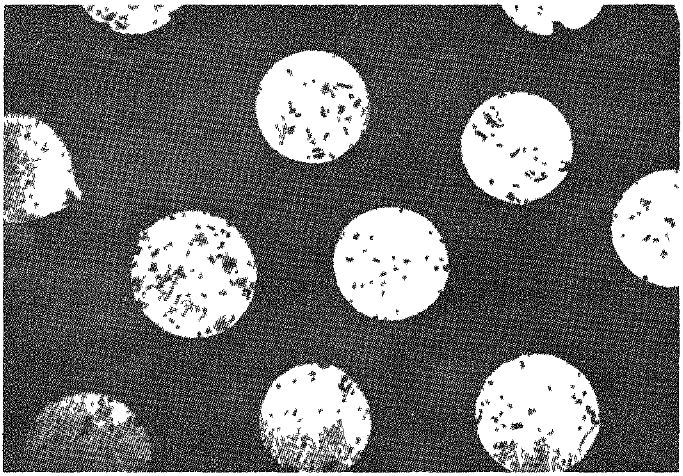

FIG.2. Microspheres from a sol with a Pu/UO_3 ratio of 0.2 (diam. ≈ ~250 μm).

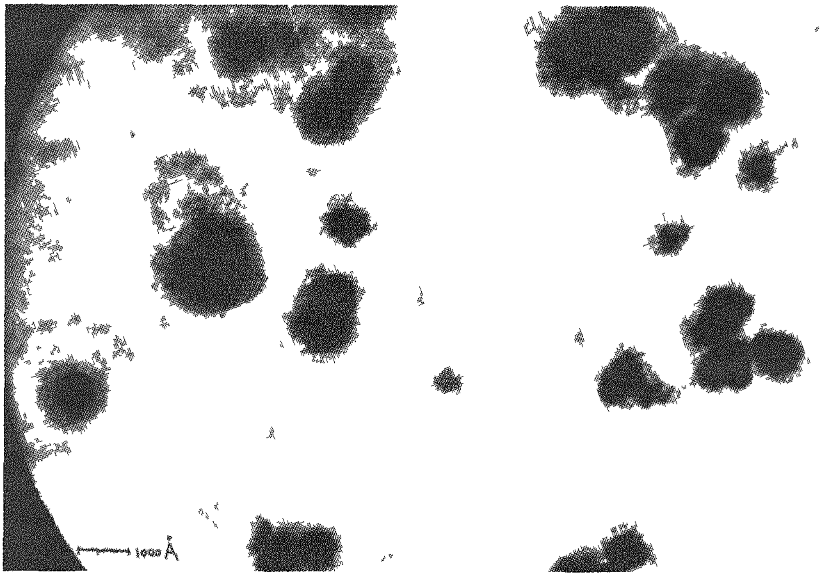

FIG.3. 1 $\underline{M}$ PuO_2 sol with initial UO_3/Pu ratio of 1.0, diluted 10 000 times at constant pH.

Diluting with water gives less agglomeration. The sol with a nitrate-to-plutonium ratio of 1 has very small particles (Fig. 6) that are absent if the nitrate-to-plutonium ratio is 0.2 (Fig. 7).

None of the sols studied showed any structure by electron diffraction, not even the aged PuO_2 sol (Fig. 9). The electron diffraction pattern of a CeO_2 sol is shown for comparison in Fig. 10. It reveals that the sol particles have a crystalline structure (cubic face centred).

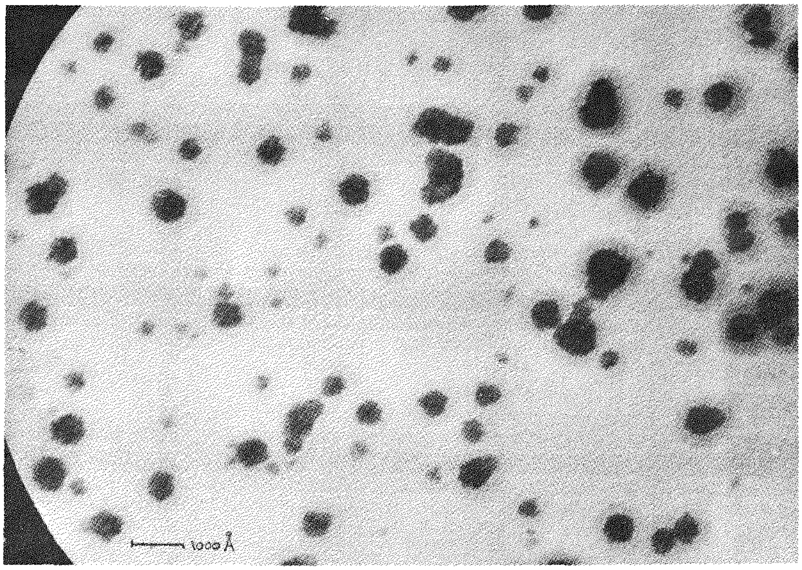

FIG.4. 1 M PuO_2 sol with initial UO_3/Pu ratio of 0.2, diluted 10 000 times at constant pH.

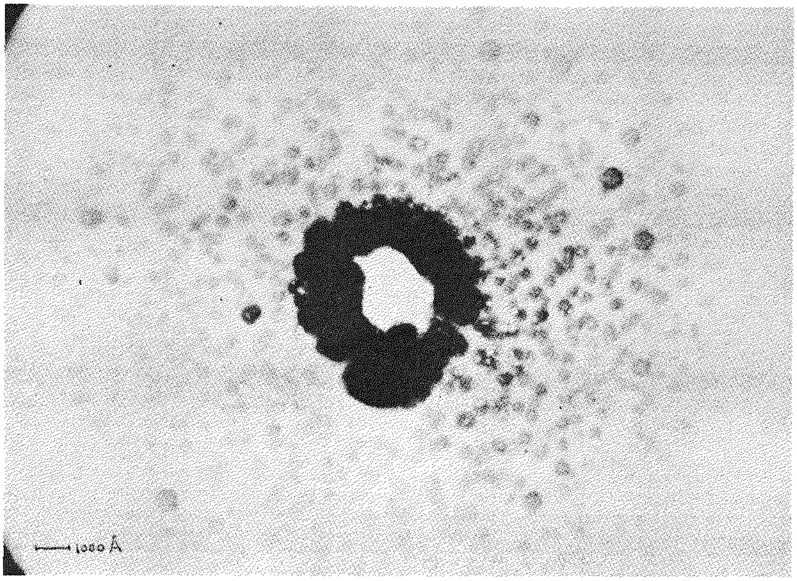

FIG.5. 1 M PuO_2 sol with initial UO_3/Pu ratio of 0.2, diluted 70 times at constant pH, 140 times with water.

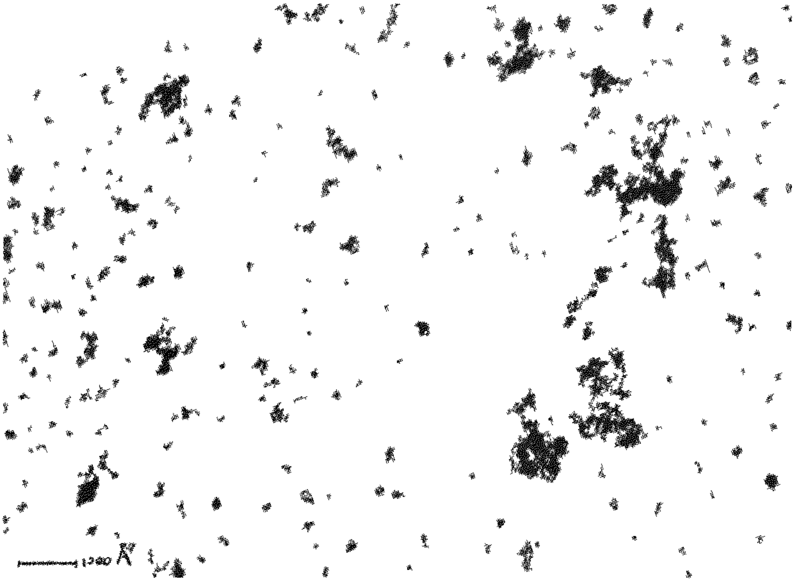

FIG.6. 1 M PuO_2 sol with UO_3/Pu ratio of 1.0, diluted 20 000 times with water.

FIG.7. 1 M PuO_2 sol with UO_3/Pu ratio of 0.2, diluted 10 000 times with water.

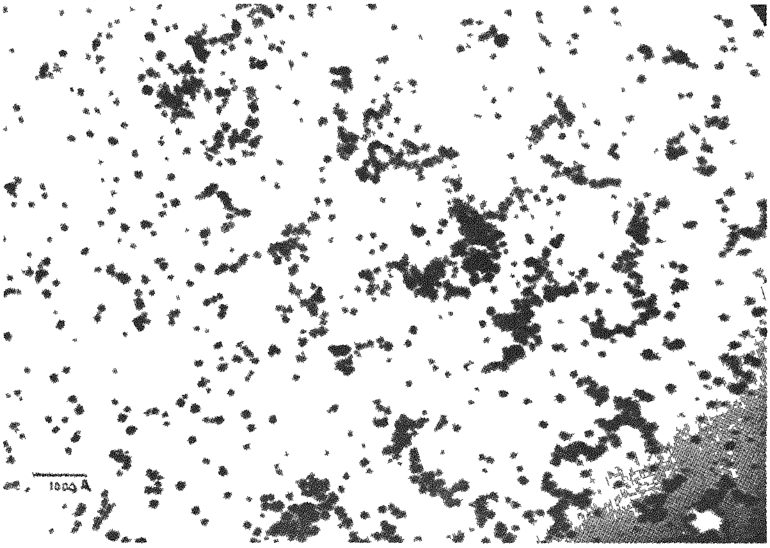

FIG.8. 1 <u>M</u> PuO_2 sol with UO_3/Pu ratio of 1.0, diluted 10 000 times with water and aged for one year.

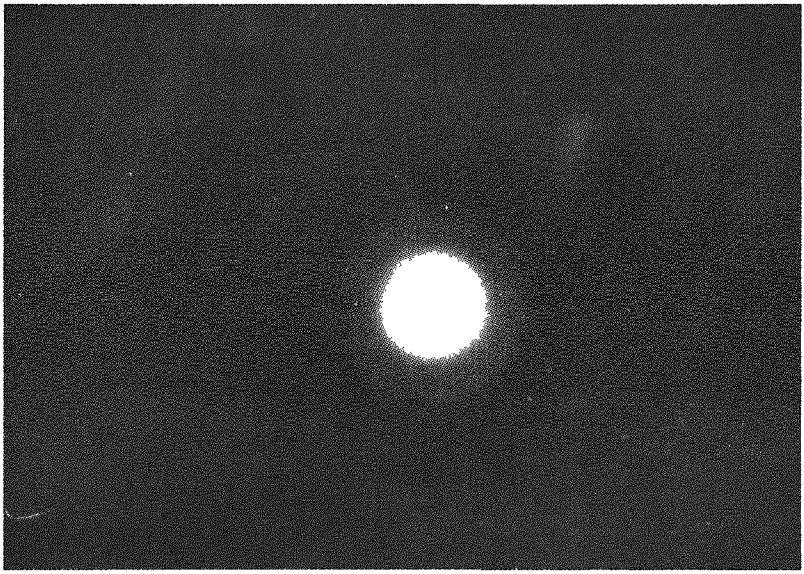

FIG.9. Typical electron diffraction image, similar in all PuO_3 sols.

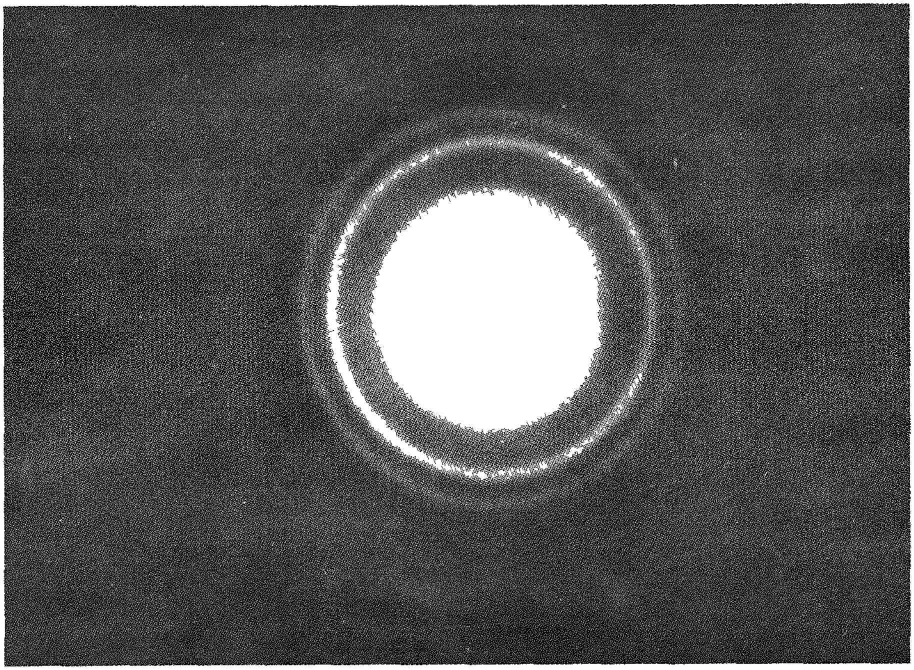

FIG.10. Electron diffraction pattern of CeO_2 sol, c.f.c. structure.

5 PROGRAM

The sol-gel research program in the Institute will be carried out along the following lines:

(1) The production of PuO_2 sol with a low nitrate content from acid Pu solutions by solvent extraction.
(2) The study of the hydrolysis of plutonium by means of light scattering.
(3) The development of a sol-gel process for ^{241}Am

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EVALUATION OF SOL-GEL METHODS AT CNEN WITHIN THE FRAMEWORK OF THE PLUTONIUM UTILIZATION PROGRAM

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Abstract

EVALUATION OF SOL-GEL METHODS AT CNEN WITHIN THE FRAMEWORK OF THE PLUTONIUM UTILIZATION PROGRAM. The ability to produce dense plutonia, homogeneous urania-plutonia or thoria-plutonia microparticles at any desired ratio by means of sol-gel processes has been demonstrated on a laboratory scale. An irradiation program is underway to evaluate the plutonium-bearing fuels together with an economic study based on a comparison of the fabrication processes.

1. INTRODUCTION

One of the most important tasks of the CNEN Plutonium Utilization Program is the development of a sol-gel process suitable for plutonium-bearing fuels.

In Italy there is a growing interest in plutonium nuclear fuels, and substantial programs for plutonium utilization have therefore been undertaken both by Enel (Ente Nazionale per l'Energia Elettrica), the Italian Government power agency, and by CNEN (Comitato Nazionale per l'Energia Nucleare), the Italian Government nuclear agency.

The Enel program was undertaken in co-operation with Euratom and it is aimed at the practical and immediate goal of thermal utilization. This program covers all aspects of the problem comprehensively, from design to experimental tests of many plutonium-fuelled assemblies in the Garigliano BWR power station.

The CNEN program covers a wider field of research and development, ranging from thermal to fast utilization. This program is an eight-million-dollar undertaking which was started in 1966 with funds allocated up to and including 1969.

2. CNEN PLUTONIUM UTILIZATION PROGRAM

The principal aim of this program is to provide CNEN in the shortest possible time with a plutonium capability – both in personnel and facilities – in the area of ceramic fuels. While the program is intended to include research work on non-oxide compounds, such as carbides or nitrides, by far the main emphasis in now being placed on oxide fuels. The fabrication methods considered are: (a) the pelletization technique, either by mechanical mixing or coprecipitation routes, where a choice between the two will be made at a later date, and (b) the vibrocompaction technique of microparticles, produced by modified sol-gel methods, two of which are now under investigation. One of these is the subject of the present paper; the other is a different method developed at the laboratories of the SNAM-PROGETTI, in Milan, Italy.

To accelerate the development of these methods, the decision was made to build a 21 000-ft^2 facility, approximately half of which consists of alpha laboratories, at CNEN (La Casaccia Centre near Rome, Italy).

At the time of writing the laboratory is in the final phase of commissioning. Cold runs have already started and hot runs with plutonium fuel are scheduled for the summer of 1968.

While the plutonium laboratory in Italy was being completed, it was decided to give impetus to the program by renting some alpha laboratory space elsewhere and start the comparison of the two sol-gel methods considered without any further delay.

To this purpose a contract was signed early in 1966 with the Centre d'Etude de l'Energie Nucléaire (CEN) and the Société Belge pour l'Industrie Nucléaire (BelgoNucléaire) for the rental of an empty 600-ft^2 alpha laboratory plus cold laboratory space and offices for about ten people in Mol, Belgium. Contractual provisions were also made to have ancillary services performed, such as health physics surveillance, analyses, etc. The laboratory was then equipped with ten glove-boxes in two parallel lines to perform plutonium chemistry (precipitation, filtration, liquid-liquid extraction, centrifugation, etc.), thermal treatments (in air, $Ar-H_2$, CO_2, Ar) and some basic characterization, chemical analyses, etc.

CNEN's previous experience in the field of nitrate extraction with strong-base amine led to the development of modified sol-gel processes capable of yielding microparticles of thorium and uranium oxide or carbide with satisfactory nuclear characteristics. The general results and findings are reported in Professor Zifferero's paper,[1] while the extension of such experience to the preparation of microparticles of plutonia, urania-plutonia or thoria-plutonia are reported here for the CNEN sol-gel method.

3. CNEN SOL-GEL METHOD FOR PLUTONIUM FUELS

Plutonium colloidal solutions with a NO_3^-/Pu ratio between 1.0 and 1.5 can easily be obtained either by peptization of the hydroxide or direct nitrate extraction from a solution of Pu(IV) nitrate. On the basis of CNEN experience the latter is by far the simplest method, since tedious operations, such as washing – with the resulting large volumes of waste solutions – or plutonium hydroxide recovery are avoided altogether. Moreover, the direct extraction technique is more amenable to continuous operation.

On a small-scale laboratory line (with a capacity of one kilogram per month) the solution of Pu(IV) nitrate is contacted in a separatory funnel with a long-carbon-chain primary amine (Primene JMT) in an aliphatic solution. The Pu(IV)/amine ratio is established to obtain a final $NO_3^-/Pu(IV)$ ratio in the aqueous phase between 1.0 and 1.5. Since the Pu(IV) nitrate

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[1] ZIFFERERO, M., Status report from Italy: Sol-gel research and development, these Proceedings.

solution generally comes from an ion-exchange column with a plutonium concentration of 0.2 - 0.3 mole/litre. the dilute aqueous phase is evaporated at 80°C to a final plutonium concentration of 1 - 2 mole/litre. The residual plutonium content in the organic phase does not exceed a few milligrams per litre and can be recovered as usual by conventional means.

A large number of batches has been processed discontinuously through the line, while a mixer-settler extractor for continuous operation is being designed.

The Pu(IV) colloidal solutions obtained as described show a low viscosity even at a high plutonium concentration and can be safely stored for months without showing any alteration whatsoever, Such a colloidal solution can be used as prepared for producing plutonia microparticles or can be properly mixed with other colloidal solutions of heavy metals, such as tetravalent uranium or thorium, to produce mixed urania-plutonia or thoria-plutonia.

The dispersion of colloidal solutions into small droplets is easily achieved with conventional techniques by either mechanical stirring or spraying two immiscible fluids: one, the aqueous colloidal solution and the other, an organic fluid with which the first is immiscible. The latter contains in solution the denitration agent to produce gelation.

The choice between the two systems, stirring or spraying, is essentially determined by the desired size of the microparticles. The gelation of small-diameter microparticles (less than 100μm after thermal treatment) is performed in a beaker with diaphragms. The gelation of microparticles of a larger diameter is made in a Plexiglas column with a conical section that is very similar to that originally developed by ORNL.

A low-cost commercial product 'Alphanol 79', which essentially consists of a mixture of high-carbon-number alcohols, is used as the organic dispersing medium. To keep microparticle coalescence to a minimum, 0.5 vol.% of a tensioactive agent (SPAN-85) is added.

Finally, the denitrating extractant, 1 - 2 vol.% of an amine mixture, commercially known as Primene JMT, is also added to the organic phase. The amines of Primene JMT also show a tensioactive action. The solubility of water in Alphanol-79 is 3 - 4 vol.%; if used in the anhydrous state the Alphanol-79 would therefore extract water from the sol droplets. In the CNEN sol-gel process water extraction must be strictly avoided, since it would form a nitrate-impervious thin layer at the surface of the microparticles with a resulting difficulty in completing the gelation of the innermost parts of the microparticles. Therefore, before using it, the organic phase needs to be saturated with water at the operation temperature. Among the many factors that affect the duration of complete gelation, the most important ones are certainly the amount of nitrate to be extracted and the microparticle diameter.

Gelation is assumed to be completed when a limit between 0.1 and 0.2 of the NO_3^-/metal ratio is reached. Such a nitrate content has been shown not to have any harmful effect on the characteristics of the microparticles after the thermal treatment.

After the gelled microparticle has been rinsed with an organic volatile solvent to free it of the Alphanol-79 excess, the product is ready to undergo the thermal treatments.

The plutonia, urania-plutonia and thoria-plutonia specimens referred to in this paper were all fired under an argon-5% hydrogen atmosphere in resistance tubular ovens for four hours to reach the soaking temperature of 1 200°C at which they were held for two hours.

