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INTERNAL GELATION FOR OXIDE AND NITRIDE PARTICLES

July 1996

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Japan Atomic Energy Research Institute

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In the fabrication of fuel containing TRU elements, flow sheets and techniques which allow a shielded and/or remote fabrication are needed. One approach, which has been proven on the laboratory- and on semiprototype scale, is the fabrication route of coprecipitation of the matrix element uranium mixed with plutonium to form spherical particles. The so-called Internal Gelation offers a simplified production route with reduced processing stages compared to the classical powder route. The individual steps (precipitation, removal of reaction products and drying) can be readily adapted for remote operation with low maintenance demand (absence of mechanical powder treatment, dust-free operation) and good operative production.

The produced ceramics holds the TRU elements homogeneously distributed in the matrix. The method has been developed for uranium as matrix element, but recently aluminium and zirconium are seen as new and interesting matrix elements to be utilized for the fabrication of new types of nuclear fuel.

The fabrication technology for the preparation of the solutions, droplets and spherical particles is briefly discussed.

This paper is a review on research activity of a foreign researcher for the JAERI inviting program during February and March, 1995.

Keywords : Uranium Plutonium Oxide, Uranium Plutonium Nitride, Internal Gelation

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内部ゲル化法による酸化物・窒化物粒子燃料の製造

日本原子力研究所東海研究所燃料研究部

Guido LEDERGERBER*

(1996年7月1日受理)

TRU元素を含む燃料の製造には、放射能に対する遮蔽のある施設において、遠隔操作による工程や技術が必要とされる。研究室規模または半実用規模の製造では、すでに確立している一つの方法に、ウラン-プルトニウム混合物の共沈による湿式の粒子製造法がある。内部ゲル化法と呼ばれるこの方法は、従来の粉末による製造法と較べて、工程が簡略化され、沈澱ゲル化、反応不用生成物の除去、乾燥といった各工程は、機械的な粉末の取扱いがないダストフリーの操作のために最少限度の設備ですみ、遠隔操作も容易になる。

出来上がった焼結体は、TRU元素がマトリックスに均一に分布した状態になっている。本来、この方法はウランをマトリックスとして開発されたが、最近では、アルミニウムやジルコニウム等をマトリックスとした注目の新型燃料にも適用しうる。

他に、供給液の調製とゲル化による粒子形成などの関連技術についても、簡単に述べた。

なお、本報は1995年2月から3月の間、原研の招へい研究員として滞在した研究報告書である。

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1 Introduction

The wet route fabrication of nuclear fuel has a long history. Arising partly out of developments in the field of HTR fuel kernels has been seen as an alternative process to the standard powder technology. It has the advantage of being entirely "wet", and thus of avoiding the hazards of the fine powders and dust of the conventional methods. A comparison of different routes for mixed oxide fuel fabrication is shown in Figure 1. Even more important are the process advantages in a fabrication of nitride as compiled by Blank in Figure 2.

Nitride particles of the actinides (U,Np,Pu,Am)N are of interest in the partitioning and transmutation system utilizing the helium cooled particle Actinide-Burner-Reactor (P-ABR)[1] and the lead cooled sphere-pac pins with reprocessing the nitride after reaching high burn-up in a pyrochemical process with molten-salt electrorefining proposed by Takano[2]. For the fabrication of the nitride the Internal Gelation process was proposed by Suzuki[3].

Coated plutonium oxide particles with an inert matrix and embedded in a pebble was proposed for burning weapon grade plutonium in a HTR with graphite moderation[4]. For the preparation of those particles the process could be well adapted. Especially, if a matrix like alumina or zirconia would be used to hold the plutonium oxide, these elements could be co-processed with the plutonium.

(U,Pu,Np)-oxide spheres of two sizes may be directly filled in a cladding tube as a reactor pin instead of the standard pelletized fuel. Such fuel pin so-called sphere-pac offers many advantages in the processing, and shows an irradiation behavior quite similar to the classical design. The sphere-pac concept has been tested for LWR oxide fuel and for FR(Fast reactor) carbide fuel by PSI in collaboration with fuel vendors and research laboratories.