The oxide microparticles so produced showed a satisfactory spherical form in all batches with different diameters from a few microns up to a maximum of about 600 microns. The carbon content of the calcined product was typically less than 100 ppm. The individual microparticle crushing strength values for 300-μm $(U\text{-}16\%Pu)O_2$ microparticles showed a variance between 6 and 10 kg. This value is very difficult to keep constant from particle to particle within a single batch and to reproduce from batch to batch. X-ray analyses showed that the urania-plutonia microparticles have a solid solution $(U, PU)O_2$ structure. The microparticle densities ranged from 98% of theoretical density for urania-16% plutonia to consistently higher than 99.5% of theoretical density for mixed oxide of urania or thoria with only a few unit per cent of plutonia (up to 5 or 6% Pu).

4. EVALUATION PROGRAMS

Evaluation programs are now under way both to qualify the fuel for reactor use and to make an economic comparison of the various sol-gel processes on a common basis.

With regard to fast reactor fuels, a joint effort with the CNEN Fast Reactor Program yielded a first specimen loaded with UO_2-16% PuO_2 that underwent irradiation in the Avogadro test reactor of SORIN in Saluggia, Italy. At present the specimen has reached a burn-up of approximately 20 000 MWd/t and irradiation is being continued.

Thermal fuels for water reactors are the subject of two sets of experiments:

(a) long-duration tests in the HBWR reactor in Halden, Norway, to study the effects of the fabrication methods or of some design parameters, such as the density, power rate, etc.;

(b) short-duration tests, of the order of minutes, in the R-2 reactor in Studsvik, Sweden, to investigate the transient structural variation of the fuel and, in particular, to determine the minimum time required at different power densities to achieve a stabilized structure.

All such experiments will first be performed with uranium and then with plutonium fuels.

Five rigs have been inserted in the Halden reactor, two of which have been unloaded and are now cooling while awaiting post-irradiation examination.

About twenty uranium capsules were irradiated in the Studsvik reactor and are now under examination, while other plutonium capsules are being fabricated to undergo irradiation shortly.

To make an economic comparison of the various sol-gel processes on a common basis, a study was started last year to arrive at a foreseeable production price by designing a plant in sufficient detail to achieve estimates close enough to yield reasonably accurate cost predictions.

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IRRADIATION AND COST

√COST OF COATED-PARTICLE FUEL

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Abstract

COST OF COATED-PARTICLE FUEL. The paper contains a tentative appraisal of the economic effect of the fabrication process for producing kernels for coated particles. It is demonstrated that the sol-gel processes, which are capable of producing satisfactory spheres of small diameter, may cause a sensible decrease in the cost of coated particles and in the electricity generating cost.

1. INTRODUCTION

The design of high-temperature gas-cooled reactors utilizing coated particles as a fuel is more profoundly influenced by the fuel than any other reactor concept. It is therefore interesting to analyse all the fabrication routes of the kernels used for the coated particles and to see how they may affect the electricity generating cost.

2. BREAKDOWN

Table I gives a general view of the contribution of each item to the total cost.

For the sake of the present study, one single value has been retained in the range of normal figures. It can be seen that the amortization costs form the largest part of the generating cost. It must, however, be noticed that within this item the amortization on the first core, which is in fact a fuel cost, accounts for a total of 2.6 to 2.8%.

The fuel cost itself is divided into its components. In Table I the net fuel consumption is computed as the difference between the expense due to the ^{235}U consumption and the plutonium credit. As can be seen, the two first items related to the value of the fissile material utilized in the reactor form 70% of the fuel cost.

The fabrication cost of coated particles may be divided, as shown in Table I, into its three fabrication steps, namely:

- kernel preparation,
- coating the bare kernel with successive layers of pyrocarbon (PyC) and possibly other materials, and
- assembly of the coated particles into a fuel element.

The relative importance of these three steps depends on the fuel design; but again for the sake of the present study, representative values were adopted.

From Table I it can be seen that the kernel preparation represents only 1.2 to 3% of the generating cost. It therefore seems that the manufacturing route, which could only partially influence the kernel preparation cost, would have a minor effect on the total electricity cost.

TABLE I. COST BREAKDOWN (%)

Item	Range	Adopted value
Generating cost		
Amortization	63-67	65
Fuel	24-27	25
Operation	9-10	10
Total	100	100
Fuel cost		
Net consumption	37-40	37
Inventory	30-34	32
Fabrication	22-30	25
Reprocessing	5-7	6
Total	100	100
Fabrication cost		
Kernel preparation	20-34	26
Coating	50-70	60
Fuel element fabrication	10-17	14
Total	100	100

3. ALTERNATIVE FABRICATION ROUTES OF THE KERNELS

The fabrication route of the kernels not only influences the fabrication cost of the kernels themselves, but also the properties of the product and therefore the design and the specifications of the fuel, and even the design basis of the reactor.

To simplify one could compare two fabrication routes, namely the powder agglomeration method, and the surface tension processes.

Table II gives the main characteristics of the products that usually result from these two processes. There is no inference that properties not mentioned in this table cannot be achieved with each process; they can be achieved, but entail a decrease in quality and an increase in manufacturing cost.

TABLE II. TYPICAL PROPERTIES OF SPHERICAL PARTICLES

Fabrication route	Powder agglomeration	Sol-gel
Shape	Spherical to ellipsoidal	Spherical to egg shaped
Size range	Wide	Narrow
Density (% TD)	70 - 90	90 - 100
Surface	Rough	Glossy

In the present state of development of the manufacturing processes the relative fabrication cost can hardly be assessed for large-scale production. This paper therefore neglects any difference in fabrication cost between these two processes.

4. EFFECT OF SPHERICITY

Defects in the perfection of the spherical shape are usually accepted in the specifications. It must, however, be realized that the coating is subjected to stresses that are easily predicted when uniformly distributed, but may have catastrophic effects when local stress concentrations occur.

Most of the fabrication techniques now yield a product quite spherical in shape. The main defect consists of ellipsoid shaping.

For the mechanical fuel design, these shapes can be treated by relating the design to the radius of curvature so that a defect of sphericity appears roughly as an additional variation of size range. For instance, a ratio of the largest to the smallest particle diameter of 1.1 is similar in effect to a size-range variation of 5% relative.

5. EFFECT OF SIZE RANGE

One of the main objectives of the coating is to act as a pressure vessel. However, only part of the layers are mechanically resistant.

The deposition of these layers amounts to 50% of the total coating cost. As an example, for a kernel in the 800-μm range, the most economical powder agglomeration kernel calls for a relative variation in sizes between the largest and the smallest kernels of 16%, while surface tension methods can achieve, without appreciable economic penalty, a size range of 2.5%.

The mechanical design needs to be performed, not on the average size of the particles, but on the maximum size, because a fission gas release of the order of 10^{-5} is requested and one of 10^{-7} is desirable, which practically means that the quality level of the particles needs to be 99.999%. Therefore, particles of the same nominal size have to be considered as being 7% larger for powder agglomeration kernels and as containing 20 to 25% more fuel.

Since not all the space necessary for gas-pressure build-up is included in the kernel, part of it being in the inner porous coating layer, the above-mentioned difference in design principle calls for the inclusion of further coating layers; it is estimated that this would cause an increase in the coating cost of 7 to 10%.

6. EFFECT OF DENSITY

The manufacture of high-density kernels is the most appropriate field of application of surface tension preparation methods. In these circumstances most of the voidage necessary within the mechanically resistant coating layers needs to be built up with porous PyC layers.

For instance, using 97% density kernels requires doubling the thickness of the porous layer as compared with a kernel of 90% TD and trebling the thickness of this layer as compared with a kernel of 80% TD. This increase of the porous layer thickness increases the average diameter of the mechanically resistant layers and therefore requires that their thickness be increased accordingly, i.e. by 3 and 7%. The total increase in coating cost related to the above mentioned cases is, respectively, 2.5 and 6%.

7. EFFECT OF SURFACE ROUGHNESS

During coating the surface of the particles is subjected to abrasion if, as is usually the case, the coating is deposited in a fluidized bed under turbulent conditions. The contamination of the coatings will therefore be related to the roughness and the hardness of the kernel surface. In this respect the sol-gel kernels usually have a dense surface and a weaker central region while the contrary is more common for kernels made by the agglomeration method.

The direct effect of the low contamination of the coatings is to lower the fission gas releases of the fuel. In the reactor design it therefore permits the maintenance of a cleaner primary circuit and decreases the necessity of costly secondary circuitry or expensive in-core devices to catch volatile fission products. The effect on the primary circuit design of a fission gas release rate of 10^{-7} as against 10^{-5} may be important and influences the generating cost appreciably due to the high proportion of the amortization accounted for by the electricity cost. This effect cannot be estimated at present with any accuracy, but it is of larger magnitude than any of the effects discussed previously.

The decrease in contamination also influences the fabrication cost since it permits a reduction of the cleaning cost of the equipment and the replacement cost of equipment parts, which are usually discarded not for failure but for contamination level. It also allows the controls of the coated particles to be reduced. On the basis of the present estimates, the effect on the fabrication cost may be as much as 3 to 7%.

8. CONCLUSIONS

If spherical, small-sized sol-gel particles could be obtained at the same manufacturing cost as powder agglomeration kernels, the total fabrication cost of the coated particles would be reduced by up to 20%. This would bring a generating cost reduction of only 0.2 to 0.6% in a HTR designed on the principles presently available. However, if the quality and availability of such improved fuel could be ensured, it would be possible to design the HTR on the basis of this higher quality fuel and thus bring about a greater reduction of the generating cost.

X SOL-GEL PROCESSES IN THE DRAGON PROJECT: A SUMMARY OF WORK

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Abstract

SOL-GEL PROCESSES IN THE DRAGON PROJECT: A SUMMARY OF WORK. A high-temperature gas-cooled reactor uses fuel in the form of microspheres coated with pyrolytic carbon and silicon carbide. Although development work on the fabrication of fuel kernels by the Dragon Project has concentrated on powder agglomeration methods, the perfection of the spheres formed by sol-gel processes is obviously attractive for kernel fabrication. In this way the coating laid around the spheres can have optimum mechanical properties.

It has been shown that, by suitable choice of sol-gel process, the wide range of carbide and oxide compositions called for by the Dragon Project irradiation program can be made in sizes up to 700 μm after sintering. Difficulties were only experienced with low thorium/uranium ratios - outside the range of practical interest for power reactors. Initial experience with plutonium fuels has also been obtained.

Irradiation experiments in the Dragon Reactor which are based on sol-gel process kernels are summarized. A detailed study of the cost of reprocessing thorium cycle HTR fuels has been commissioned by the Dragon Project and probable costs are given for a plant processing 30 tonnes of heavy metal/yr.

1. INTRODUCTION

The progress of the high-temperature gas-cooled reactor (HTR) project [1] has been made possible by a small number of key advances. One of the most important has been the development of ceramic fission-product retaining fuels. In such fuels, the particle, which may contain fissile or fertile isotopes and be in oxide or carbide form, is coated with layers of pyrolytic carbon and silicon carbide. The coated particles are then incorporated into a graphite fuel element of suitable size and form.

Good neutron economy of the all-ceramic core of an HTR makes it possible to achieve a high burn-up and the requirement generally is to achieve a fifa value of ~1.1 for low-enrichment reactors and higher values for thorium cycle HTR's. With the high burn-up it is necessary to accommodate the resultant increase in volume of the kernel material, otherwise the usefulness of the coating as a barrier to actinides and fission products is likely to be impaired. This can be achieved by incorporating porosity into the kernel, by laying down an initial coating which is porous or by a combination of these two methods. These concepts led, in the Dragon Project, to the development of a coated particle with a porous fuel kernel. It was therefore necessary to investigate, inter alia, methods of fabricating such fuel kernels. Spherical or near spherical porous and dense particles can be made by agglomeration of powders and from spherical droplets as outlined in the following section.

2. METHODS OF PREPARING SPHERICAL PARTICLES

2.1. Powder agglomeration processes

Powder agglomeration processes for the fabrication of fuel kernels have several advantages·

(1) They are simple to use and give a high yield Particles of the correct size and shape can be fabricated in the unsintered state when recycling costs are minimal.
(2) The kernel composition and size can be varied over wide limits
(3) Porosity can easily be incorporated

There are two main variants of the powder agglomeration process·

(a) Powder mixtures are granulated and then subjected to simultaneous consolidation, abrasion and agglomeration to spheroidize and densify the granules.
(b) .The mixtures are pressed to a spherical shape in a die This process is probably not suitable for direct pressing of particles much less than 1000 μm in diameter.

In both cases the 'green' kernels are heat treated or sintered

2.2. Spherical droplet methods

The two main methods of forming spherical droplets are·

(1) Spraying liquid droplets into a second phase (liquid or gas) followed by changes designed to solidify and thereby retain the spherical shape produced. The sol-gel family of processes [2] involves injecting a solution or a sol containing the appropriate fuel into a second liquid so as to form discrete droplets which then gel, e g. by removal of water or by increase of the pH. The gelled particles have then to be heat treated.
(2) Fabrication of fuel agglomerates which are then wholly or partially melted. Again a second phase (liquid, gas or solid) is necessary to avoid coalescence of the liquid droplets.

Various methods of melting have been investigated, but these experiments were terminated mainly because of concern relating to the irradiation swelling behaviour of dense melted kernels and also because melting processes were judged to be more costly and less flexible than the alternatives

3. SOL-GEL PROCESSES

3.1. General

Stimulated by the development of sol-gel processes at Oak Ridge National Laboratory [3, 4], the Dragon Project has assessed their application to the manufacture of fresh and recycled fuel for thorium cycle HTR's. Initial research, which commenced in January 1964, benefited from the experience of N.V. KEMA, Arnhem, Netherlands, whose work under contract to the

Dragon Project assisted technological studies in the Project's laboratories by G.W. Horsley and L.A. Podo at Winfrith, United Kingdom.

It is fair to say that the work by the Project has relied on the extensive experience of CNEN, KEMA and ORNL for the fabrication of sols and their gellation. The special feature of the Dragon work has been the development of processes to make porous fuel kernels aimed at minimizing swelling under irradiation.

The work was integrated with a detailed study under contract of the cost of reprocessing and refabrication of HTR thorium cycle fuels by UKAEA, Risley, United Kingdom and CNEN, Rome, Italy. As further support for this study CNEN was also engaged to develop an appropriate sol-gel process for the large-scale manufacture of fuel kernels

3.2. Preparation of sol-gel particles by the Dragon Project at Winfrith [5]

3.2.1. Preparation of Th/U sols

The sol preparation method normally adopted was that used by KEMA since 1959 as part of their sol-gel process for the manufacture of 5-μm diameter $(Th, U)O_2$ spheres. Other methods were investigated but none was as simple and effective in producing stable sols. The process, which has been described elsewhere [6] consists in peptizing freshly precipitated and washed thorium hydroxide with uranyl nitrate and nitric acid at about 100°C. The batch size has been up to 1 kg heavy metal. Horsley et al.[5] have indicated how the properties of such sols are significantly affected by the nitrate, uranium and thorium concentrations. They found that very stable sols can be prepared which do not precipitate during concentration, provided that the $NO_3/Th + U$ mole ratio is between 0.25 and 0.3 and the Th·U atomic ratio in excess of 7·1. It may be noted that for homogeneous thorium cycle HTR's the Th:U atomic ratio will be in the region 10-12:1, and in the breed fuel of feed and breed systems it will be about 30-40·1 [1].

Virtually all the sols prepared at Winfrith have been tailored to the fabrication of porous carbide and porous oxide microspheres and, for both types of fuel, it was necessary to add carbon to the sols. The use of carbon in the preparation of porous $(Th, U)O_2$ particles was an essential feature to counter the normally excellent sintering behaviour of sol-gel oxides. The amount of carbon to be dispersed in a sol to make a carbide fuel was equivalent to 4.4 mole per mole of heavy metal. It was considered desirable, because of the high carbon loading, to adjust the density of the sol to be the same as the theoretical density of carbon. The molarity of U + Th to give a density of ~2 g/ml was ~4. A consequence of this approach was that the ratio of diameter of sprayed droplet to finished sintered microsphere was ~2. It was believed that the only carbon powders sufficiently fine to be incorporated satisfactorily in a sol were carbon blacks. The surface properties of the wide spectrum of carbon blacks can exhibit large differences [7, 8]. Accordingly, four proprietary carbon blacks, whose properties are given in Table I, were examined, and it was concluded that of these United 15 (whose pH was similar to that of the sols) was the best.

3.2.2. Preparation of gelled microspheres by internal gellation

Internal gellation and dehydration were used as methods of forming gelled spheres. When the concentrations of nitrate, uranium and thorium are such as to cause precipitation were water to be removed, internal

TABLE I. PROPERTIES OF CARBON BLACKS

Carbon black designation	Surface area (m^2/g)	Particle diameter (nm)	Volatile content (%)	Ash content (%)	pH
United MT	6	470	0.5	0.5	8.5
United 70	117	24	1.5	0.5	9.1
United R	105	30	4.6	0.02	4.5
United 15	370	23	11.5	0.03	3.0

gellation is used instead and is effected by introducing an ammonia donor into the sol to increase the pH, following the method of KEMA [9]. To form spheres by internal gellation, ice-cold hexamethylene tetramine is introduced into the sol immediately before spraying. The sol-hexamine mixture is then sprayed to form droplets via a two-fluid nozzle similar to that used by Oak Ridge National Laboratory [10] into 2-ethyl hexanol saturated with water (1.0 - 1.5%) to prevent dehydration. At room temperature this gives a gelling time of about 30 minutes which reduces to 5 minutes at 45°C. Coalescence of the droplets is prevented by the addition, to the 2-ethyl hexanol, of 0.2 - 0.3% of a surface active agent, sorbitan mono-oleate (Span 80), as had previously been used by the KEMA investigators. The internal gellation method results in spheres containing ~40 wt.% water and ~6 wt.% ammonium nitrate. There would be obvious difficulties during heat treatment of these spheres. The particles are therefore washed with: (a) carbon tetrachloride, to remove 2-ethyl hexanol, (b) 2 $\underline{M}$ ammonia solution at 60°C for 2-3 minutes to remove ammonium nitrate, and (c) 60% carbon tetrachloride/40% acetone mixture to remove surface water.

3.2.3. Preparation of gelled microspheres by dehydration

Although the majority of the fuel manufactured for the Dragon Project by sol-gel processes has used the internal gellation method, some work has been carried out on gellation by dehydration following the method of Oak Ridge National Laboratory [11]. Preliminary experiments on dehydration with 2-ethyl hexanol of sols whose $NO_3/Th + U$ mole ratios were ~0.4 showed that as dehydration proceeded the particles disintegrated However, if dehydration of the sol does not cause precipitation (see section 3.2) then the droplets can be gelled satisfactorily. It is necessary to take care that the water is extracted uniformly and not too rapidly from the droplet surface, otherwise the particles may be malformed.

Particles prepared by dehydration are merely washed with carbon tetrachloride to remove 2-ethyl hexanol.

3.2.4. Heat treatment of sol-gel kernels

A standard drying schedule of: 2 h at 80°C, 2 h at 120°C and 2 h at 180°C was used throughout the work. In the case of carbide kernels, the kernels were then heat treated in vacuo, care being taken to use a

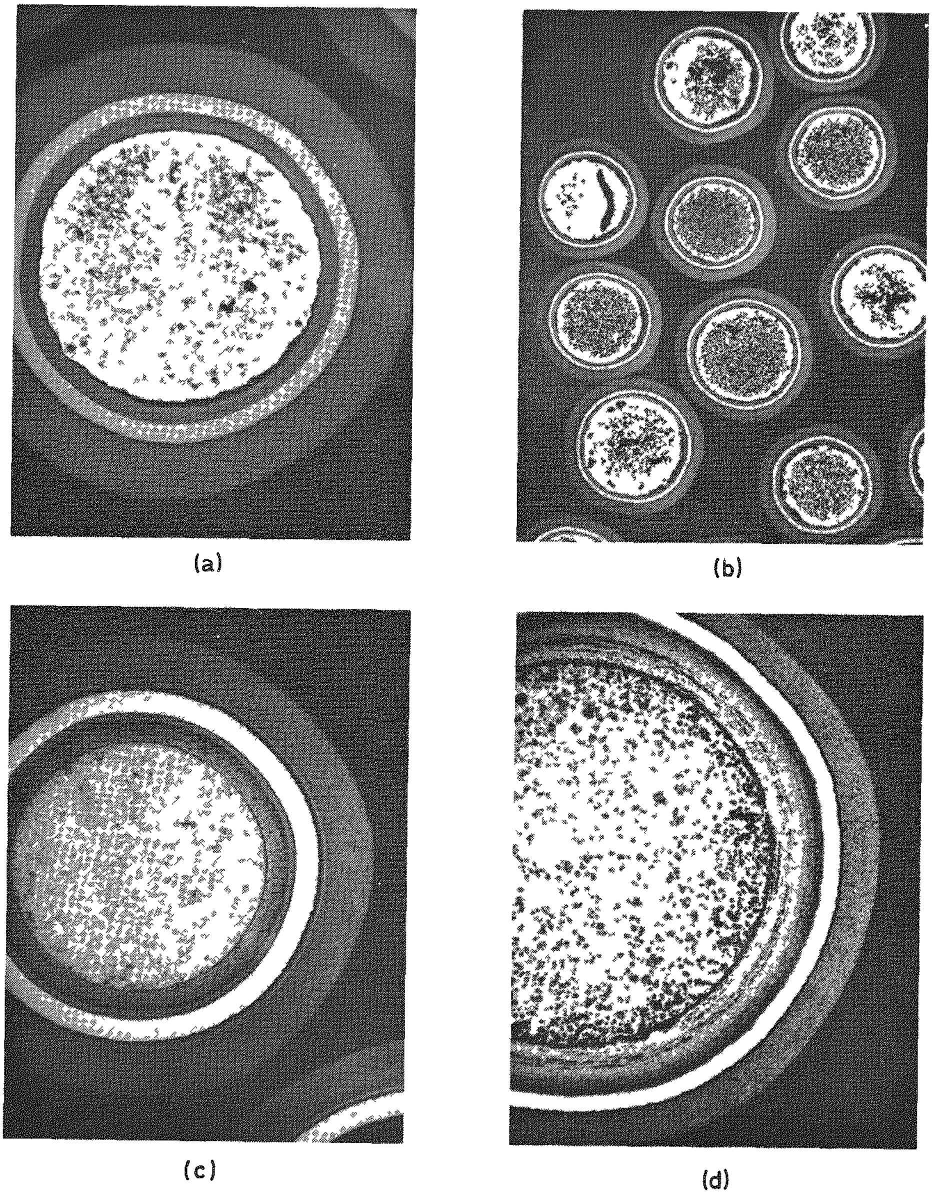

FIG.1. Photomicrographs of unirradiated coated-particle fuels produced by the sol-gel process: (a) kernel type 14M M4743, ×90, (b) kernel type 14M M5525, ×90, (c) kernel type 17M M5540, ×90, (d) kernel type 23C M6367, ×90.

reduced rate of heating near the temperatures at which considerable gas evolution had been observed (200, 400, 1050 and 1800°C) [12] Batches of up to 1 kg were successfully treated up to 2000°C on an 8-h cycle to give particles of 250 - 800 μm diameter and porosity 20 - 30%

In the case of $(Th, U)O_2$ spheres, the carbon-containing dried kernels were heat treated at up to 1600°C in 1 atm. carbon monoxide to avoid carbon/$(Th, U)O_2$ reactions. The carbon was removed from the particles by a second-stage heat treatment in oxygen at 800 - 900°C. Finally, the particles were densified by sintering at up to 1600°C in carbon monoxide Kernels in the range 400 - 700 μm diameter with well distributed porosity were produced by these treatments. The porosity, of which the greater part is closed, was varied over the range 20% to more than 40% by adjustment of the carbon content or the final heat treatment

3.2.5. Subsequent treatment of sol-gel kernels

The preparation of sol-gel kernels is only one stage of the fabrication of fuel for an HTR. Satisfactory heat-treated kernels are coated in fluidized bed furnaces with a multilayer pyrolytic carbon and silicon carbide coating which is the principal barrier to the escape of fission products. Properties *of sol-gel particles irradiated in the Dragon Reactor are given in Table II* and photomicrographs of unirradiated particles in Fig. 1. All these particles were consolidated into a graphite matrix in the form of fuelled cylinders approximately 1.75-in. diameter, which were then assembled into standard Dragon graphite fuel elements.