The processes are generally titled "Sol-Gel Process". This name is appropriate for the water extraction method[5] and the external gelation of uranium[6], but is not for the internal gelation process. This process does not involve the preparation of sols in the sense of a colloid being suspended in a liquid. Pure newtonian solutions are transferred into a gelatinous solid materials, in which the precipitates are formed. All gelation processes have the unique feature in producing microspheres of well adjusted sizes which again give major advantages in processing e.g. in the coating of the particles or in the utilization as fuel in the sphere-pac pin design for LWR and FR. The sphere-pac pin means in the strict sense of the words that spherical particles in two or three sizes are packed directly in a cladding tube instead of the well known pellet. The processes are in general also suited for coprocessing different metals together with a matrix element mostly Uranium or Thorium, but others are anticipated like Aluminum and Zirconium.

2 The Internal Gelation Process

2.1 The Basic Chemistry for Uranium

The internal gelation process was first developed and described for the production of nuclear fuels in the form of microspheres at KEMA by van der Bruggen et al. in 1970 [9] and Kanij et al. (Keuring van Electrotechnische Materialen at Arhem in the Netherland) in

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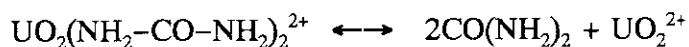
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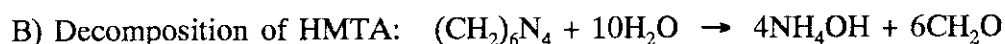
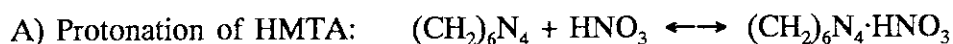
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1974[10]. The process bases on the precipitation and thermal decomposition of ammonium-di-uranate (ADU). The precipitation is achieved by the thermal acceleration of the acid (NO_3^-) catalyzed decomposition of hexamethylenetetramine (HMTA) and hence formation of ammonia. Detailed examinations showed the formation of an amorphous gel in a heated droplet of concentrated stoichiometric or acid-deficient uranyl nitrate hexahydrate (UNH) solution during the initial stage of the process and a subsequent formation of a crystal structure of distinct compounds of ADU[11]. Urea is added to the UNH solution to complex the uranyl ions and to prevent the formation of a weaker complex with HMTA, which would precipitate in the feed solution prior to anticipated precipitation in the gel during the solidification of the formed droplets. According to the following equation:

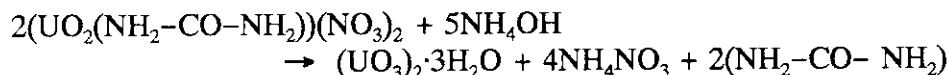
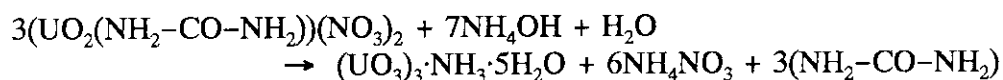


In a second function it has been shown by Collins[12] that urea promotes the deprotonation of HMTA, which seems to be the key reaction for the whole process. The reactions involved are the following:



The uranyl ion precipitates by hydrolysis: $\text{UO}_2^{2+} + 2\text{H}_2\text{O} \longleftrightarrow \text{UO}_2(\text{OH})_2 + 2\text{H}^+$

In the precipitation during gelation, and subsequent washing are as follows:



During ageing at elevated temperature in the gelation medium and successive washing step in ammonia solution, the crystallites are growing. Large crystals will give a porous structure which allows the volatile reaction products to escape during the drying and calcination step. Hence such a structure prevents from cracking. The region of gelation for the uranium system depending on the parameters of the gelation have been evaluated by Baran[13] and Urbanek [14]. Very high concentrations of HMTA for the uranium and the uranium-plutonium system have been applied by Förthmann in the so-called H-Process[16].

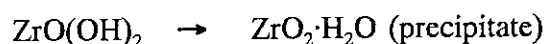
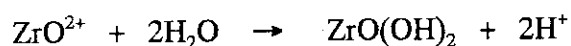
2.2 Gelation of Uranium and Plutonium

If uranium and plutonium are coprecipitated from a mixed nitrate solution, the acidic conditions are to be adjusted either by nitrate extraction, and mixing of acid deficient metal solutions of the two components uranium and plutonium or by pre-neutralization with ammonia hydroxide solution. The addition of ammonia hydroxide does not cause any problems, since pre-neutralization of the free acid is only needed and no precipitates should occur. Plutonium precipitates in the gelation step as the so-called plutonium polymer. This special form of the plutonium oxide was identified and characterized by Lloyd[15]. The very

fine crystals are intimately dispersed in the more open structure of the ADU crystallite structure[11]. The depolymerization rate, as defined by Lloyd, of the plutonium precipitates formed by the internal gelation depends on the ratio uranium to plutonium. Slower depolymerization rates for the polymer is formed at low plutonium contents which indicates more crystalline primary particles rather than formation of extensive polymerization.

2.3 Gelation of Zirconium

According to Baes and Mesmer [17] the hydrolysis of zirconyl ions shows similarities with uranyl ions, i.e., the hydrolysis occurs in strongly acidic solutions ($>0.1\text{M}$) and is dominated by the formation of one or more polymeric species. These characteristics are essential to expect a good gelation and a homogeneous distribution of the metal precipitates and the carbon black.



The mononuclear species of these ions are dominant only at very low metal concentrations. The principal species formed by reversible hydrolysis at concentrations of acid greater than several tenths molar are polynuclear $\text{Zr}_4(\text{OH})_8^{8+}$ along with $\text{Zr}_3(\text{OH})_4^{8+}$ and/or $\text{Zr}_3(\text{OH})_5^{7+}$. At lower acidities, a slow irreversible hydrolysis appears, which is accompanied by an increase in polymerization and perhaps a change in structure from OH^- to O^+ bridging. The distribution of hydrolyzed products at solutions saturated with ZrO_2 respectively for uranium can be compared in Figure 3. The similarities are obvious, and the good gelation behavior of zirconium makes this element to be a prime candidate as inert matrix which carries actinides for their transmutation.

2.4 Gelation of Americium

Americium precipitates as an amorphous hydrous gel, when ammonia is added. The precipitates consist of small particles about 2 nm in diameter[18]. The different behaviour in the precipitation of americium compared to uranium and plutonium will not allow a direct coprecipitation, but during the washing step with ammonium hydroxide solution, americium precipitates in the pore structure of the ammonia-di-uranates and the plutonium oxides. The behaviour of americium in a zirconium gel needs to be investigated.

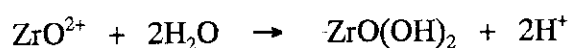
3 Fabrication of Microspheres

As an example, a flow sheet for the preparation of nitride particles is given in Figure 4. The flow sheet consists of three main process parts; a) preparation and adjustment of solutions, b) conversion of nitrate solutions into oxides, and c) thermal treatment with the first step yielding a dry product, which is seen as an intermediate product. Calcination and sintering might be followed depending on the anticipated product. Similar conditions are applicable to the fabrication of uranium-plutonium oxide, where the detailed conditions are

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to be altered depending on the utilization of the particles. The equipment used by PSI for the fabrication of significant quantities of microspheres on a semi automated equipment is given in Figure 5.

3.1 Solution Preparation

3.1.1 Uranium Nitrate Solution

A) Uranium-tri-oxide is dissolved in boiling nitric acid to a substoichiometric, highly concentrated uranyl nitrate solution with concentrations in a range of 1.4 to 1.8 mol/kg uranium and a nitrate to metal ratio in the range of 1.5–1.9 mol/mol. The highest concentration is reached at a nitrate to uranium ratio of 1.6 mol/mol. Data for uranyl nitrate solutions are given by Haas[19] and Botts[20].

B) Uranium nitrate solution from a reprocessing plant is concentrated to the appropriate concentration by a vacuum distillation and adjusted with ammonium hydroxide solution as given in [12].

3.1.2 Plutonium Nitrate Solution

Diluted plutonium nitrate solution is concentrated in a vacuum distillation at about 20 mbar to a concentration of about 1.8 mol/kg and adjusted with water to easy treatable solution of about 1.2–1.3 mol/kg with a nitrate to metal ratio 3.9 to 4.3. Plutonium polymer formation was not encountered in all the solutions prepared for the carbide fabrication for the AC-3/FFTF experiment[22]. Vacuum distillation is also seen as nitrate removal step. Thin layer distillation at reduced pressure might be the appropriate technique to be used for the concentration step in a up-scaled fabrication.