3.3. Investigation of sol-gel processes by Dragon contractors

A process had already been developed by N.V KEMA for the production of 5-μm diameter $(Th, U)O_2$ spheres [6]. The main object of the research contract placed by the Dragon Project with KEMA in 1964 was to extend this process to produce larger spheres. This work has already been published [9] and incorporated into a recent summary of sol-gel development at KEMA [13]. The satisfactory outcome of the Dragon contract was the adoption of the KEMA sol preparation and internal gellation methods for the preparation of irradiation specimens, as described in section 3.2

Amongst the topics studied by CNEN in support of the reprocessing and refabrication design and cost studies was gellation by external denitration. The CNEN gellation system is based on extraction of nitric acid to increase the pH. The acid was extracted with a commercially available mixture of higher alcohols (Shell Alphanol 79) containing 1% vol /vol. Primene JMT (long chain aliphatic primary amines of composition approximately $C_{18}H_{37}NH_2$, produced by Rohm & Haas Co.), and 0.5 - 1% of a surface active agent (Span 85) and saturated with water (~3%). The gelling time for particles of 500 - 1000 μm was 15 - 30 minutes

The effects of the additions to the Alphanol were studied For a Primene concentration of 0.5% the gellation time increased to 120 minutes, while for concentrations higher than about 1.5% the droplets became misshapen. For the Span 85 an optimum range was also found. Under 0.5% vol./vol. the droplets tended to coalesce and above 1% there was a large loss of carbon.

Some very preliminary experiments were carried out by the BelgoNucléaire-CEN Plutonium Project, Mol, Belgium, to prepare plutonium-bearing sol-gel particles [14] $Pu(OH)_4$, precipitated from a solution containing 0.18 M Pu/litre and 1.9 M NO_3/litre by concentrated ammonium hydroxide solution, was washed with dilute ammonium hydroxide solution and water The plutonium hydroxide was peptized at 70 - 80°C in a portion

TABLE II. PROPERTIES OF SOL-GEL COATED-PARTICLE FUELS IRRADIATED IN THE DRAGON REACTOR

Kernel identification	Kernel type	Mean kernel size (μm)	Kernel density (g/cm^3)	Mean Th·U-235 atomic ratio	Average thickness of individual coating layers (μm)			Spread of total coating thickness
					Inner pyrocarbon layer (s)	Silicon carbide	Outer pyrocarbon	
Dragon fuels								
14M/3/Sol 36/1-3	(Th,U)C$_{2+}$	502	~6.9	10.1	23 (no porous layer)	29	71	108-135
17M/3/Sol 37/1-2	(Th,U)O$_2$	495	~7.6	9.4	39	32	66	124-151
17M/3/Sol 37/3	(Th,U)O$_2$	477	~7.6	9.4		137 (No SiC)		127-148
5C/3/Sol 43/2-5	(Th,U)C$_{2+}$	535	7.0	9.9.	28	28	85	124-151
23C/3/Sol 44/1-4	(Th,U)O$_2$	460	8.3	10.2	59	34	55	137-162
ORNL fuels								
ORNL 32	(Th,U)O$_2$	286	10.15	3.4		124 (No SiC)		104-147
ORNL 46	(Th,U)O$_2$	281	10.11	4.75		124 (No SiC)		105-150

TABLE III. IRRADIATION TEMPERATURE AND BURN-UP OF SOL-GEL PROCESS COATED PARTICLES IRRADIATED IN THE DRAGON REACTOR

Kernel identification	Range of irradiation temperatures in a fuel element (degC)	Calculated average burn-up at discharge or to 1 May, 1968 (fima %)	Fuel element No.
Dragon fuels	700°C minimum at base of fuel; 1200°C peak; temperatures reduce by 70 degC at end of life		
14 M/3/Sol 36/1-3		2.2, 5.2, 6.2 6.2	700, 701, 703, 704, (i.e. four identical elements with irradiation time as variable)
17 M/3/Sol 37/1-2			
17 M/3/Sol 37/3			
5C/3/Sol 43/2-5		4.5	430
23C/3/Sol 44/1-4		4.7	433
ORNL fuels			
ORNL 32		9.5	413
ORNL 46		7.5	443

Note: The approximate peak fast neutron dose for the fuel in elements 430 and 433 is 1.1×10^{21} n cm^{-2} and in elements 413 and 443 is 1.0×10^{21} n cm^{-2}.

of the original solution. The NO_3/Pu mole ratio fell from 10.5 to 0.65 during the peptization. United 15 carbon black was then added to yield a sol with a C:Pu atomic ratio of 22:1, and a Pu content of about 1 M/litre resulted. This and other sols were used to spray droplets, but insufficient work was carried out to establish other than tentative experimental conditions for gellation.

4. IRRADIATION TESTS

The number of types of sol-gel process coated particle which have been irradiated, although small (reflecting the higher priority given to powder agglomeration methods), nevertheless represents a very significant weight of fuel, amounting to over 250 g ^{235}U. Irradiation tests in the Dragon Reactor are summarized in Table III. This table includes data on two fuels which are being irradiated on behalf of Oak Ridge National Laboratory and were designed on the basis of the original Prados & Scott model for coated-particle fuel [15]. Of the fuels in Table III, since the tests are essentially of a long-term nature, only 14 M and 17 M particles have so far been discharged from the reactor, and the particles examined had an average burn-up of about 22.9% fifa.

14 M particles exhibit damage to the inner pyrocarbon layer but no other significant features. 17 M particles show little sign of damage, the only feature worth mentioning being the opening up of a slight gap between kernel and coating.

It is premature from these results to draw any conclusions regarding the behaviour of sol-gel process kernels. However, the significant difference between the behaviour of the pyrocarbon layer adjacent to the kernel in the cases of 14 M and 17 M is attributed to the interposing of a porous, sacrificial layer to modify fission recoil effects as has been discussed elsewhere [1].

5. REPROCESSING AND REFABRICATION COST STUDIES

The Dragon Project commissioned UKAEA, Risley, and CNEN, Rome, to prepare a conceptual design and cost study for a centralized fuel reprocessing and refabrication plant, sited inland on a medium size river in Europe. This plant was to service HTR's operating on the Th/^{235}U/^{233}U fuel recycle system with an installed capacity of 10 000 MW(th).

It is not appropriate in this paper to detail this study. However, a sol-gel process was selected as the basis for kernel refabrication by either the remote or direct refabrication routes and, after consideration of the alternatives, the sol was chosen to be prepared by external denitration, according to the recommendations of CNEN [16], and gellation by dehydration with 2-ethyl hexanol. This combination was considered to be the most readily adaptable to continuous operation at a high throughput rate

An advance estimate of the overall cost of the low decontamination, remote refabrication route is given in Table IV together with the costing assumptions. The studies have shown [17] that the capital investment and operating costs are similar for both the high decontamination, direct refabrication and the low decontamination, remote refabrication routes The ultimate choice is likely to depend more on an assessment of the amount of engineering design and development necessary and the high decontamination, direct refabrication route might then be preferred.

6. POSSIBLE ADVANTAGES AND DISADVANTAGES OF SOL-GEL PROCESSES FOR COATED-PARTICLE FUEL FABRICATION

Possible advantages of sol-gel processes for coated-particle fuel fabrication are:

(1) More uniform kernel shape and size.
(2) Slightly lower contamination levels for the finished coated-particle fuel and lower rejection rate at the coated-particle stage.
(3) Potential adaptability to continuous large-scale fabrication or refabrication.

Amongst possible disadvantages are higher fabrication cost, insufficient irradiation experience and increased difficulty of recycle at the kernel stage. The majority of the advantages and disadvantages can eventually be assessed in economic terms, (e.g. what is the value to a reactor operator of fuel with

TABLE IV. ADVANCE ESTIMATE OF COSTS FOR LOW DECONTAMINATION REPROCESSING AND REMOTE REFABRICATION OF HTR FUEL

10 000 - MW(th) program; Design capacity 30-tonne heavy metal/yr;
Th : fissile U atomic ratio 12:1; Inland location on medium size river

	Cost (£/kg heavy metal outpout)				
	Reprocessing		Refabrication		Total
Direct works cost	26.9		22.8		49.7
Indirect works cost	10.8		15.4		26.2
Depreciation (see note 1)	18.0		19.6		37.6
Insurance (see note 2)	2.1		2.3		4.4
Interest on investment (see note 3)	12.8	13.3	9.2	11.8	25.1
Interest on stock (see note 4)	0.2		1.8		
Interest on added value (see note 5)	0.3		0.8		
Graphite components (see note 6)			12.0		12.0
Pre-production costs (see note 7)	1.0		1.0		2.0
	72.1		84.9		157.0

Notes concerning costing convention used as basis for Table IV

1. Plant capital depreciated linearly over 10 yr. Capital invested in site facilities allocated 50% to reprocessing and 50% to refabrication and depreciated linearly over 20 yr.
2. Insurance charged at 1% capital investment/yr. Capital invested in site facilities allocated 50% to reprocessing and 50% to refabrication.
3. Interest on capital investment charged at 8% yr on average present worth. Reprocessing capital investment comprises £ 2.754 × 10^6 plus certain site facilities which are integral with the requirement to reprocess fuel, (e.g. medium-activity and low-activity effluent treatment plants, fuel reception and storage) together with an annual charge of £ 110 000/yr to take account of varying storage tank requirement by an average charge. Capital investment allocated to refabrication comprises £ 4.9 × 10^6. Residues of site facilities are divided equally between reprocessing and refabrication.
4. Interest on stock charged at 8%/yr. Stock is defined as the cost of one month's operations.
5. Interest on added value charged at 8%/yr. Added value defined as total works costs plus the outlay on insurance for a time interval related to the hold-up time and the integrated added value during the hold-up. This time interval is one month for reprocessing because the fuel reception time is similar to the buffer store time and three months for refabrication because of the need to quantize deliveries to the reactor site.
6. It is assumed that the weight ratio of structural graphite to heavy metal is 10, that the utilization of unmachined graphite is ~0.7 and that the unmachined graphite costs £800/t, inclusive of machining costs.
7. Pre-production working-up is assumed to require 0.5 yr and is amortized over 20 yr. It is based on total works costs plus insurance.
8. Corporation expenses, research and development and profit not allowed for.

a lower contamination level in terms of access to plant for maintenance) and for this reason the cost of the unit process of kernel fabrication is a continuing area for study by the Project.

ACKNOWLEDGEMENTS

A short review of this nature must of necessity draw from the work of a large number of people to whom detailed acknowledgement cannot be given. The author apologizes for this and to colleagues in the Dragon Project, BelgoNucléaire, CNEN, KEMA and the UKAEA for his all too brief treatment of their valuable contributions. The development of the porous fuel kernel, of which the sol-gel work was a part, was carried out under the enthusiastic direction of Messrs R.A.U. Huddle and G.W. Horsley. The Deputy Chief Executive, Dr. L. R. Shepherd, directed the reprocessing and refabrication cost studies.

Thanks are due to the Chief Executive, Dragon Project, for permission to publish this paper.

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LABORATORY AND ENGINEERING STUDIES OF SOL-GEL PROCESSES AT OAK RIDGE NATIONAL LABORATORY*

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Abstract

LABORATORY AND ENGINEERING STUDIES OF SOL-GEL PROCESSES AT OAK RIDGE NATIONAL LABORATORY. A brief description of a model for sols, based largely on studies on ThO_2 sols, is given. Processes based on solvent extraction of nitrate ion by secondary amines to prepare ThO_2-UO_2 and UO_2 sols are discussed, and the flow sheets and equipment used in preparing these sols are illustrated. A method suitable for preparing 150-g batches of PuO_2 as sol is described, along with the properties of the typical PuO_2 and UO_2-PuO_2 products. Demonstrated processes for preparing, drying, and firing microspheres of ThO_2, ThO_2-UO_2 are described, and results of some experiments on low-energy compaction of microspheres in tubes to form fuel elements of predetermined density are discussed. Finally, miscellaneous sol-gel processes for preparing carbides, porous oxides, nitrides, and carbonitrides are briefly described.

INTRODUCTION

The work on sol-gel processes at Oak Ridge National Laboratory has been summarized recently in a series of our reports.[1,2,3,4] In this paper much of what has already been reported is summarized, and recent observations and developments have been added. The emphasis is on the applied work rather than the basic work being carried out. Much remains to be done in both areas. The present emphasis is on exploiting sol-gel processes to produce improved fuels for fast breeder reactors, especially liquid-metal-cooled fast breeders, and for high-temperature gas-cooled reactors, especially those of the Fort St. Vrain (Public Service of Colorado) type. This emphasis is reflected in the order of presentation of the material. The order also reflects the state of the art at ORNL. Thoria and thoria-urania microspheres represent the products of the most higly developed processes; urania, the next; plutonia and plutonia-urania, the next; the carbides next, and the remainder fall into a sort of miscellaneous category.

PROPERTIES OF THORIA SOLS

Much of our understanding of the nature of sols, as well as the physical chemistry of sol-gel processes, stems from fundamental studies of the colloidal properties and the surface chemistry of thoria sols and gels. A large part of this work, particu-

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larly as it is related to the nature of thoria sols, is summarized and interpreted in a comprehensive and well-documented doctoral thesis.[5] More recently, the work has been supplemented by detailed studies of rare-earth oxide sols.[6] From these studies has emerged a model that the concentrated sols that are suitable for the preparation of dense ceramic materials are composed of well-formed crystallites having a well-defined surface stoichiometry for the adsorption of ions from solution. In addition, the rheologically significant particle appears to be a loosely bound aggregate or floc containing several crystallites, the shape and average size of the floc being mainly determined by the surface chemistry of the crystallites and the electrolytic environment. The concept of a definite, well-defined surface stoichiometry is ideally represented by thoria sols; but it is felt that other oxide sols also show this property to some degree, and the concept has proved to be useful in the development of sol-gel processes for urania, plutonia, zirconia, and the rare-earth oxides.

At ORNL, thoria to be used for dispersion to sols has been prepared in a variety of ways; however, the largest quantities have been made by passing steam at a pressure of 1 atm over a thin layer of thorium nitrate at a temperature that is gradually increased to 485°C. The thoria powder thus produced has a NO_3^-/ThO_2 mole ratio of about 0.025 and contains about 1% H_2O. When this thoria is stirred vigorously at 80°C in sufficient dilute nitric acid to give a NO_3^-/ThO_2 mole ratio of 0.11, a stable thoria sol results within a few hours.

In general, thoria sols are of two main types: the crystalline thoria sols, which are prepared from the steam-denitrated oxide, and hydrous amorphous thoria, which is produced by precipitation or dialysis of a solution of thorium nitrate or chloride at 25°C. The crystallite size of thoria prepared by steam denitration of thorium nitrate was found, by x-ray line broadening and electron microscopy, to be about 80 A. The presence of an anisometric floc in crystalline thoria sols has been confirmed visco-

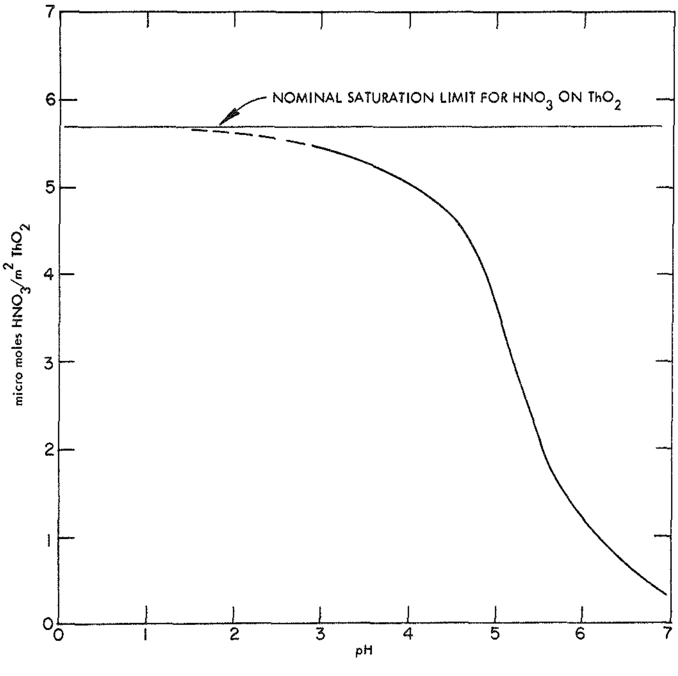


FIG. 1. Adsorption of HNO_3 on colloidal ThO_2.

metrically. An indication that the flocs of crystallites are not tightly bonded is that the area calculated from the x-ray crystallite size is, within experimental error, the same as that measured by the BET area.

Thoria rapidly adsorbs water and a variety of other chemical species that are generally acid or amphoteric. Completely dispersed thoria is probably rapidly and completely hydrated. Acid metal oxides, as a class, are adsorbable. For monomeric acids, a saturation value of 4 to 6 micromoles per square meter of ThO_2 surface is obtained.

Figure 1 shows a graphic representation of nitric acid adsorption as reflected by solution depletion. It appears that thoria adsorbs nitrate in two forms: as ionic nitrate, and as a distorted "nitrato" species, with amounts of the latter increasing as the colloidal thoria is progressively dried.

The peculiarly strong adsorption of U(VI) on thoria is well known.[7] If the U(VI) is adsorbed on pre-formed thoria crystallites, the expected 4 to 6 micromoles of uranium per square meter of surface are adsorbed. If, however, the crystallites are formed in the presence of U(VI), the U(VI) content appears to exceed this value by as much as 100%.[8]

Detailed study of the electrophoresis of colloidal thoria has shown numerous, severe false-boundary and false-mobility effects due to traces of dissolved thorium nitrate or possibly other trace ionic contaminants. Further, it was only possible to obtain consistent trends of electrokinetic mobility with electrolyte composition for a given sample. Different thoria samples would sometimes give opposite trends. The electrokinetic behavior of thoria, and of other oxides as well, is apparently a very complex function of its preparative history, as has been suggested by others.[9]

ThO_2—UO_3 SOL PREPARATION BY SOLVENT EXTRACTION

The ability of amines to extract acids and metal complexes from aqueous solutions provided the basis for the development of the process in which amines were used for the partial denitration of thorium and/or uranium[8] and for the preparation

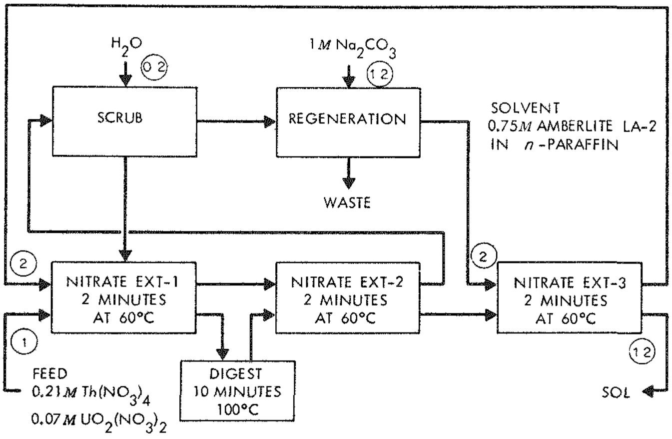


FIG.2. Flow sheet for preparation of $ThO_2 - UO_3$ sol by amine extraction of nitrate.

of colloidal suspensions containing thorium and uranium.[10] More recently, it was utilized in a two-stage solvent extraction process that was developed at ORNL for the preparation of thorium-uranium oxide sols.[11]

In the solvent extraction process, ThO_2-UO_3 are prepared directly from aqueous solutions containing thorium and uranyl nitrates The nitrate is removed from the aqueous solution by contacting it with a long-chain aliphatic amine dissolved in an inert diluent. The aqueous phase is digested at 95 to 100°C during the interval between the first two extractions.