3.1.3 Zirconium Nitrate Solution

Zirconium nitrate solution is prepared from zirconyl nitrate. The salt is dissolved in water or nitric acid of low concentration. The concentration limits and amount of precipitates occurring in the dissolution of the $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ have been determined by Shiratori[21]. As shown in Figure 6, it was found that the maximal concentration of the solution was reached with 1.8 mol/kg zirconium in pure water or 0.5 mol/kg nitric acid, while for practical reasons a concentration of 1.56 mol/kg zirconium was chosen.

3.1.4 HMTA-Urea Solution

A) *for oxides*: HMTA (hexamethylenetetramine) and urea according to their mol ratio in the feed solution are dissolved in water close to their solubility limits (typical values are given in Figure 4).

B) *with carbon for carbides and nitrides*: A stock solution of water, HMTA, urea and surfactant similar to a solution for oxides is prepared. The surfactant prevents the later dispersed carbon black from coagulation during the intermediate storage time prior to the gelation of the mixed feed solution. High purity carbon black with a low sulphur content and a surface area in the order of 130 m²/g gave good results.

3.1.5 Mixed Feed Solution

The solution has to be prepared just prior to the formation of the droplets. Nevertheless the solution has a shelf-life of two to three hours, if cooled at 0°C. In the laboratory scale, the HMTA-urea solution is precooled to 0°C and the metal solution held at room temperature is added. Continuous mixing without cooling in a static mixer has been applied for uranium gelation at JAERI. For the fabrication of nitrides, the ratio of the two solutions needs to be accurately measured, since the carbon to metal ratio, one parameter for the carbothermic reduction, is determined in this way.

3.2 Drop Formation

Depending on the size of the drops to be formed, different techniques are required[32]. In laboratory scale, large droplets might be formed from the tip of a needle. The outer needle diameter determines the size of the drop falling by gravity force. For breaking up a liquid jet of feed solution, a laminar flow in the nozzle is most favourable. The arrangement of nozzle and gelation medium is given in Figure 7 for spheres with diameter of 0.15 to 0.6 mm, and arrangement for the smaller droplets in the range of 0.03 to 0.20 mm is shown in Figure 8. In the case of gelation by microwaves instead of the hot oil, the droplet might be formed in the cavity.

3.3 Gelation

The gelation is accelerated at higher temperature, where the heating rate has an influence on the formation of the gel and the precipitation of either an amorphous structured hydroxide or clearly defined crystalline compounds. The application of heat on to the formed droplets may be accomplished by a hot liquid as heat carrier or microwave radiation.

A) *heat carrier*: For the pure uranium system a low temperature gelation in trichloroethylene has been applied by Haas[19] for spheres in the range of 0.3 to 1.2 mm, where small spheres (>40 µm) were gelled in 2-ethyl-hexanol which supports the gelation by water extraction and allows a combination of the two gelation processes.

The fast gelation anticipated by Förthmann[16] requires temperatures in the order of 100°C. He proposed a paraffin oil. In PSI we apply a silicon oil with adjusted viscosity, which has favourite properties as far as fire protection and ability to be recirculated is concerned. For a fast gelation temperature up to 110°C can be reached.

B) *microwave gelation*: Microwaves serve today as electromagnetic waves telecommunication applications and are widely used in industry and household for heating food and other water containing goods. Falling drops of water can be effectively heated by applying microwave radiation within a cavity. For the application in the internal gelation process the two properties are most important:

- the heat is generated within the falling drop. Surface heating does not occur.
- the energy transport is easily accomplished with standard wave guide technology with low transmission losses.

The transfer of heat into water depends on the frequency and the relative permittivity of the material according:

$$P = 0.556 \cdot E^2 \cdot \epsilon_r'' \cdot f$$

where P is the power converted into heat per unit volume, E the effective (root mean square) electric field strength in V/m, ϵ_r'' the imaginary part of the relative permittivity of the material and f the operating frequency. The relative permittivity is highest between 10 and 15 GHz. Details of the first experiments performed in PSI are found in [23] and a description of the laboratory equipment is found in [24]. Patents were granted by many countries[25].