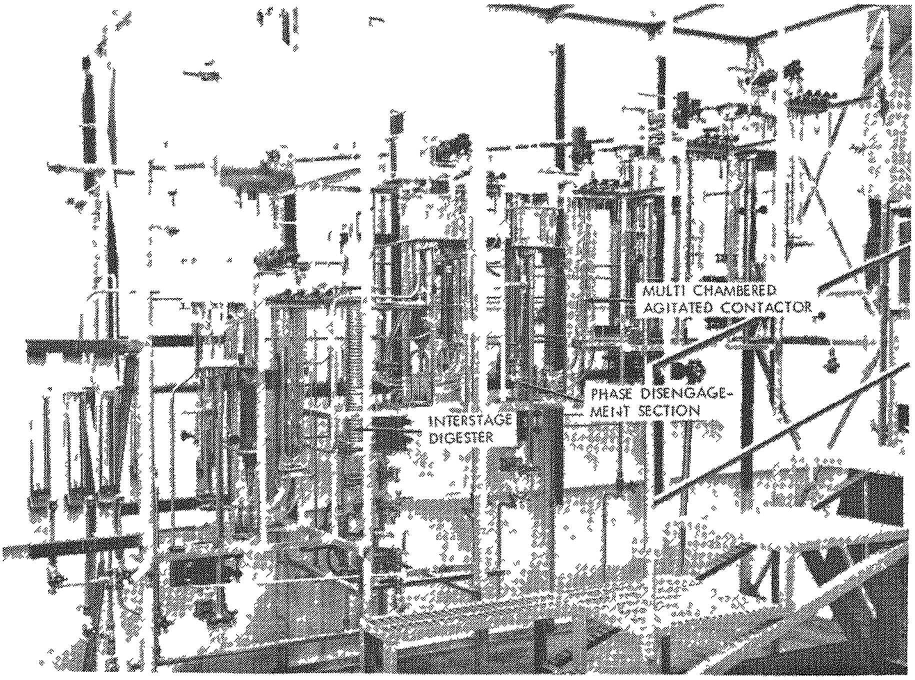


FIG. 3. Mixer-settlers used for continuous preparation of ThO_2 - UO_3 sol by amine extraction of nitrate.

A typical flowsheet for the preparation of a sol having a Th/U atom ratio of about 3 is presented in Fig. 2. One volume of aqueous solution about 0.21 $\underline{M}$ in $Th(NO_3)_4$ and 0.07 $\underline{M}$ in $UO_2(NO_3)_2$ is contacted for at least 2 min with two volumes of 0.75 $\underline{M}$ Amberlite LA-2 (a commercial, extensively branched secondary amine, *n-lauryltrialkylmethyl amine) in n-paraffin. To ensure rapid phase separa*tion, the extraction is made at 50 to 60°C with the organic phase continuous.

After the initial contact, the phases are separated, and the aqueous phase, which has a NO_3^-/metal ratio of about 1, is heated for at least 10 min at 95 to 100°C. This heat treatment causes the aqueous to change from a yellow solution *to a dark red sol containing approximately 10- to 40-A crystallites.* Also, more nitrate is released for extraction in the second stage. Although the flowsheet shown uses cocurrent flow, countercurrent flow is equally effective. In any event, operation of the second stage is identical to that of the first; but, after the phases are separated in the second stage, the organic is regenerated.

Mixer-settlers are used as the contacting devices (Fig. 3). They are constructed of 3-in.-diam glass pipe and are geometrically safe for enriched uranium. Each mixer is divided into six compartments, with an agitator in each compartment. This minimizes bypassing and ensures efficient mixing. The solvent and the aqueous phases enter at the top and flow cocurrently through the mixer to the settler, which is a pipe tee located at the bottom of the mixer. The interface is maintained in the tee below the mixer to ensure an organic-continuous dispersion in the mixer, which is very important for preventing emulsions. The interface position is controlled by a simple jackleg and an adjustable weir on the aqueous outlet of the settler. The digester is merely an enlargement of the jackleg of the first-stage settler. The temperature is controlled by circulating heated water through the baffles in the mixers and through a coil in the digester.

The process was demonstrated at the design rate of 1 kg of ThO_2—UO_3 sol per hour. About 900 liters of 0.3 M sol was produced. The NO_3^-/metal mole ratio was consistently less than 0.10. The crystallite size of the sol was 42-46 A, which is slightly larger than that obtained in laboratory preparations.

The equipment has operated very smoothly. Organic-continuous dispersions were maintained without difficulty and interface control was very stable. Some emulsions accumulated in the first-stage settler during the early runs; however, coalescence occurred in subsequent stages such that the sol product contained less than 0.1 vol % solvent. During the latter runs, the scrub solution was recycled to the first stage, and virtually no emulsion was formed. Entrainment of aqueous in the solvent caused difficulties only for the solvent stream leaving the extraction section; it was directly dependent on the agitator speed in the mixer, ranging from 0.15% at 300 rpm to 0.8% at 600 rpm. Entrainment was the only significant cause of loss of metal, which usually amounted to about 0.1%. We believe this loss can be reduced by improved scrubbing of the solvent before regeneration. The efficiency of the mixers was 90 to 95% at agitator speeds of 300 to 500 rpm.

Batches of sol have been concentrated 5-fold (to 1.5 M) in a forced-circulation vertical-tube evaporator (Fig. 4). A high degree of turbulence and a large heat exchange area are used to minimize drying of the sol on the tubes. De-entrainment is accomplished by introducing the superheated sol tangentially into the body of the evaporator; additional de-entrainment occurs in the stripping section, where the vapor contacts the feed in a packed tower. Very few solids have formed, and no foaming has occurred, even with operation at a vacuum of 25 in. Hg. The concentrate is fluid and stable at all Th + U concentrations up to 1.5 M.

Seven kilograms of microspheres were formed, dried in a steam atmosphere, and calcined at 1150°C in an Ar atmosphere to form 350-500-μ-diam spheres. The microsphere forming column was operated with the surfactants 0.6 vol % Ethomeen S/15 and 0.5 vol % Span 80 in the 2-ethyl-1-hexanol. No microsphere cracking was detected at either the drying or calcining steps.

Engineering studies of the amine extraction process are now being extended to include high specific alpha activity materials, e.g., ^{233}U. Towards this end, an alpha enclosure containing amine extraction equipment (the Pu Solex Development Laboratory) has been designed and built.[12] This laboratory will permit the preparation of concentrated hydrosols containing fissionable isotopes at a rate of about 1 kg/day. Three stages of amine extraction with two stages of digestion are permis-

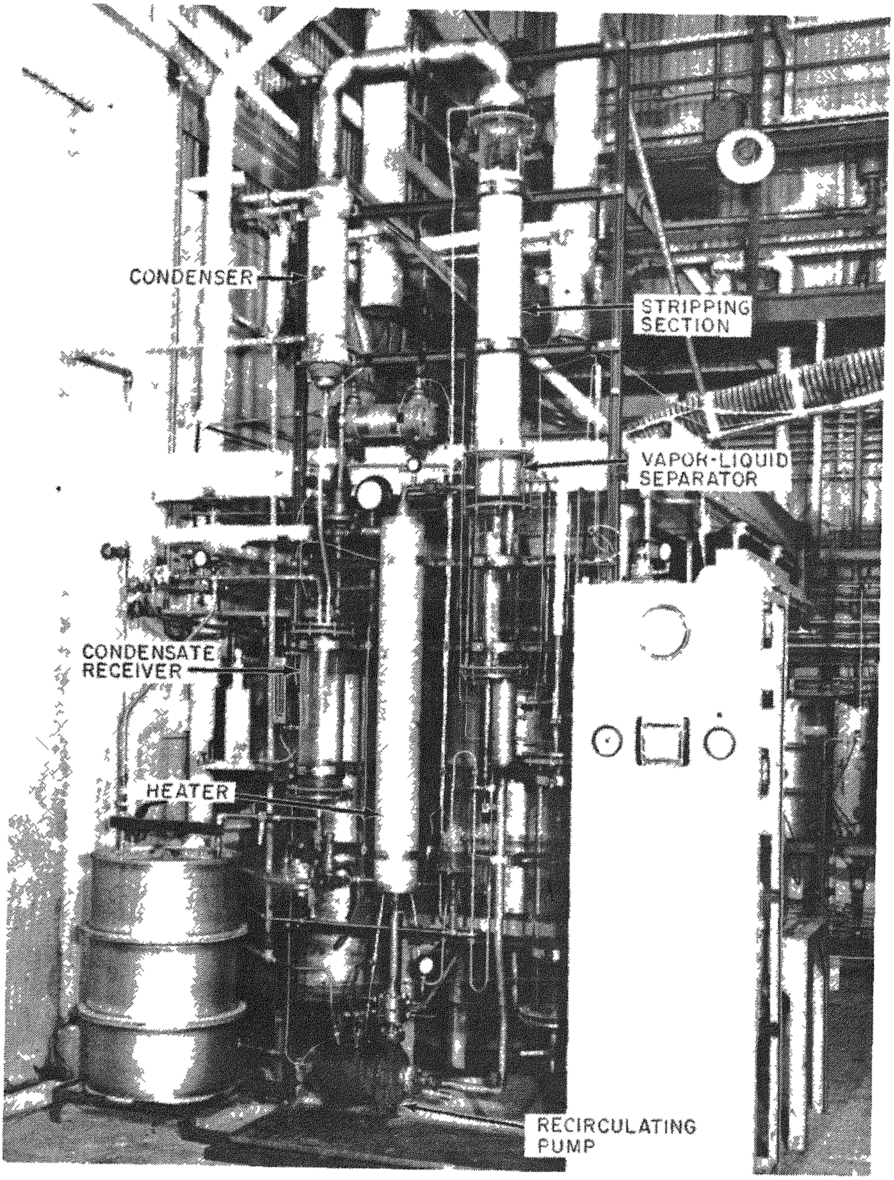


FIG.4. Forced-circulation evaporator for concentration of sols.

sible. Three contactors without the interstage digestion are available for amine regeneration. These six contactor assemblies are mounted on a frame with the services located between the hydrosol forming stages and the amine regeneration stages. The assembled unit fits onto a track inside an alpha enclosure to facilitate equipment modifications (Fig. 5).

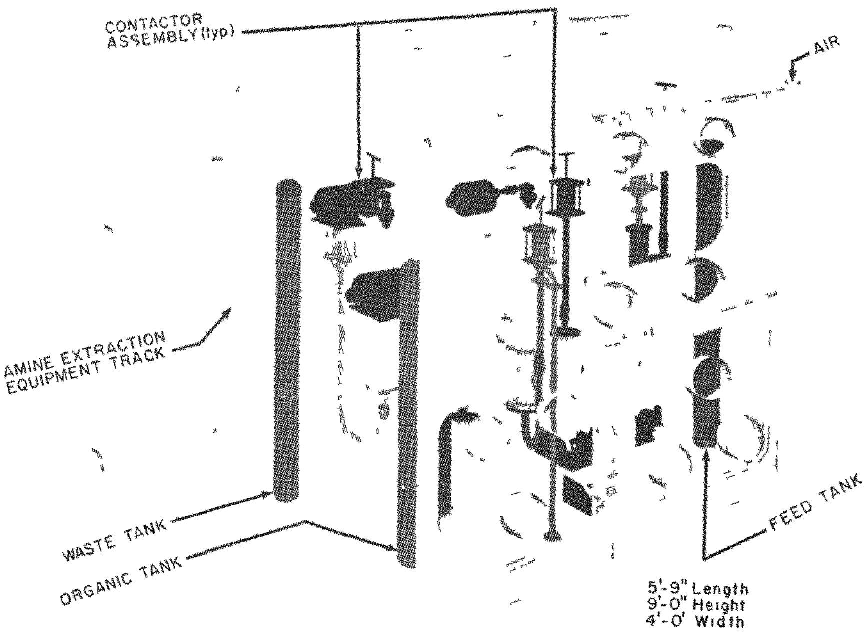


FIG.5. Amine extraction equipment alpha enclosure.

A second alpha enclosure of identical design contains the vacuum evaporator. This critically safe vacuum evaporator is designed for batch operation, and is capable of removing about 4 liters of condensate per hour. It is very similar to the evaporator described earlier.

UO_2 SOL PREPARATION BY SOLVENT EXTRACTION

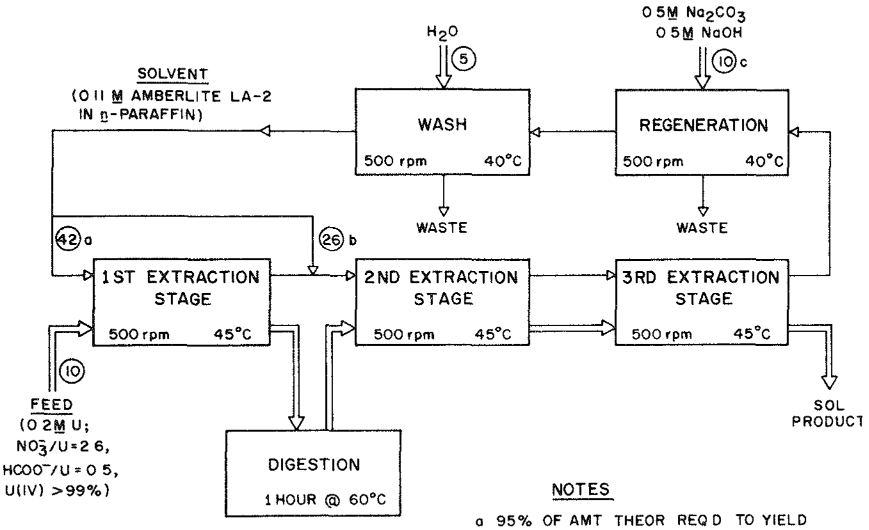
The development of a sol-gel process for the preparation of urania microspheres was prompted by their potential use as thermal and fast reactor fuels, in which urania would be the bulk constituent. A solvent extraction process analogous to that developed for preparation of ThO_2—UO_3 sols was developed for preparation of UO_2 sols. The process has been successfully scaled up and operated continuously in engineering experiments. A total of 40 runs has been made, each producing about 2 kg of UO_2 in the form of dilute (about 0.2 M) sol. Laboratory studies have been continued to characterize the sol and aid in the engineering studies. Some of the operating parameters affecting sol properties that were studied are: nitrate-to-uranium ratio during digestion; digestion temperature; and method of preparing the U(IV) solution.

The reference flowsheet for the preparation of UO_2 sol by solvent extraction (Fig. 6) was developed from laboratory batch studies.[13] It consists of extracting nitrate from an aqueous solution of U(IV) nitrate-formate with a long-chain amine (e.g., Amberlite LA-2, Rohm and Haas Company) dissolved in a paraffin diluent.

Digestion of the nitrate deficient solution thus formed results in formation of the UO_2 sol. Final nitrate adjustment is obtained in subsequent extractions. The amine is regenerated by contact with sodium carbonate and is recycled.

Preparation of U(IV) Solution

During the laboratory studies, the U(IV) solution was prepared by contacting 0.2 M $UO_2(NO_3)_2$—0.1 M HCOOH with hydrogen using 5% Pt on Al_2O_3 powder as the catalyst. Although this procedure usually produced good results, it did not appear very practical for the larger engineering tests because of the time required for settling and filtration for removal of the catalyst. Several alternative methods of reduction were tried. The first method was continuous reduction in a pressurized fixed bed of Pt on Al_2O_3 pellets. Attempts to make sol using U(IV) from this reductor failed because of the formation of viscous sol in the second extraction stage. The next reduction method tried was batch operation of the fixed catalyst bed at nearly atmospheric pressure. This allowed better control of the reduction, and the resulting sol was improved; no thickening of the dilute sol occurred. However, the sol could not be concentrated (by vacuum evaporation) to 1 M without getting thick or setting up as a gel. The U(IV) solution contained a nitrogen-bearing basic material which acted like ammonia during chemical analysis but degraded on standing. The fact that ammonia can cause thick sol was demonstrated in laboratory tests by adding ammonia (mole ratio $NH_3/U = 0.02$) to the laboratory prepared U(IV) solution, which then was formed into sol by the usual batch extraction technique.



NOTES

a 95% OF AMT THEOR REQ D TO YIELD $NO_3^-/U = 0\ 15$

b 150% OF AMT THEOR REQ'D TO YIELD $NO_3^-/U = 0\ 15$

c 200% OF AMT THEOR REQ'D TO REGENERATE THE AMINE

FIG.6. Preparation of UO_2 sol by solvent extraction.

Our preferred reduction method now is based on use of a slurry-type reductor wherein finely divided PtO_2 catalyst is suspended in a well-mixed uranium nitrate solution and hydrogen is introduced through a sparger. The PtO_2 is reduced to metal, which becomes flocculated in the presence of excess hydrogen, so that when the reduction of the uranium is nearly complete the catalyst settles very rapidly and is readily retained on a filter. The filter is a flat disc of porous stainless steel (10μ pore) which forms the bottom of the reductor. The reduction is monitored by measuring the redox potential of the solution using a Pt electrode *vs* a reference glass electrode system. (Other reference electrodes, such as silver–silver chloride or calomel, will work but are not as rugged and free of trouble as glass.) The end point is readily detected as a sharp break in emf which occurs when reduction has progressed to between 96 and 100% U(IV). The feed composition was fixed at 0.6 $\underline{M}$ $UO_2(NO_3)_2$ containing about 0.4 $\underline{M}$ HNO_3 and 0.3 $\underline{M}$ HCOOH so that NO_3^-/U was 2.6, and HCOOH/U was 0.5.

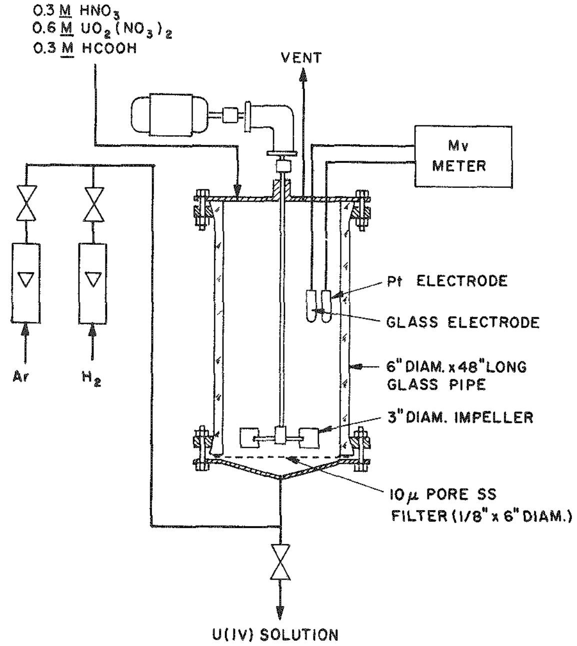


FIG.7. Batch slurry uranium reductor.

The slurry reductor has been tested both in a laboratory unit of 1.6 liter capacity and a larger unit of 14 liter capacity to supply feed for the engineering tests of the solvent extraction sol process. A total of about 10 kg of U was reduced in the small reductor, thus demonstrating the feasibility of the slurry catalyst. The large reductor was designed and built using the laboratory data. The results of 20 runs, producing a total of 40 kg U(IV), show excellent performance. The Pt catalyst has shown no sign of loss in activity or in ease of filtration (gravity filtration time was 12 min for 14 liters). Greater than 99.5% U reduction was easily obtained, very little ammonia was formed ($NH_3/U \leq 0.002$), and less than 10% of the HCOOH was destroyed. The rate of U reduction with 30 g of PtO_2 ranged from 2 moles/hr when only a small excess of hydrogen was used (96% utilization) to 3.3 moles/hr at 77% hydrogen utilization.

Figure 7 is a schematic representation of the reduction equipment used to prepare feed for the engineering scale solvent extraction equipment. Table 1 shows the effect of agitator speed and H_2 flow rate for a fixed feed and catalyst concentration.

Table 1. Batch Reduction of 0.6 M $UO_2(NO_3)$—0.3 M HCOOH 0.3 M HNO_3 Solution (14 liters) in a Stirred Slurry Catalyst (30 g PtO_2) Reductor.

Agitator Speed (rpm)	Excess H_2 (%)	Reduction Rate (mole U/hr)
570	12	1.9
820	12	2.5
1070	12	2.8
1070	4	2.0
1070	12	2.8
1070	22	3.7

Preparation of Sol

The equipment for the engineering study of the sol preparation process is the same as was used for the preparation of ThO_2—UO_3 sol.[14] It uses mixer-settlers as the contacting devices for extraction, water scrub, and amine regeneration. The mixer-settlers are geometrically safe with regard to criticality. The design capacity of the equipment is 6 liters of sol per hour; capacity is set by the size of the digestor and the flowsheet requirement of about 1-hr residence time in the digestor.

The operation of the solvent extraction equipment with the reference flowsheet has been very good (during 20 runs about 1000 liters of 0.2 M UO_2 sol has been produced). Table 2 summarizes some operating conditions and sol product properties. No emulsion or entrainment problems have occurred. The entrainment of solvent in the sol product has been consistently less than 0.01 vol %. A small entrainment of sol in the used solvent is removed by a water scrub stage to prevent loss of uranium to the regeneration waste. Although three extraction stages have been used in most of the runs, only two are needed because the nitrate content of the sol changes very little in the third stage. The stage efficiency has been consistently greater than 90% at a mixer speed of 500 rpm.

Variation of U concentration from 0.15 to 0.3 M (the reference concentration is 0.2 M) did not cause any trouble, and good sol was produced; however, two attempts to run at 0.5 M U were unsuccessful because the sol became thick in the second extraction stage.

The digestion temperature was found to be an important variable. At 50°C the sol product contains a significant amount of amorphous UO_2 (determined by x-ray diffraction). This sol gels at about 0.5 M if evaporated immediately after preparation; however, after aging overnight it can be evaporated to greater than

Table 2. UO_2 Sol Formation by Solvent Extraction in Continuous-Flow Engineering Tests

Run No.	Excess Amine (%)	Digestor Temp. (°C)	Dilute Sol, NO_3^-/U mole ratio	Shelf Life* of 1 M Sol (day)
15	50	50	0.17	13
16A	50	50	0.26	50
16B	50	65	0.08	90
17	50	50	0.27	43
18	50	50	0.24	40
19	70	50	0.24	60
20	50	60	0.09	35
21	50	60	0.09	36
22	50	60	0.10	60
23A	65	60	0.17	25
23B	65	50	0.24	-
24	50	50	0.24	50
27	20	60	0.13	50
28	20	60	0.14	50
29	50	60	0.10	50
30	50	60	0.09	10
31	50	60	0.09	25
32	50	60	0.09	15
33	50	70	0.07	8
35	50	60	0.10	-
36	50	60	0.09	-

*Shelf life refers to the number of days the sol remained fluid. In some cases, the sol thickened after the interval listed; in others, it gelled. In all cases the sol had been concentrated from the concentration given in column 4 to 1 mole/liter.

1.0 M and will remain fluid for over 30 days. When the digestion temperature is increased to 60°C, the sol contains more UO_2 crystallites, and the fresh sol can be concentrated without gelling. To minimize oxidation of the uranium at the higher digestion temperature, the laboratory flowsheet was modified by using an excess of amine in the first stage. This results in the nitrate being extracted down to a NO_3^-/U less than 0.5. At a digestor temperature of 70°C, the sol has a shorter shelf life after concentration; perhaps because too much oxidation of uranium occurs, even at the low nitrate-to-uranium ratio. The digestor temperature also affects the nitrate-to-uranium mole ratio in the sol product; it averages 0.24 when digestion is carried out at 50°C, 0.10 when carried out at 60, and 0.07 when carried out at 70°C. The amount of amine in excess of the stoichiometric quantity required to extract the nitrate from the feed has very little effect on the nitrate content of the sol over the range of 20 to 70% excess. The average size of the UO_2 crystallites is 35 to 40 A and does not seem to be dependent on either digestor temperature or length of the aging period.

Evaporation of Sol

The dilute sol must be concentrated to about 1 M U to facilitate forming microspheres. Vacuum evaporation is used to avoid over heating the sol. The temperature is kept below about 35°C. The sol is quite sensitive to oxidation, and exposure to air is a common cause of thickening or, in extreme cases, flocculation of the sol.

Seven batches (each 2 kg U) of dilute sol have been successfully concentrated in the forced circulation vertical tube evaporator[15] to yield 1 M sol for use in making microspheres. The evaporation has been very smooth without foaming or scaling at the design boilup rate of 15 liters/hr and at an absolute pressure of 30 torr. The shelf life of the large batches of concentrated sol has not been as good as product from the small laboratory evaporator. We believe this is caused by some inleakage of air and resultant oxidation of uranium in the large evaporator. In several runs where large leaks were discovered, the sol thickened overnight, while in other runs the sols were still fluid after 30 days.

PuO_2 SOL PREPARATION

A sol-gel process for the preparation of dense oxide forms of PuO_2 has been developed and tested on a 150-gram scale. The sols produced by this method are 1 to 3 M in plutonium and have NO_3^-/Pu of 0.1 to 0.15. They are stable for many months and are compatible with thoria and urania sols that have been prepared at Oak Ridge National Laboratory. Dense PuO_2, as well as PuO_2—UO_2 or PuO_2—ThO_2 microspheres at any desired Pu/U or Pu/Th atom ratio have been produced.

A total of 7.4 kg of Pu was converted into stable PuO_2 sols during the past year. Approximately 90% of this was formed into PuO_2 microspheres of greater than 94% theoretical density. The remainder was mixed with UO_2 sols and formed into microspheres for fuel fabrication studies. These preparations demonstrated the operability of equipment and the reproducibility of the flowsheet, and provided sol for the formation of mixed-oxide and plutonia microspheres. The present flowsheet for the preparation of Pu sol is shown in Fig. 8. Prior to the operations shown on the flowsheet, an adjustment of the valence of the plutonium (to Pu^{4+}) is made, if necessary, by bubbling NO gas through the $Pu(NO_3)_4$ solutions. A minimum HNO_3 concentration of 1 M is maintained in the feed to prevent polymerization of the plutonium; free HNO_3 concentrations as high as 3 M have been used successfully.

The $Pu(NO_3)_4$ feed solution is added to NH_4OH at rates as high as 30 cc/min, with moderate agitation, to ensure rapid neutralization and precipitation of the $Pu(OH)_4$. As little as 40% excess NH_4OH proved to be satisfactory as long as the concentration of NH_4OH in the final solution was $\geqq 1$ M. The NH_4NO_3 and the excess NH_4OH are removed through a porous stainless steel (G porosity) filter. The precipitate is washed thoroughly (four washes), with resuspension of the filter cake in each wash. A high-nitrate sol is then formed by peptizing the washed cake in dilute HNO_3 at a NO_3^-/Pu mole ratio of about 2. All the steps just mentioned are carried out in an 8-in.-diam precipitation-filtration vessel having a porous stainless steel filter in the bottom (Fig. 9). Filtration time is about 20 min per wash. Four such washes give adequate NH_4^+ removal. The high-nitrate sol is removed through the bottom of the vessel, leaving no solids on the filter.

A minimum NO_3^-/Pu mole ratio of 1 is necessary for forming plutonia sol. Although ratios as high as 4 have been used, a ratio of 2 is sufficient to bring about sol formation upon heating to about 90°C. Under these conditions, a sol having approximately 20 A crystallites exists. However, microspheres formed from this material have low densities and low strength.

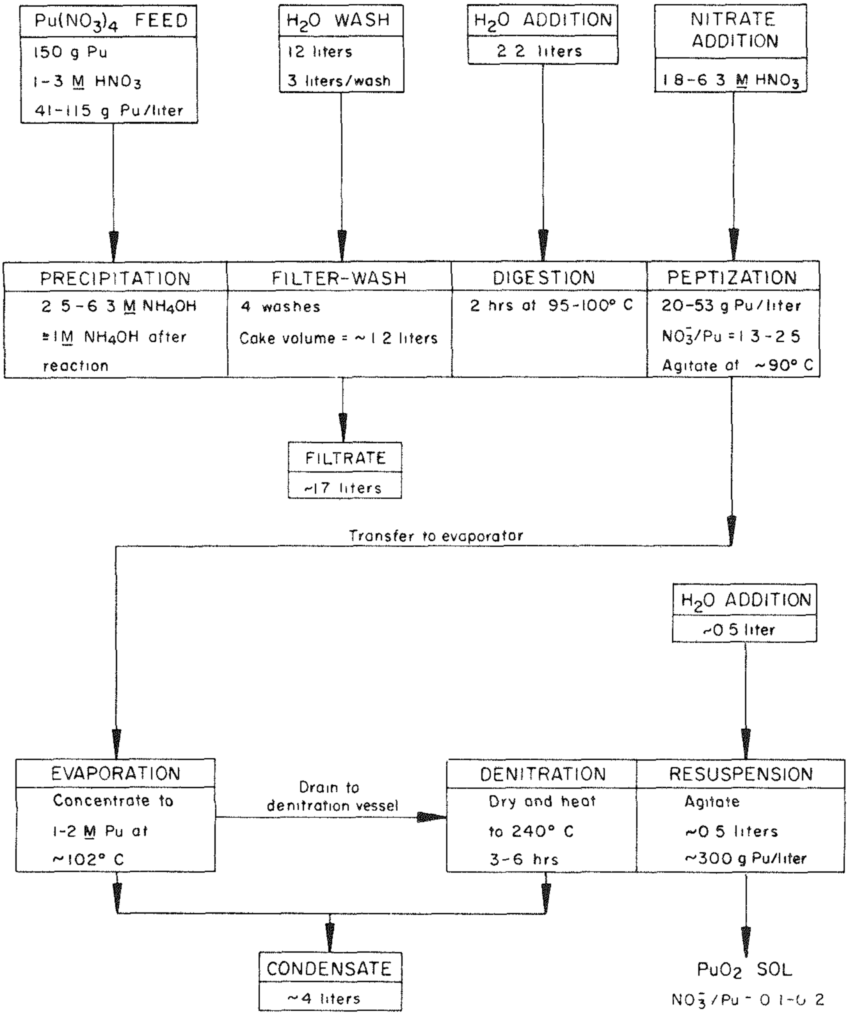


FIG.8. Flow sheet for preparation of PuO_2 sol.

The NO_3^-/Pu ratio of the sol must be reduced to 0.1 to 0.2 by thermal denitration (or baking) and resuspension before the sol will form dense microspheres. This is a crucial step requiring careful control of temperature and time. The sol is first evaporated to dryness at 100°C and then heated to a temperature of about 240°C. A thin, porous cake which forms as the sol dries is maintained intact throughout the cycle. During the reduction to dryness, excess HNO_3 is evaporated such that the initial NO_3^-/Pu mole ratio in the dry solid is 0.8 to 1.0. Progress of the denitration is followed by resuspending a weighed sample of the dry material and titrating with NaOH to determine the NO_3^- content. It is important that the heating of the solid be uniform in order to obtain a uniform product. If the denitration is allowed to proceed until the NO_3^-/Pu mole ratio is less than 0.1, the PuO_2 cannot be resuspended as a sol. Laboratory results relating temperature and time to the removal of NO_3^- from the cake being denitrated are shown in Figs. 10, 11, and 12. A diagram of the denitration vessel, which allows independent control of the temperatures of the top and bottom surfaces and limits radial gradients to approximately 2°C, is shown in Fig. 13. Crystallite growth and agglomeration also occur during baking. After the denitration step, the basic crystallite size is approximately 80 A. These form

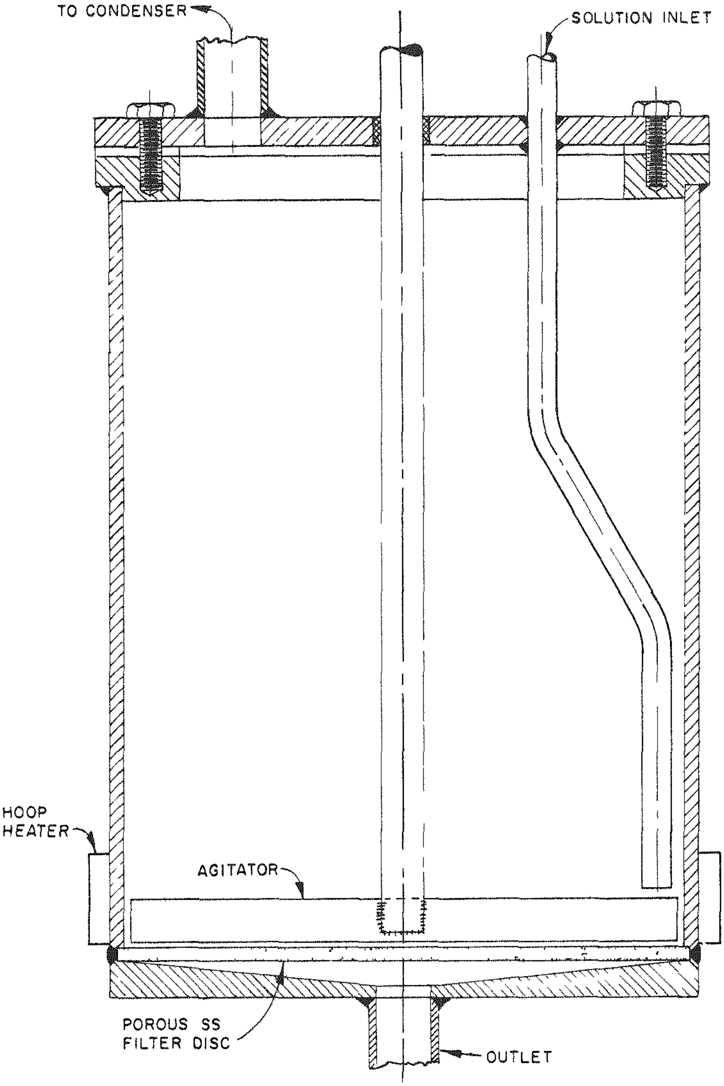


FIG. 9. Vessel for the precipitation, filtration, and peptization of PuO_2 sol.

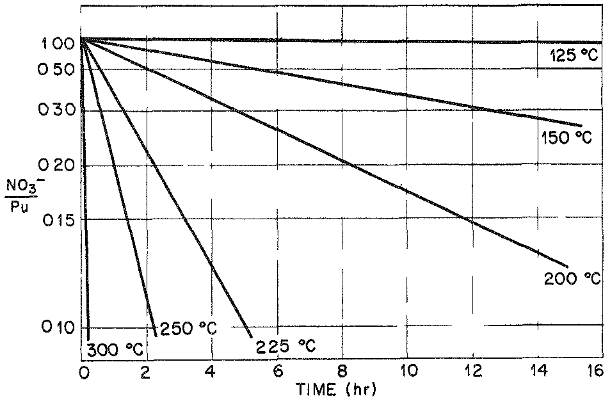


FIG. 10. Denitration of plutonium by baking at different temperatures.

agglomerates as large as 1000 A. The amount of agglomeration must be limited to ensure a stable sol. Material having NO_3^-/Pu mole ratios of 0.1 to 0.15 can be resuspended by mild agitation in water to give plutonium concentrations as great as 2 M; more concentrated sols may be produced by evaporation after resuspension.

Plutonia sols can be dried and calcined to dense hard fragments, or they can be formed into microspheres that are subsequently calcined to dense oxide spheres. They can also be mixed with thoria or urania sols and formed into microspheres or fragments. Formation of gel microspheres from these sols is accomplished by using the procedures developed for thoria sols.

Microspheres have been prepared from mixed PuO_2—ThO_2 sols containing 2, 5, 10, 20, 30, 50, and 80 wt % PuO_2 and from mixed PuO_2—UO_2 sols containing 5, 15, 20, 25, and 50 wt % PuO_2. Calcined microspheres that are 50 to 600μ in diameter can be obtained. After calcination at 1150°C, these products are characterized by high density, low surface area, and high resistance to crushing. Mercury porosimetry indicates densities of 95 to 99% of the theoretical crystal density for typical products. Surface areas of 0.02 m^2/g are obtained from 300- to 600-μ-diam microspheres. Crushing loads for microspheres calcined at 1150°C average above 550 g for a 250-μ-diam microsphere, and increase to greater than 1 kg for a 500-μ-diam sphere. Crush resistance is approximately the same for microspheres calcined at 1600°C or 1150°C.

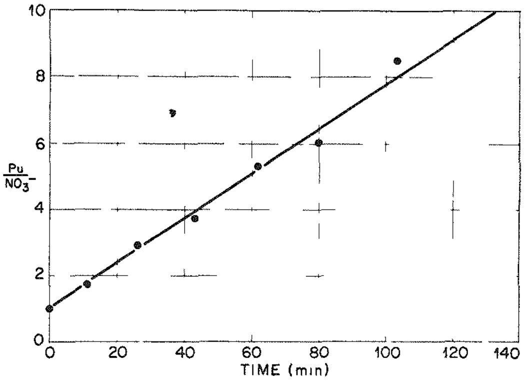


FIG. 11. Denitration of plutonium by baking at 250°C.

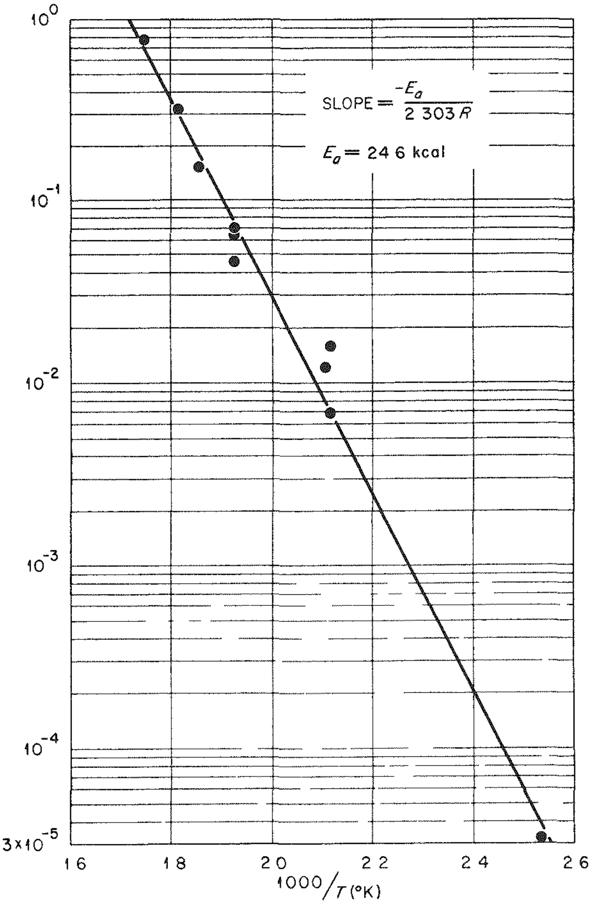


FIG. 12. Variation of k with temperature.

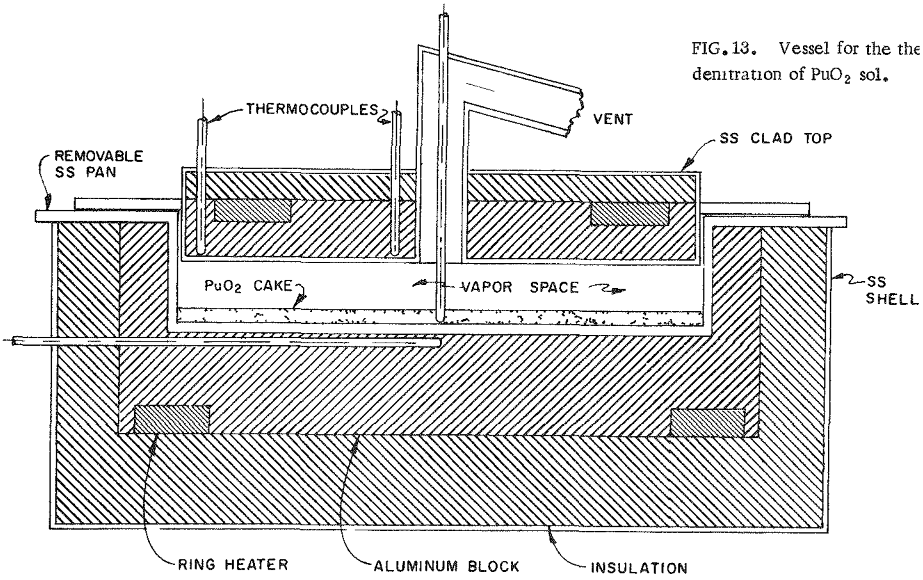


FIG. 13. Vessel for the thermal denitration of PuO_2 sol.

X-ray analysis indicated a crystallite size of 1000 A for PuO_2 spheres that had been calcined in air at 1150°C. Crystallite size increases with temperature; for example, 1700 A crystallites were observed in material that had been calcined for 0.5 hr at 1550°C. It was found that $^{239}PuO_2$ microspheres can be washed free of smearable alpha contamination. Calcined spheres were water-washed, dried in air, and smeared. Extensive contact with 50 to 100 spheres produced counts on the order of 20 dis min^{-1} $smear^{-1}$.

The homogeneity of UO_2—20% PuO_2 microspheres was investigated using the electron microprobe technique. Since no plutonium standard was available, analysis was limited to uranium. Data obtained indicated the presence of a homogeneous mixture having a uniform distribution of urania. The maximum deviation of the uranium concentration over the entire surface of the sectioned microspheres was ± 1.5%.

MICROSPHERE PREPARATION

The initial development of the process for the preparation of ThO_2 microspheres and its application to UO_2 or UO_2–ZrO_2 sols have been previously reported.[16,17] Our work has included the operation of a microsphere pilot plant, with procedures and equipment required for a remote facility, the application of the process to a variety of sols on a larger scale, and the continued development of dispersers for sols.

Full-scale prototype units for microsphere preparation in a remotely operated facility have been operated during the past two years to produce ThO_2 microspheres. The prototype equipment incorporates all operations that are essential for the conversion of aqueous sols into microspheres (see Fig. 14). The design capacity is 1 kg of oxide spheres per hour. The improved equipment flowsheet presently used requires fewer equipment pieces and is simpler to control than earlier pilot plant flowsheets. The sol is dispersed into droplets that are released into the enlarged top of the tapered column. These droplets are suspended or fluidized by a recirculated, upflowing stream of the 2-ethyl-1-hexanol (2EH). As the water is extracted and the droplets gel into solid microspheres, the settling velocity increases. The column configuration and the fluidizing flow rates are selected to permit the gelled particles to drop out continuously while sol droplets are being formed in the top of the column. Separation of the gel spheres from the 2EH is accomplished by discharging the product collector into a dryer and draining off the liquid through a woven wire cloth. The gel spheres are dried and calcined batchwise. Fresh or purified 2EH is continuously added to the column; this displaces a stream of wet 2EH to a recovery system. Water is removed from the 2EH by distillation.

The entire system has been emptied and filled twice with 2EH, and 300 kg of 210- to 250-μ-diam and 20 kg of 500- to 590-μ-diam ThO_2 microspheres have been prepared. Each charge of 2EH (about 45 gal) was used for 6 months (equivalent in our operating mode to about 300 hr of operation in the column-distillation system). Operation was smooth throughout both periods; the solvent could have been used for a longer period of time, if necessary or desired. The largest monthly production was 137 kg of ThO_2 microspheres.

Surfactants must be added to the 2EH to prevent coalescence of droplets, sticking of droplets on column walls, and clustering of partially dried drops. Each time the column was filled with fresh 2EH, 0.3 vol % Ethomeen S/15 and 0.07 vol % Span 80 were added. Satisfactory column operation was maintained by adding 10 ml of Ethomeen S/15 and 2.5 ml of Span 80 per liter of sol fed. Excessive Span 80 concentrations result in distortion of large sol droplets and thus in nonspherical gel particles; therefore, the additions of Span 80 were discontinued while making 400 μ ThO_2 microspheres.

Samples of 2EH were analyzed for nitrate, amine, total nitrogen, and thorium periodically throughout each of the two 6-month periods. Results of analyses obtained during the last four months of the second 6-month period showed no trend with time (see Table 3). Only the thorium (ThO_2) concentration built up steadily throughout the period, causing turbidity of the solvent. This buildup was the result of occasional equipment malfunction. Turbidity hindered visual observations of microspheres through the column walls and was the primary reason for discarding both the 2EH loadings. The thoria causing the turbidity was present as extremely fine particles (300 A), which settled out upon long standing (~15 days), leaving clear 2EH.

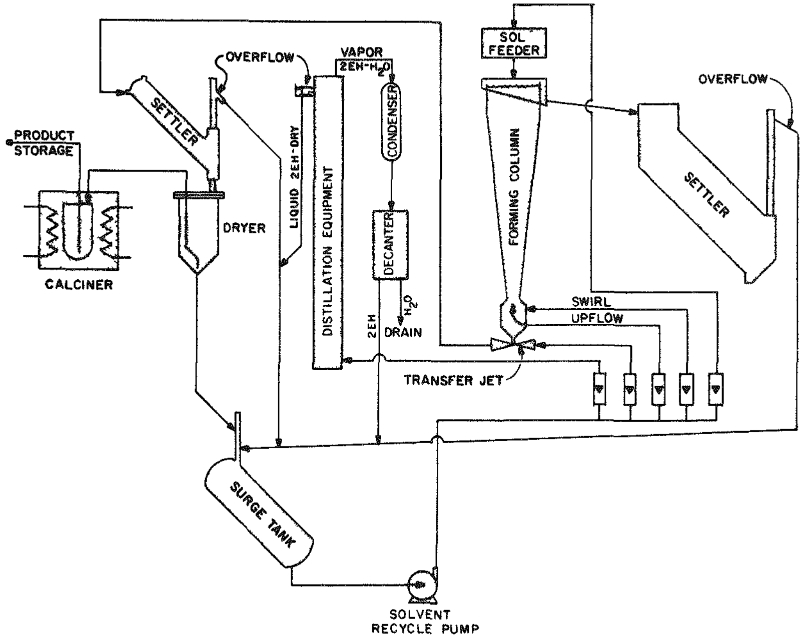


FIG.14. Improved and simplified equipment flow sheet for microsphere preparation.

To monitor the extent of column loading, a bubbler tube was installed with its lower tip placed in a sidearm off the column bottom. As the column loaded with microspheres, the back pressure increased to about 4 in. of water and then leveled off. This plateau has been used as a means of controlling the loading of the column.

The present geometry of the glass column (Fig. 15) appears to be nearly optimum for producing microspheres in the size ranges of interest. The 500- to 590-μ-diam particles settle in a sharply defined zone in the tapered section just above the throat; the stainless steel top section gives ample settling capacity for the 210- to 250-μ-diam particles.

Table 3. Analyses of Species Present in the 2-Ethyl-1-Hexanol Used in a Microsphere Column over a 4-Month Period

Species	Concentration Range	Comment
Nitrate ion	(1.5 to 4) x 10^{-4} $\underline{M}$	No trend with time
Total nitrogen	(2.0 to 5) x 10^{-4} $\underline{M}$	No trend with time
Amine	(6.0 to 10) x 10^{-4} $\underline{M}$	No trend with time
Thorium	(2.0 to 7) x 10^{-4} $\underline{M}$	Increasing with time

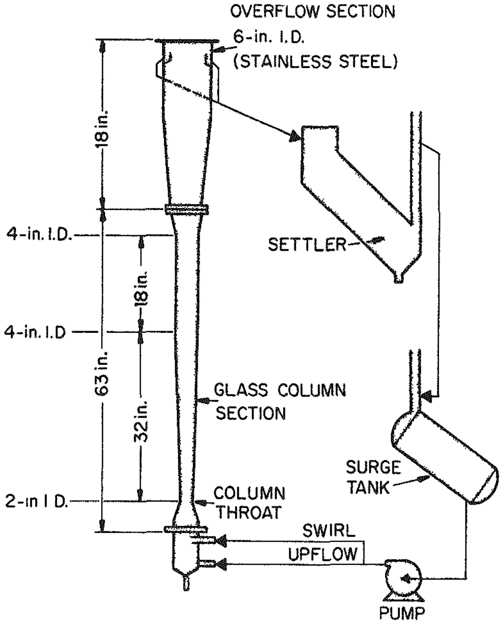


FIG. 15. Microsphere column: configuration and dimensions.

A filter was placed in the 2EH circuit to remove suspended fines; it was also effective in removing small gelled particles. Use of filtration, in an overall sense, was not satisfactory since any operational upsets allowed soft, half-gelled sol to enter the circulating system and to plug the filter. A large settler (Fig. 16) is now used to remove any entrained sol or gel particles before they reach the pump.

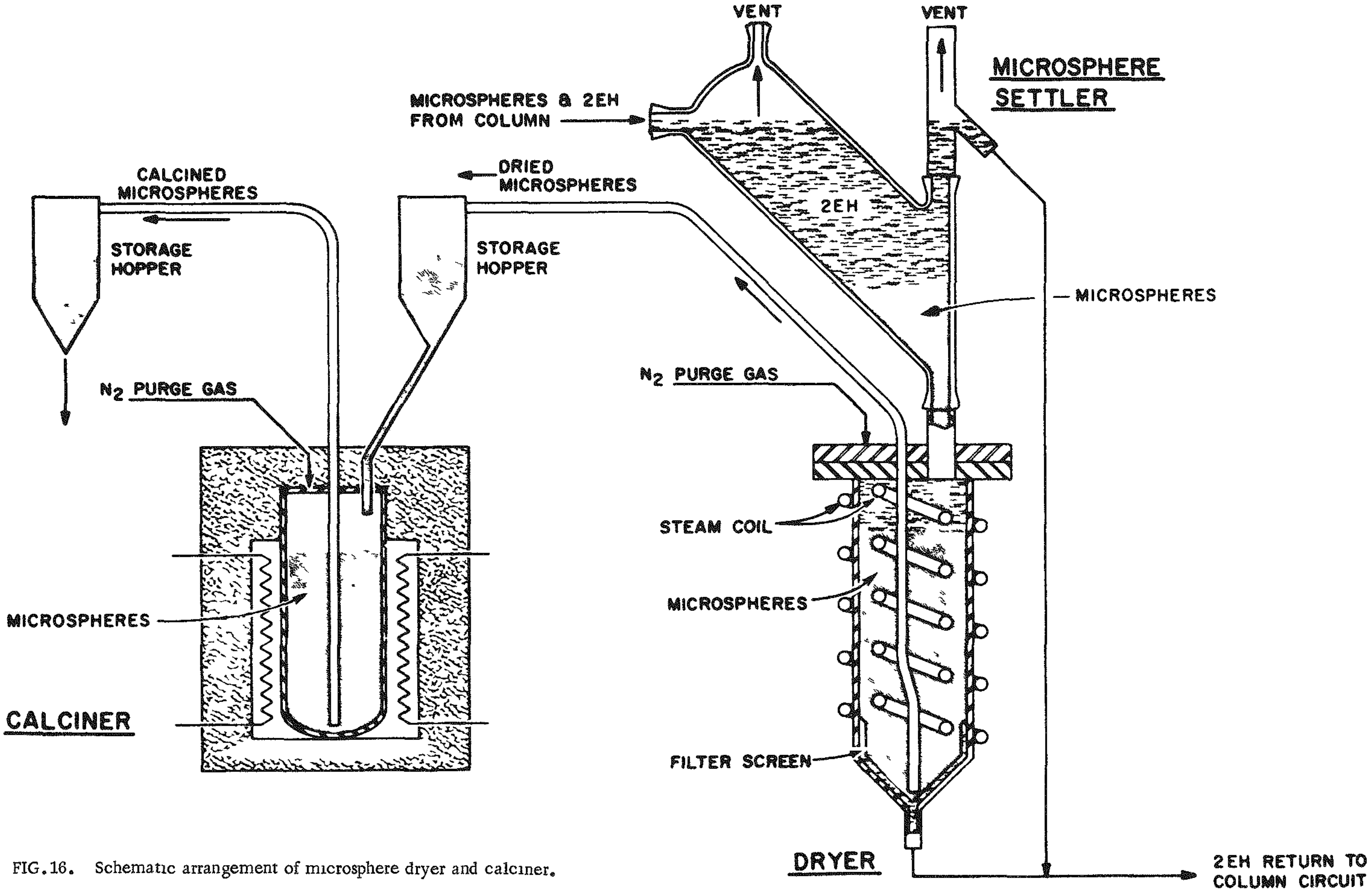


FIG. 16. Schematic arrangement of microsphere dryer and calciner.

A liquid-driven (2EH) jet was mounted on the bottom of the forming column to transfer the microspheres continuously to the dryer. This transfer method has worked satisfactorily.

A prototype gel microsphere dryer design is shown in Fig. 16. The ThO_2 microspheres enter the settler with the 2EH transfer fluid. Part of the 2EH flows down through the stainless steel wire cloth in the dryer bottom, while the rest overflows the settler. Both streams combine and return to the column circuit. The microspheres remain on the screen. The settler was installed to allow the transfer jet to operate at constant pressure, since the pressure drop across the bed of microspheres increases as the dryer is filled. When the dryer is filled with microspheres, excess 2EH is blown down through the screen with nitrogen, the steam is turned on, and the bed is allowed to dry (150 to 250°C). After drying, microspheres are transferred pneumatically to the calciner.

In the conceptual design of the remotely operated calciner the charge is contained in a crucible that is fixed in the furnace. The charge will be loaded by gravity and discharged pneumatically. The present calciner is actually a muffle furnace containing crucibles that are loaded manually.

The use of the liquid and pneumatic microsphere transfer systems represents a significant improvement in our flowsheet, serving to eliminate mechanical transfer of canisters, or crucibles, within the cell.

The ThO_2-UO_3 sols prepared by amine extraction of nitrate (Th/U ratios = 3 to 5) were formed into gel spheres using Span-80/Ethomeen S/15 volume ratios of about 2. Span 80 alone tended to give wrinkled or "raisin" surfaces, while Ethomeen S/15 alone tended to give deep dimples or "cherry pits." Small-scale tests with freshly prepared sol and new 2EH required low total surfactant concentrations ($\leq 0.2\%$) to prevent cracking of the gel spheres into fragments. This cracking did not occur for surfactant concentrations as large as 0.8 vol % in larger-scale tests with aged sol (storage period, 1 to 3 months) and 2EH that had been used 20 to 40 hours. The drying and firing conditions were similar to those used for microspheres prepared from ThO_2 sols containing small amounts of $UO_2(NO_3)_2$ or UO_3.

The UO_2 sols can be formed into gel microspheres in the equipment developed for use in preparing ThO_2 microspheres. However, provision must be made for an inert gas blanket to prevent oxidation of the UO_2 during microsphere preparation. The UO_2 sols are more prone to stick, coalesce, or cluster, and require more careful control of the surfactant concentrations than ThO_2 or ThO_2-UO_3 sols. Also, the urania sols have many more composition variables. The UO_2 sols generally require the presence of both Span 80 and Ethomeen S/15 in the 2EH. High total surfactant concentrations or high Span/Ethomeen volume ratios tend to result in badly distorted particles having the appearance of raisins. High Ethomeen S/15 concentrations seem to favor production of particles having a deep dimple or "cherry pit" on one side. High surfactant concentrations also appear to contribute to the cracking of the spheres in some cases.

Equipment for the forming, drying, and calcination of microspheres containing PuO_2 was operated to produce 5-20% PuO_2-UO_2, 5% PuO_2-ThO_2 and PuO_2. Batch sizes were 50 to 150 g, and densities generally were $\geq 95\%$ of theoretical. The equipment is installed in two 6-ft glove boxes; the first is used for sol mixing, microsphere forming, and drying; the second, for calcination and size classification. To

Table 4. Examples of PuO_2-Containing Microspheres Prepared in a Glove Box Facility

		Density by Hg Porosimetry				Surface Area	
			10,000 psi				
Type of Material	Size Range (μ)	Bulk (g/cc)	(g/cc)	Theoretical (%)	Carbon (ppm)	Gas Adsorption Method (m^2/g)	Calculated (m^2/g)
20% $PuO_2-{}^{235}UO_2$	300-600	10.3	10.5	95	<10	0.02	-
15% $PuO_2-{}^{238}UO_2$	300-600	10.5	10.6	97	<90	-	0.06
5% $PuO_2-{}^{238}UO_2$	300-600	-	-	-	-	-	-
5% PuO_2-ThO_2	300-600	9.48	9.84	97	<10	0.02	-
PuO_2	250-600	11.13	11.22	98	<30	0.02	0.03
	50-250	11.06	11.19	98	<70	0.01	0.02

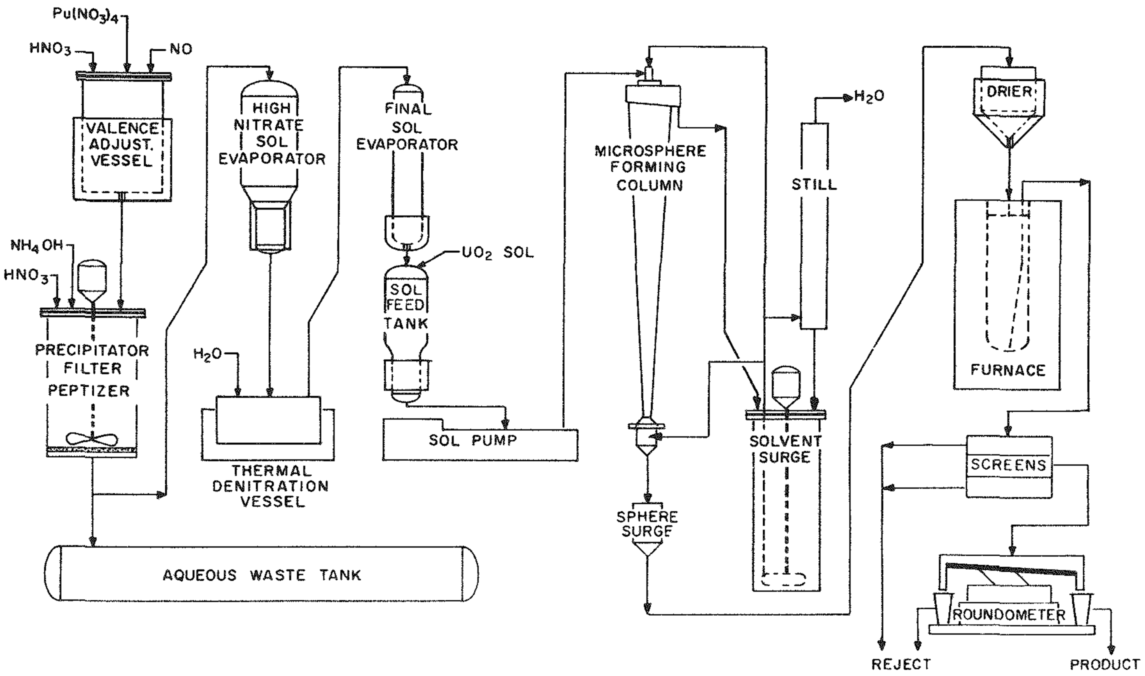


FIG.17. Schematic flow sheet of shielded sol preparation and microsphere forming equipment for PuO_2 and mixed oxide sols.

obtain mixtures, the sols are prepared separately and then blended to the desired proportions; thus, any Pu/Th or Pu/U atom ratio can be easily achieved. The PuO_2 and PuO_2—ThO_2 sols are formed into spheres using the procedure that is routinely used for ThO_2 spheres. Plutonia-urania mixtures, like urania, must be processed in an inert atmosphere. After firing, the microspheres may be handled in air, but prolonged exposure to moist air is not advisable because of a slight hygroscopicity of the fired spheres.

Microspheres containing PuO_2 are prepared using equipment and procedures similar to those developed for thoria microspheres. The primary differences were the use of glove boxes for containment and somewhat different surfactant requirements for optimum microsphere formation. The PuO_2 and PuO_2—ThO_2 sols were formed by using 0.3 to 0.5 vol % Ethomeen S/15 as the surfactant. The 20% PuO_2—UO_2 spheres are best formed using a surfactant system of 0.1 vol % Ethomeen S/15—0.4 vol % Span 80. Plutonia and ThO_2 sols and mixtures require no atmospheric protection, and the gel spheres are fired in air.

Some types of material, size ranges, and physical properties are shown in Table 4 for materials produced in the glove box facility. No significant differences were observed in the range 5-20% PuO_2—UO_2. Crushing resistance for the coarse material was about 1 kg/sphere.

A larger, shielded system for preparing PuO_2 and PuO_2—UO_2 microspheres has been fabricated and installed (Fig. 17). The design capacity is 1 kg of microspheres per day and 200 g of Pu (as PuO_2 sol) per day. The equipment is basically the same as that described earlier for PuO_2 sol preparation and microsphere forming.

Development of Dispersion Devices

Many column operating difficulties would be minimized if sol droplet sizes were absolutely uniform. A variety of sol dispersion devices have been tested to achieve this. Sol droplets can be formed by applying one or more forces, such as gravity, centrifugal field, shear, inertia, interfacial tension, and electrostatic repulsion. To obtain uniform droplet size and controlled diameters, both the force and the configuration of the sol (where the force is applied) must be uniform, and

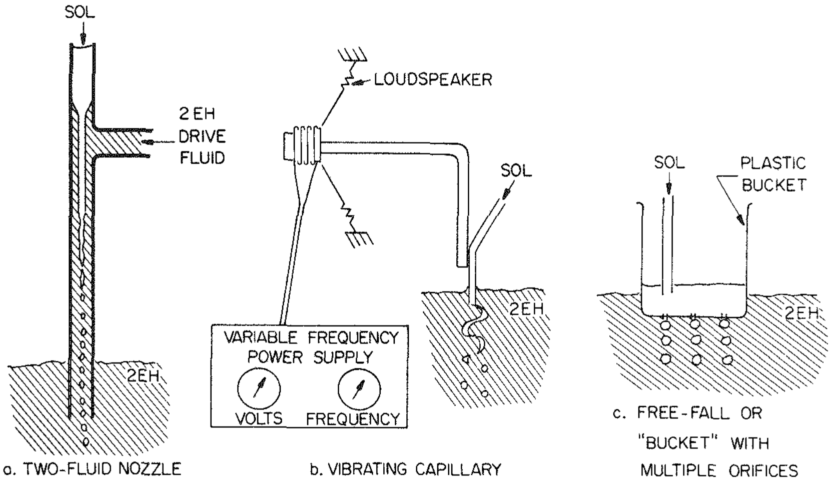


FIG.18. Devices for dispersing sol in gelling media.

Table 5. Sizes of Calcined Thoria Microspheres from Three Dispersers

Sol feed: 3 M ThO_2; diameters of sol droplets were 2.35 times those of theoretically dense ThO_2 product

	Two-Fluid Nozzles		Vibrating Capillaries			Free-Fall Drop Method
No. of feed capillaries	Single	Two	Single	Four	Four	19
Capillary diameter, μ	250	425	425	480	480	400
Sol feed rate, cc/min	1.2	9.9	1.2	19.2	9.6	9.6
Vibration frequency, cps	-	-	40	200	50	-
Predicted mean size, μ	270[a]	230[a]	330[b]	310[b]	390[b]	-
Amount of sample, g	540	10,200	-	314	720	480
Mesh[c] or diameter size of product, wt %:						
30/35 or 500-590 μ						97.9
35/40 or 420-500 μ					0.1	0.8
40/45 or 350-420 μ			0.2		61.9	1.1
45/50 or 297-350 μ	2.9	0.2	98.3	30.4	37.6	
50/60 or 250-297 μ	92.0	3.0	1.5	62.6	0.4	
60/70 or 210-250 μ	0	85.8		7.0		
-70 or <210 μ	5.3	10.9				

[a] Calculated from equation developed for two-fluid nozzle.

[b] From number of drops per cycle and flow rate.

[c] From use of U. S. Sieve Series screens.

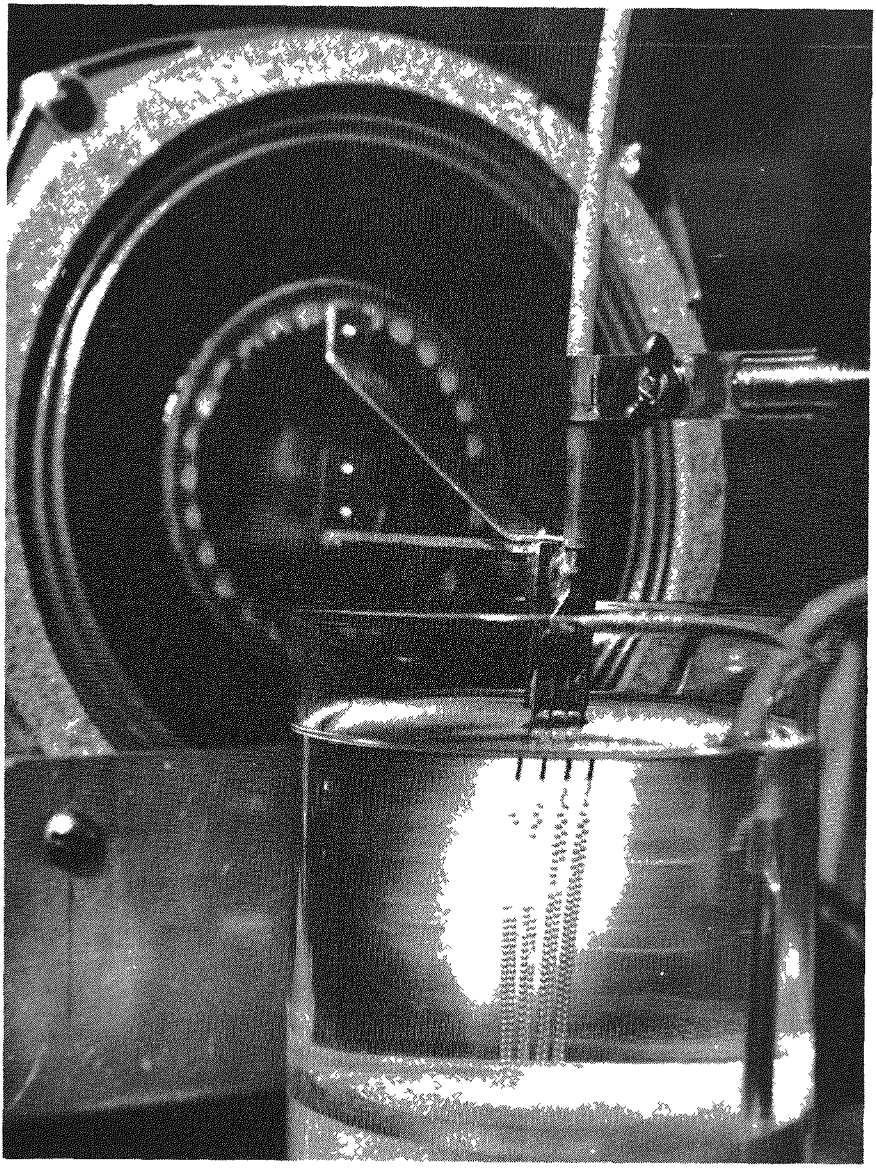


FIG. 19. Dispersion of a ThO_2 - 25% UO_2 sol by a vibrating capillary. Four capillaries are vibrated at 90 Hertz to form 950-μm-diam. droplets.

one or both of these factors must be controllable. For all dispersers tested, a uniform configuration is obtained by feeding the sol through orifices or capillaries that are 0.004 to 0.030 in. in diameter

Two-fluid nozzles (Fig 18) have been our most-used sol dispersion devices[16,17] They are reliable, give a very uniform product, and are easily controlled over a wide sol droplet size range (200 to 2000 μ). With single two-fluid nozzles, 90 wt % of the product consistently had diameters within ± 15% of the mean diameter (Table 5). The capacity of single two-fluid nozzles was unacceptably low for pilot plant operations. Therefore, multiple arrays of two-fluid nozzles arranged in parallel were tested; the sol and the 2EH were fed to their respective feed locations from single pumps. Two arrays tested consisted of 6 and 11 parallel two-fluid nozzles. The yields within ± 10% of the mean diameter for extended periods of operation were 70% for the 6-nozzle arrangement and 50% for the 11-nozzle arrangement.

Sol droplets formed from capillaries that are vibrated by an electrodynamic device (Fig. 19) are more uniform at optimum conditions than those from any other disperser. The best results are obtained with a continuous, approximately sinusoidal liquid stream that breaks at the midpoint position with respect to amplitude (Fig. 18). The amplitude for this type of operation varied from 1/4 in. at 20 Hertz to 1/32 in. at 200 Hertz and was obtained by 1.5 to 4.0-v inputs to commercial loudspeakers.

The free-fall drop mechanism and the relationship between droplet size, orifice size, and interfacial tension are well known. The use of plastic buckets with a large number of holes provides a practical capacity and avoids droplet size variations caused by variable wetting of the orifice by the sol. This disperser is useful for large drops only; the orifice sizes necessary to produce drops smaller than 1000 μ in diameter are too small to be practical. The interfacial tension between the sol and the 2EH depends on the amounts of surface-active agents present.

DRYING AND FIRING

Drying and firing of both microspheres and shards of gel are necessary to remove volatile constituents, to effect chemical reactions, and to sinter the particles to a high density. Both the temperature and the atmosphere are controlled while the gel is heated to the sintering temperature and then cooled to room temperature. Particles containing UO_2 or most carbides must be protected from oxygen. Cracking of particles, densification during sintering, and the amount of carbon and gases in the calcined product can vary greatly depending on the conditions used.

ThO_2 and ThO_2—UO_2

Thoria or thoria-urania fragments have been fired principally in standard muffle furnaces with time-controlled temperatures and atmospheres.[18] The dried gel is heated in air to 1150°C at a rate of 300°C/hr. The charge is held at 1150°C for 4 hr; if uranium is present, an Ar--4% H_2 atmosphere is used to reduce it to UO_2. A continuous, vertical tube, moving-bed calciner was also successfully operated with thoria—3% urania fragments. The temperature profile along the tube is carefully controlled so the moving charge undergoes the correct temperature-time program. The countercurrent flow of gas up the tube provides excellent utilization of hydrogen and helps maintain the required temperature profile. The moving-bed-type calciner appears to be practical for large production (≥ 50 kg day), while batch units appear more attractive for small-scale preparation.

The most efficient drying conditions for microspheres required superheated steam to final drying temperatures of 200°C.[1] The conditions in Table 6 were successfully used for firing gel microspheres in muffle furnaces. Argon—4% H_2 is used to avoid the explosive hazards of pure H_2. If hydrogen is present throughout cooldown, excessive amounts of it may be adsorbed.

Table 6. Conditions for Firing ThO_2, ThO_2—UO_3 and PuO_2 Microspheres

Temperature (°C)	Time	Atmospheres Used for: ThO_2 or PuO_2	ThO_2—UO_3
25	16 hr	-	-
25 to 100	300°C/hr	Air	Air
100 to 1150	300°C/hr	Air	Air
1150	4 hr	Air	Ar—4% H_2
1150 to <100	<500°C/hr	Air	Ar

UO_2 Drying and Firing

Drying and firing studies of sol-gel UO_2 have been made in a variety of atmospheres to establish conditions that will yield products having low carbon contents (<100 ppm) and near-theoretical densities (>95%). Products having the desired properties were obtained by drying and firing spheres to 1000°C in H_2O—0.2 vol % Ar. Final reduction was accomplished in Ar—4% H_2 for 2 to 4 hr. Other atmospheres tested included CO_2, Ar, Ar—4% H_2, and O_2; however, none of these gave results that were reproducible with respect to density and carbon removal when a variety of gel preparations were used. Differential thermal analysis (DTA), thermogravimetric analysis (TGA), and measurements of shrinkage rate, crystallite growth, and surface area were used as guides in studying the effect of gaseous atmospheres on sintering and carbon removal.[19,20,21] The source of the carbon is the drying solvent and surfactants used in the microsphere forming column. The sorbed organic materials must be removed prior to sintering to achieve a consistently high-density product. If these materials are not removed, they are often trapped within the pores, giving a product that has a high carbon content and a density less than 95% of theoretical.

The formic acid present in UO_2 sol (and also in the gel microspheres) is not difficult to remove. Analysis of shards prepared by evaporating UO_2 sols in argon and firing in Ar—4% H_2 showed that the final product contained <30 ppm of carbon and had a density 97 to 100% of theoretical. Comparison of TGA curves for shards and gel microspheres shows that formic acid is decomposed at 250 to 400°C.

Since the organic materials are very strongly sorbed, heating in an inert atmosphere or vacuum for prolonged periods is not sufficient. A gaseous atmosphere that can either oxidize the sorbed organic compounds to a more volatile species or displace them is needed. In an H_2O atmosphere the sorbed organic species are not removed below 450°C; for example, they were not completely removed after "soaking," with 5 to 10 g of H_2O (as gas) per gram of microspheres, for periods of 4 to 24 hr until a temperature of greater than 450°C was reached (Table 7). At any fixed tempera-

Table 7. Soaking of Gel Microspheres in Gaseous H_2O

Conditions: Heated to temperature at 100°C/hr after drying first in argon to 105°C for 4 to 24 hr; 10- to 50-g samples; flow rates linear

Temperature (°C)	Quantity of H_2O (g of H_2O/g of gel)	Net Carbon[a] (wt %)
110	3	2.9
110	18	2.7
210	5	1.0
350	5	0.6
450	10	0.1-0.02
850	10	0.001-0.005
1000	10	0.001-0.005

[a] Net carbon is defined as total carbon minus the formate carbon.

ture, the rate of removal became very slow (a few ppm per gram of steam) after about 3 g of H_2O per gram of gel microspheres had been used, and rapidly diminished thereafter. Experiments indicated that the removal of the sorbed organic species was more dependent on the total amount of steam used than on the steam flow rate.

The following heating schedule in H_2O (gas) was used to consistently produce a product having a uniform black color, a density of 95 to 99% of theoretical, a carbon content of <50 ppm, and an O/U atom ratio of <2.005.

(1) The gel spheres are dried in a flowing stream of H_2O vapor to 200°C at 50°C/hr and held for 4 to 6 hr; 10 to 15 g of H_2O per gram of gel spheres is used. The spheres are then heated to 1000°C at 300°C/hr, using 5 g of H_2O per gram of gel. Flow rates of about 300 scfh for steam and 0.7 scfh for argon are generally used in firing 50- to 100-g batches of UO_2.

(2) At 1000°C, the sample is reduced in a stream of Ar—4% H_2 (1 scfh) for 2 to 4 hr.

Studies are being made to determine the feasibility of shortening the firing schedule and decreasing the amount of steam. Preliminary results indicated that a temperature of 850°C may be sufficiently high to achieve near-theoretical density and low carbon content (<50 ppm). Tests indicate that 3 g of H_2O per gram of UO_2 in the temperature range 200 to 1000°C is not sufficient for obtaining a product that has the characteristics just mentioned. However, we believe that the quantity of H_2O, particularly in the firing region above 600°C, can be decreased substantially from the quantities listed in Table 7.

The effect of a variety of atmospheres and soaking conditions on the sintering of UO_{2+x} gels and the removal of carbon have been studied.[19–22] Differential thermal analysis (DTA), thermogravimetric analysis (TGA), and measurements of crystallite growth, shrinkage rate, and surface area showed that gaseous atmospheres of H_2O or CO_2 promote sintering in the region where the carbon-bearing volatiles are being removed. Carbon dioxide promotes a very rapid sintering of the UO_{2+x} gels, as is evidenced by: (1) DTA, which showed that the release of surface energy began at 400°C and rose to a sharp maximum at 500°C, (2) x-ray measurements, which showed rapid crystallite growth in this temperature region, and (3) surface area measurements, which showed a tenfold decrease in surface area. Thermogravimetric measurements indicated that either a very rapid surface oxidation of the UO_2 crystallites or a very strong surface adsorption of CO_2 was also occurring. The gain in sample weight during sintering in the CO_2 was found to be 0.25%. Thermogravimetric measurements also indicated that the carbon compounds were not removed by CO_2 at appreciable rates until a temperature of about 550°C was reached. With H_2O, however, the rate of sintering did not become significant until a temperature of 450°C was reached, and then it increased more slowly from 450 to 550°C than was observed with CO_2. Thermogravimetric measurements indicated that either a very rapid surface oxidation of the UO_2 crystallites or a strong surface adsorption of the H_2O was taking place. Carbon removal occurred at appreciable rates at 450 to 550°C. All these data strongly suggest that removal of the sorbed organic materials prior to sintering could be more easily accomplished with H_2O than with CO_2.

In Ar—4% H_2, sintering occurred over a higher and much broader temperature range (600 to 900°C); however, at these higher temperatures, hydrocarbons are decomposed, leaving free carbon within the gel, unless sufficient excess oxygen is present in the UO_{2+x} to react with the sorbed materials or their decomposition products. Thermogravimetric studies indicated that air could be employed to remove the carbon, by combustion of the sorbed organics at 150 to 200°C, with subsequent firing in argon to 1000 to 1200°C to give a product having a low carbon content. Since this type of reaction is highly exothermic, the rate must be controlled by limiting the quantities of the reactants (to prevent excessive temperature rises and oxidation of the UO_2). Studies of carbon removal and sintering are continuing.

PuO_2 Drying and Firing

During the past year the gel microsphere drying technique was modified to include steam drying at 95 to 105°C over a period of 4 to 5 hr to remove the residual drying solvent, and then continuing the flow of steam up to 150 to 170°C for 5 to 6 hours. Approximately 3 to 4 g of steam/g Pu was passed through the bed of microspheres. This technique results in microspheres of slightly higher density, and a process advantage is realized in that steam suppresses or eliminates the thermal excursion occasionally observed in drying deep beds of gel. To reduce microporosity in the finished microsphere, the firing technique was modified to include passing humidified air over the microsphere bed throughout the firing step.

LOW-ENERGY MICROSPHERE PACKING (SPHERE-PAC)

High-density microspheres of $(U,Pu)O_2$ are ideally suited for fuel rod fabrication by the Sphere-Pac process. We are developing the Sphere-Pac fabrication process to produce fuel rod loadings with smear densities in the range of 80 to 90% of theoretical.[3,23] The process involves pouring a large size-fraction of microspheres into the cladding tube and vibrating the tube to settle the poured bed, then infiltrating this bed with a fine size-fraction of microspheres. The bed of large size microspheres is restrained during addition of the small-size fraction.

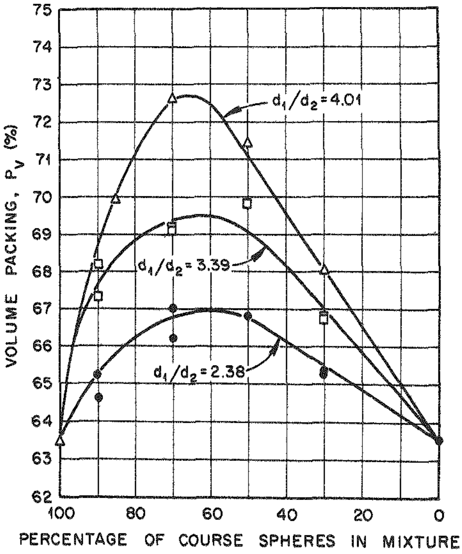


FIG.20. Volume packing of blended spheres of two sizes for various diameter ratios.

These studies yielded samples of about 85% of packing density for characterization and irradiation testing.

We are now attempting to form sphere beds in the higher density range (88% and higher) by blending two sizes of large spheres to form the initial poured bed prior to infiltration with the fine-size fraction. The blending studies are carried out by placing about 60 g of coarse and medium size spheres in a 3.5-cm-diam 120-cc bottle, rolling the bottle at 275 rpm for times up to 5 min, pouring the blended spheres into a 1.07-cm-ID graduated tube, and packing the unrestrained bed by vibrating for from 1 to 120 min. Blending is found to be complete after about 1 min, and the poured bed is fully settled after about 1 min of vibration. The conditions of vibration were 60 cps with about 7 g acceleration of the bed.

Figure 20 illustrates our results on blended bed volume packing (P_V) as a function of the volume percentage coarse and medium spheres for three sphere diameter ratios. These results agree well with those obtained by McGeary[24] and extend them to lower diameter ratios and smaller size spheres. The data obtained from the maximum density point (~65% coarse and 35% medium) on these curves may be used to calculate the efficiency (P_E) of the medium size spheres in filling the void available to them around the coarse spheres. In order to calculate this efficiency on a uniform basis, we assume an artificial packing efficiency for the coarse spheres of 63.5%. This is the limit for packing efficiency of a single size sphere in a large tube as presented by Ayer.[25]

Using this basis for the packing efficiency of smaller spheres in a packed bed of large spheres, the data in Fig. 21 was obtained. Some data from the work of McGeary and Ayer is also shown in this figure. The agreement is excellent for diameter ratios up to 8 or 10. Above this range, Ayer's work deviates significantly from our findings and those of McGeary.

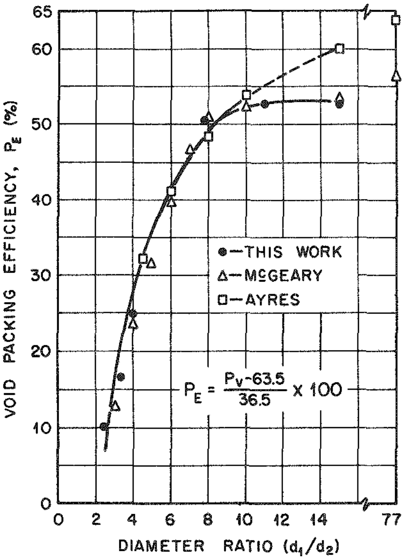


FIG.21. Packing efficiency of small spheres in a packed bed of large spheres.

Using this information on blended bed densities and packing efficiencies, we have developed a graphical construction which may be used to correlate and generalize all of our information relating to the Sphere-Pac fabrication procedure. This is shown in Fig. 22 where the horizontal axis represents the volume packing of spheres in a container or bed (packing efficiency) and the vertical axis represents the void volume associated with this volume packing. If a 45° operation line is established between the two zero points of the axes then the void volume associated with any packed volume may be determined by reading up and then across (line A-B-C). If we now construct a line joining the volume packing efficiency of a given size sphere (% of available void volume filled by spheres) to the void volume zero point, the horizontal distance between this line and the operation line is always proportional to the packing efficiency multiplied by the void volume associated with that packed bed density. Thus, the line A-D represents the packing of a single size sphere in a large tube or in a packed bed (according to Ayer) where the diameter of the sphere is less than approximately 1/25 that of the smallest sphere in the packed bed.

This curve may be used to illustrate the effect of serial infiltrations with spheres having d_1/d_2 greater than 25. We will obtain 63.5% packing with the coarse spheres. If we then infiltrate a small size sphere at this same efficiency, we obtain from point E an 87% dense bed, and a second infiltration produces a 95% dense bed. This type of line must also be plotted for the packing of spheres of varying diameter ratio with respect to the bed. These data are shown by the dotted lines for spheres of 1/4, 1/7, and 1/10 the size of the spheres in the bed, and are obtained from the plot of P_E vs d_1/d_2 (Fig. 21).

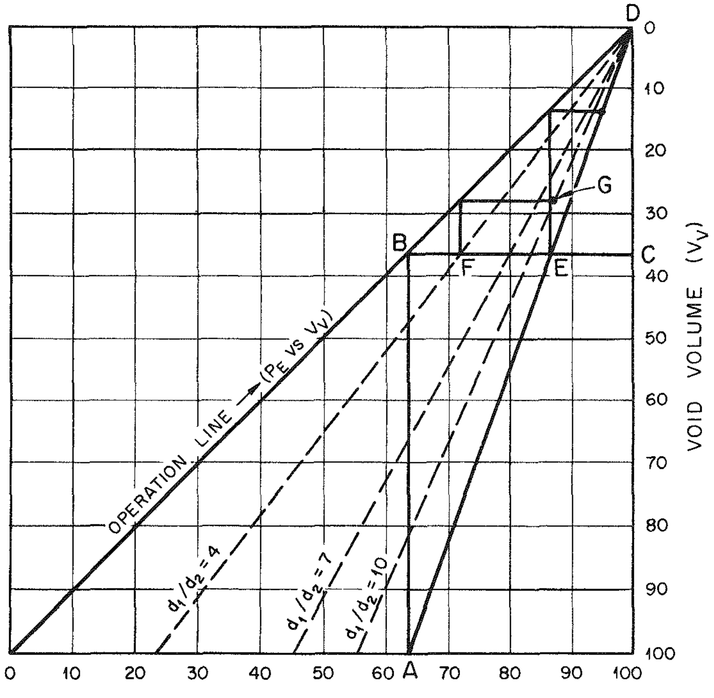


FIG.22. Analysis of sphere-pac beds.

We may now see the effects of using a blended bed, or the effect of infiltration at less than the optimum 63.5% packing efficiency. If a d_1/d_2 ratio of 4.0 is used for a blended bed, the bed density (volume packing) is increased to 72%, point F. Infiltration with spheres 1/10 the size of the medium fraction produces an 88% dense bed, point G. This is exactly the density which we have obtained and reproduced by this technique. We have also produced 86.5% dense beds by infiltration of a blended bed ($d_1/d_2 = 3.4$) with the 10/1 size ratio of medium to small. This is the density predicted by the graphical correlation for these conditions.

From the above discussion it may be seen that to produce a 90% dense fuel, we must use either a double infiltration with very carefully controlled sphere sizes or a blended bed at d_1/d_2 of about 5.8/1, followed by a single infiltration. This requires investigation of the behavior of beds blended at this diameter ratio. They tend to segregate.

The Sphere-Pac process is a promising technique for bulk oxide fuel fabrication over the range of 80 to 90% volume fuel loading. The use of blended beds to raise the fuel column to the 90% dense range is an attractive approach since it would eliminate the need for more than one infiltration step and be quicker and easier to control than a double infiltration approach.

Our experience with irradiation tests on Sphere-Pac fuels at this time is limited. We have examined twelve test rods fabricated by this process, all at relatively low burnup levels, with a maximum of 16,000 Mwd/tonne. One group of four rods with a peak burnup level of 40,000 Mwd/tonne has been removed from the reactor, but has not been examined. There are fourteen additional test rods in-reactor in uninstrumented tests and one 2-rod instrumented test. With the exception of the two rods discussed at Turin,[3] which failed during a power transient under severe overpower conditions (50 kw/ft), all rods have performed well. Based on the microstructures of the uninstrumented fuel rods and some preliminary in-reactor thermal conductivity measurements in the instrumented tests, it appears that the Sphere-Pac beds have in-reactor thermal conductivities essentially equivalent to pellet fuel rods with the same loading density. In-reactor fuel restructuring is also similar to pellets. The data are still too meager to report on relative fission gas release rates.

PREPARATION OF ThC_2 AND ThC_2–UC_2

The dicarbides of thorium and of thorium—3% uranium have been prepared by the sol-gel process. In this process, carbon-containing sols are prepared by dispersing carbon black in ThO_2 or ThO_2—3% UO_3 sol. Gel microspheres are formed from the final sol and are then converted to dicarbide microspheres by firing at 1800 to 2000°C. Thorium dicarbide microspheres with densities that are 91 to 93% of theoretical have been prepared by this method; the preparation of UC and ThC_2—20% UC_2 microspheres is in progress.

Extensive studies of the preparation of oxide-carbon sols have been made, since fluid, stable hydrosols containing the required amounts of carbon are essential to the process. In addition, an understanding of the interactions between the oxides and carbon in our presently used oxide-carbon sols will be useful in preparations of other sols of future interest such as PuO_2–C, UO_2–PuO_2–C, and UO_2–ZrO_2–C. Results to date have shown that the oxide crystallites in ThO_2, UO_2, or ThO_2–UO_3 sols disperse carbon aggregates by a strong interaction with them. This interaction results in very intimate association of the oxide and carbon, with the oxide acting as a protective colloid. The extent of adsorption of the oxide depends primarily on the relative surface areas of the oxides and the carbon. Some colloidal oxides do not show this strong type interaction.[1,3] For example, ZrO_2 and $Eu(OH)_3$ as currently prepared at ORNL, boehmite (AlOOH: duPont Baymal), and silica (duPont Ludox) do not. These colloidal oxides do not disperse carbon to the extent that the ThO_2, UO_2, or ThO_2–UO_3 sols do. Plutonia sols prepared at ORNL interact sufficiently to produce a mixed sol containing the amount of carbon required for carbide or nitride conversion.

Electron microscopic techniques, viscosity, electrophoretic and specific surface measurements are employed in studies of the oxide-carbon interactions.

Urania and ThO_2–UO_3 sol behaviors are virtually identical to that of thoria sol. The extent to which carbon was dispersed by all of these sols was dependent upon the relative surface area of the oxide and carbon and was demonstrated by viscometric titration.

Stable, fluid sols containing carbon in sufficient quantity to produce mono- or dicarbides or to produce porous oxides could be prepared from the UO_2, ThO_2, or ThO_2–UO_3 sols produced at ORNL. The amounts of dispersed carbon required to produce monocarbides and dicarbides from these oxides are 3 and 4 moles of C per mole of oxide, respectively. The amount of carbon required to produce porous oxides over the range of 10 to 60% porosity is 0.5 to 6 moles C per mole of oxide.

The most important variables in the sol-gel method of preparation of ThC_2 are the firing conditions during conversion, and control of the carbon content in the ThO_2–C gel. To obtain densities >90% of the theoretical density of ThC_2 (9.6 g/cc), the conversion must be effected under a controlled CO overpressure at temperatures where a critical balance among rate of chemical conversions, grain growth, and sintering is maintained. If porous carbides are the desired product, the reactions are carried out under vacuum. Product densities of 91 to 93% are obtained when the reaction is carried out at a controlled rate under argon until nearly complete, and then vacuum is applied to complete the reaction. The argon sweep gas contained about 4000 ppm CO, which was maintained by controlled diffusion out of the sample crucible. An infrared inline CO analyzer (Beckman Model 315) was used to monitor the progress of the reactions. This conversion technique also produced $(Th_{0.78}, U_{0.22})C_2$ and UC microspheres that were 90–93% of theoretical density in a few demonstration runs.

Control of the carbon-to-metal oxide mole ratio in the gel starting material is most important for good conversion and attainment of high density. When the initial carbon-to-ThO_2 mole ratio was too low, objectionable amounts of monocarbide were formed; when it was too high, a highly porous product was obtained. Excess carbon contents of 0.50 to 2.58% in ThC_2 resulted in highly porous products. A mole ratio of carbon-to-oxide of 3.9 to 4.0 appears optimum for preparing dense ThC_2. In practice, the carbon-to-metal oxide ratio must be adjusted empirically. This adjustment is necessary because of pickup of additional carbon by the sorption of the carbon-bearing organic materials in the sphere-forming process, and because of the reaction of carbon with the nitric acid during firing of the gel. A few attempts were made to remove the additional carbon imbibed during sphere formation by oxidizing it with air on a recording thermogravimetric balance where the rate of reaction could be carefully monitored; however, the degree of oxidation was found to be difficult to control. We have not yet tried removing the sorbed organic material by treating with steam to 600°C; this is a method found to be effective for organics from UO_2 gel spheres.

A few experiments on the conversion of ThO_2–UO_3–C gel spheres to $(Th_{0.78}, U_{0.22})C_2$ spheres gave very encouraging results (Table 8). The products were solid solutions of the monoclinic ThC_2 structure with slightly contracted parameters due to the uranium content. A reaction temperature of 1900°C was sufficient for complete reaction, whereas approximately 2000°C was necessary for ThC_2. The presence of the uranium permits conversion at a lower temperature and also seems to promote a desirable sintering pattern. Densities were 76 to 94% of the theoretical value, depending on the original carbon content. Even at the higher porosities, the spheres had a uniform cross section and the pores were approximately 1 μ in diameter. Preliminary results equally as encouraging as those obtained in preparing $(Th, U)C_2$ were obtained on converting UO_2–C gel spheres to UC and UC–UN microspheres.

Table 8. Analyses of $(Th_{0.78}U_{0.22})C_2$ Microspheres
(Conversions in argon at 1900°C)

	Run Number		
	IV-82	IV-84	IV-86
Carbon-to-metal mole ratio of reactants:			
Desired	3.90	3.95	4.00
By analysis	4.00	4.06	4.15
Composition of product			
% Thorium	70.3	69.7	69.4
% Uranium	20.4	20.2	20.0
% Carbon	8.87	9.02	9.37
% Oxygen	0.081	0.127	0.173
Material balance (Σ of above)	99.65	99.05	98.94
% Free carbon	0.097	0.264	0.146
Mercury density of product, g/cm^3			
1 atm	9.45	8.92	7.75
10,000 psi	9.56	9.09	8.65

PREPARATION OF POROUS OXIDES

We have shown that ThO_2 microspheres or shards of controlled porosity can be prepared from ThO_2–C gels by volatilizing the carbon by air oxidation after the oxide structure has been preset by firing to 1400°C in argon.[1,13,26] The amount of porosity could be controlled by varying the amount of carbon; the volume of porosity introduced was nearly equal to the volume of carbon added. In subsequent work, the technical feasibility of preparing porous ThO_2–UO_2 and UO_2 by this same approach was demonstrated. For the ThO_2–UO_2 preparations, ThO_2–UO_3–C gels were employed and air oxidation was used to volatilize the carbon. However, in the porous UO_2 preparations, CO_2 or H_2O was the preferred reactant for removing the carbon because air caused too much oxidation of the UO_2.

Experiments on preparation of 60% porous ThO_2–22% UO_2 indicated that higher porosities were obtained with ThO_2–UO_3–C gel shards than would have been expected by analogy with ThO_2–C gel shards of the same oxide to carbon ratio. The amount of carbon which produced 47% porosity in ThO_2 produced 59% porosity in ThO_2–UO_2. Also, the pore sizes in the ThO_2–UO_2 were 400 to 800 A in diameter, whereas the size was about 400 A in the ThO_2.

In our attempts to prepare porous UO_2 in a way that prevented excessive air oxidation of the UO_2, two methods for removing carbon from the prefired UO_2–C have been tested: the reaction $H_2O + C \rightleftharpoons CO + H_2$ and the Boudouard reaction ($CO_2 + C \rightleftharpoons 2CO$). Both require a temperature of about 1000°C to remove the carbon at a practical rate. Technical feasibility of porous UO_2 preparation by this approach was demonstrated by removing carbon from a gel sample of shards containing 6 moles of carbon per mole of urania. Although in these experiments only 80% of the original carbon was reacted, a 48 vol % porous product was produced.

PREPARATION OF UN AND UN–UC MIXTURES

Initial studies of the preparation of UN microspheres from UO_2–C gel microspheres were promising.[27] In the preliminary experiments, UO_2–C gel microspheres having a C/UO_2 mole ratio of 2.8 were converted to $UN_{0.92}C_{0.13}$ by firing the UO_2–C gel in nitrogen to 1600°C. The density of the final product was 13.7 g/cc. It is expected that conversion to the nitride will improve with adjustment of the C/UO_2 mole ratio to the proper value and with optimization of the firing schedule.

The sol-gel approach for preparing nitride microspheres consists in dispersing high-surface-area carbon back in a UO_2 sol, forming gel microspheres by dispersing droplets of the sol in 2-ethyl-1-hexanol, and then converting the microspheres to nitride by firing to a high temperature. There are two possible approaches to conversion of the UO_2–C gel to UN: (1) The spheres are heated in a stream of nitrogen to form a nitride according to the following reaction:

$$UO_2 + 2C + 1/2N_2 \rightarrow UN + 2CO$$

(2) The monocarbide is formed first; it is then reacted with nitrogen according to the following reactions:

$$UO_2 + 3C \rightarrow UC + 2CO$$

$$UC + 1/2N_2 \rightarrow UN + C$$

The second method leads to the presence of free carbon in the UN product. In one preliminary test in which conversion was accomplished by the second method at 1600°C, carbon could not be removed from the $UN_{0.81}C_{0.40}O_{0.24}$ product with hydrogen at 1000°C without destruction of the microspheres. The hydrogen treatment caused the spheres to crumble to powder. It is apparent that with either method careful control of the C/U and the C/O atom ratios must be exercised to achieve a relatively pure UN product that is free of carbon and oxide impurities. Actually, UO_2 sols are UO_{2+x} sols, where x may vary from 0.15 to 0.25; this must be taken into account when the amount of carbon required for the reaction is calculated.

Test conversions were made of UO_2–C gel microspheres having a C/UO_2 ratio of 2.3. A UO_2–C sol was prepared by dispersing Spheron 9 carbon black (BET surface area = 105 m^2/g) into a UO_2 sol, by means of an ultrasonic generator probe, while the sol was cooled by an ice bath. The required weight of carbon (2.3 moles per mole of U) was added to a 0.83 M UO_2 sol, and the resultant sol was diluted with water to a UO_2 concentration of approximately 0.55. The UO_2–C sol was formed into gel microspheres in a sphere forming column, using 94.5 vol % 2-ethyl-1-hexanol —5 vol % 2-octanol and 0.5% Amine "O"; the spheres were dried in argon at 120°C for 16 hr.

Attempts to convert the UO_2–C gel microspheres to nitride by heating at 1600°C for 2 hr in a stream of nitrogen were unsuccessful as a result of the formation of an impervious nitride coating on the spheres. This thin, mirror-like coating of UN impeded the entry of nitrogen. It was found, however, that the coating could be made permeable to nitrogen by cooling in nitrogen to 950°C and then reheating to 1600°C. Presumably, $UN_{1.6}$ formed, then decomposed on reheating to make the coating permeable. By starting with UO_2–C gel microspheres containing exactly enough carbon to remove all of the oxygen as CO, it should be possible to prepare essentially pure UN.

SOME PROPERTIES OF LANTHANIDE OXIDE SOLS PREPARED BY SOL-GEL METHODS

Lanthanide sols were prepared by precipitating the hydroxides from lanthanide nitrate solutions with ammonium hydroxide, washing the precipitates thoroughly, and heating them for 1 hr at 80°C. These sols were concentrated by evaporation until they were 2 to 3 M in the metal ion and contained 0.06 to 0.25 mole of residual nitrate per mole of metal ion.

Spectroscopic methods were used to determine the nitrate and metal ion concentrations in the sols, to study the form of bonding of the components (e.g., nitrate) of the sols and gels, and to estimate the sizes of the aggregates of colloidal particles. Electron microscopy and electron diffraction and x-ray analyses showed that the initial precipitates of lanthanide hydroxides consisted of amorphous particles of 30 to 60 A in diameter. When aged in water, these particles changed into rods or tubes, up to several thousand angstroms in length. In the periodic arrangement of the lanthanide elements, the trends of decreasing ionic radii and basicity with increasing atomic number are well known; similar trends are expected for the actinides. The results of the studies on the sol-gel preparations reflect these systematic changes. It has been found that the lanthanides can be divided into two groups on the basis of their crystallization behavior; namely, the time required for crystallization, and the crystalline structure or form obtained. The first group would consist of the elements lanthanum through dysprosium. It is characterized by shorter crystallizing times and needle or rod-like crystalline structures that range up to 7000 A in length and several hundred angstroms in width. The remaining lanthanide elements fall into the second group; they have much longer crystallizing times and form predominately sheets that are up to 7000 A on each side. In each group the crystallizing time and size of the crystalline forms increase as the ionic radii of the elements decrease.

The development of a sol-gel process for preparing dense Am-Cm oxides for incorporation into targets for the High Flux Isotope Reactor is continuing. Preliminary and process feasibility demonstrations have been made.[28]

To date, ^{241}Am and mixed ^{243}Am–^{244}Cm sols, gels, and oxide microspheres have been prepared by the standard lanthanide sol-gel procedure[6] or a slight modification of it. The first procedure utilizes centrifuging to accomplish washing, whereas the modified procedure uses a sintered-glass filter. The essential advantage of the latter is that it eliminates solids handling.

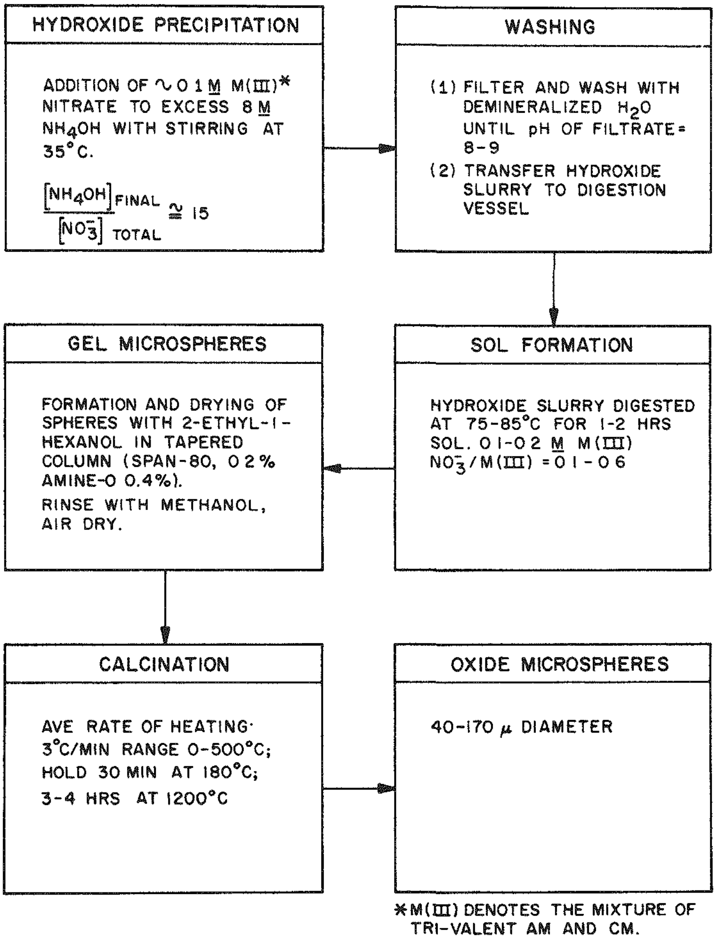


FIG.23. Preparation of ^{243}Am-^{244}Cm sols, gels, and oxide microspheres.

Americium-241 sols have been prepared by both centrifugal and filtration methods. The sols are orange-brown in color, translucent, iridescent, and stable, exhibiting no sediment for as long as six weeks, and are capable of being concentrated to nearly 2 M.[28] Americium hydroxide shows no tendency to peptize during extensive washing; however, if a washed hydroxide is allowed to stand for a day or two, it will spontaneously convert to a sol.

Americium hydroxide sols with americium concentrations as low as 0.36 M have been formed into nearly perfect spheres of uniform size. The gel spheres were calcined at 1175°C to give stable, strong, dense oxide microspheres.

An ^{243}Am–^{244}Cm sol (20% ^{243}Am) has been prepared by the centrifuge technique; however, we have now developed a process based on filtration and washing which produces sol suitable for forming into microspheres. This process is shown in Fig. 23. With the actinide elements americium and curium, needle or rod-like structures are obtained, and the diffraction patterns are isomorphous with the first group of lanthanides.

ACKNOWLEDGEMENT

A summary paper of this kind is necessarily based on the work of a great many individuals working together as a team. Most of the direct contributors are represented in the references. Perhaps the best way to acknowledge all those whose work this paper summarizes is to thank those people in the Chemical Technology, Metals and Ceramics, and Analytical Chemistry Divisions who make up the Oak Ridge National Laboratory team working on sol-gel processes.

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SUMMARY

SUMMARY OF THE PANEL

1. INTRODUCTION

Sol-gel processes are being actively developed for the economic production of reactor fuel materials in a large number of countries. The processes combine well-known principles of solution chemistry and colloid chemistry to prepare materials of closely-controlled composition, shape and size, and are well suited to the aqueous reprocessing techniques used at present.

The bulk of the published work on sol-gel processes for ceramic fuels is on pure and mixed oxides and carbides of thorium, uranium and plutonium, but the processes are also suitable for the preparation of other ceramic and non-ceramic materials. A variety of processes has been developed in the laboratory and a few of these have progressed to the pilot-plant stage. Irradiation experiments on several types of fuel, and economic evaluations of the processes, have been started and some results are available.

This Panel on Sol-Gel Processes was convened to review the state of the art and to make recommendations to the IAEA on its future policy in this field.

2. THE NATURE OF SOL-GEL PROCESSES

In the wide range of sol-gel processes colloid chemistry is used as a general principle in some way. A fundamental step is the formation of a gel of controlled composition, shape and size. This has been achieved in two main ways, either directly from a salt solution or by first forming a sol. Both sol and gel forms consist of sub-micron colloidal particles dispersed in a liquid medium, the sol retaining the properties of a liquid, the gel having properties approaching those of a solid. The existence of the material in the form of a gel leads to advantages in subsequent densification, because of the high reactivity and the homogeneous distribution of the ultimate colloidal particles and of pores.

3. POSSIBLE USES OF PRODUCTS OF SOL-GEL PROCESSES

The ability of these processes to produce spheres of closely controlled composition and size is of great interest in the development of coated-particle fuels for high-temperature gas-cooled reactors, of vibrocompacted fuels for thermal and fast reactors, and of particles dispersed in suspension reactors. On the other hand, the possibility of obtaining sol-gel products in an extruded form, and in the form of irregularly shaped particles suitable for making pellets and for vibrocompaction, is of interest for present-generation thermal or future fast reactors.

4. STATE OF THE ART

Much information has recently been published on the development of detailed process flow sheets and equipment, on supporting background research, on properties and irradiation behaviour of products, and on preliminary cost estimates.

The most extensive work has been on processes for thoria and thoria-urania. This has led to the continuous operation of pilot plants for periods of months with a capacity of up to 25 kg/day for thoria-urania and up to 100 g of fissile element/day for pure and mixed plutonia and enriched urania. One tonne of ThO_2-U(233)O_2 fuel has been prepared in a heavily shielded semi-remote plant, and fabricated into fuel rods by vibrocompaction.

Supporting background research has been done to a limited extent in the past and its importance is becoming increasingly recognized for the better understanding and improvement of the processes. Most of the work has been done on thoria, and satisfactory models are available for the structure and properties of sols and gels of thoria and for their conversion into dense oxide. It is expected that these will form a basis for the understanding of other systems.

There has been extensive characterization before irradiation and a small amount of work has been reported on irradiated products. Vibrocompacted thoria-4.5% urania fuel has shown satisfactory behaviour after irradiation to 125 000 MWd/tonne metal, and urania particles coated with pyrolytic carbon were taken to 50% fima without failure. An extensive program of irradiation in thermal and fast neutron fluxes is planned by a number of countries on fuels containing oxides and carbides of thorium, uranium and plutonium.

It appears that sol-gel processes may have significant technical advantages, but only preliminary cost estimates have been published so far, and it has not yet been possible to compare them directly with conventional processes for a given reactor fuel.

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