The simplification of the whole internal gelation process with all the recycle stream of liquids is illustrated in Figure 9.

3.4 Washing

The nitrate has to be removed to a large portion from the converted uranium and plutonium microspheres to prevent the spherical particles from cracking. This necessity unique to all gelation processes was mostly performed in a batch system with a bed of spheres as proposed by Naefe[6] and Haas[19]. In PSI we have developed a continuous counter current column wash system[33]. Fresh ammonia solution is moving counter current to the spheres in relatively short (1 meter) tube of 15 to 25 mm diameter. The electric conductivity of the particle bed is measured on-line and determines the degree of cleanness of the particles. The effluent solution has a high loading on ammonia nitrate. This wash solution is further concentrated in a distillation step and the readjusted ammonia solution recycled to the process.

3.5 Drying

The thermal treatment used in all fabrication routes for the preparation of uranium oxides controls the crystallite size and the structure of the dried powder, granulates or microspheres. The drying performed in a rotary dryer gives free flowing microspheres with a upscaleable device (see Figure 10). Most elaborated processes like the AUC-Process developed by Assmann[34] and Dörr[35], also developed for the coprecipitation with plutonium make use of the control of the oxidation potential of the atmosphere in the thermal treatment. This method may also be applied to the thermal treatment of microspheres prepared by internal gelation for the preparation of microspheres to be compacted to pellets as demonstrated by PSI in a collaboration with Siemens[29] and later on for microspheres prepared with carbon black by Ganguly[36].

3.6 Sintering, Carbothermic Reduction

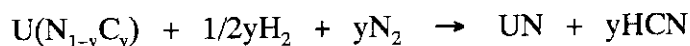
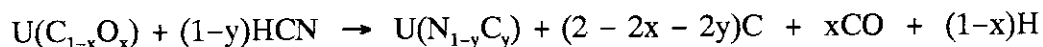
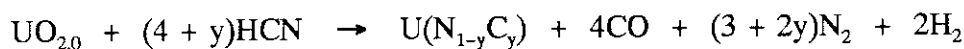
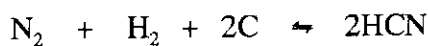
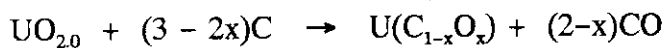
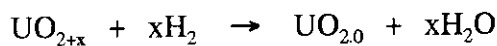
3.6.1 Oxides

Dense and porous oxides of uranium or uranium-plutonium are received according to the thermal treatment as proposed by several authors and practiced in the industry.

3.6.2 Nitrides

Condition for the thermal treatment of uranium nitride microspheres have been reported in [27]. The influence of hydrogen as reaction gas was recently evaluated by Bardelle[38] and conditions for the pellet fabrication are given by Blank[39] and Ganguly[42].

The microspheres are reacted in a particle bed with a controlled gas flow from bottom to top of a cylindrical reactor. This arrangement is ideal for the carbothermic reduction and nitriding with gaseous reactants. According to the sequence and the specific gas flow of the purge and reaction gases, and the thermal conditions the following chemical reactions take place:



4 Fuel Fabrication

PSI has successfully demonstrated the production of mixed carbide[22], [23], [24], [25], [26], nitride [27] and oxide [28] particles. Pellets from uranium oxide spheres have also been produced[29].

Uranium-plutonium carbide spheres of 800 and 80 μm in diameter have been successfully irradiated in a comparative test in the Fast Flux Test Facility(FFTF) within a collaboration with the Los Alamos Laboratory(LANL)[30],[31]. All sixty-six pellet fuel pins and twenty-five sphere-pac fuel pins irradiated for 630 full power days to peak burn-ups of 8.4 at.% at a linear powers of 84 kW/m and cladding outer temperature of 465°C, appeared to be in good condition when removed from the assembly. The post irradiation examinations also confirmed the good and generally similar behavior of pellets and sphere-pac fuel pins. A pronounced difference was found concerning fission gas release and cesium migration. The low fission gas release and low migration of cesium in the sphere-pac fuel must be related to the specific differences in the structure of fuel with a smear density in the order of 80% of the theoretical density of the carbide.

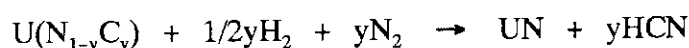
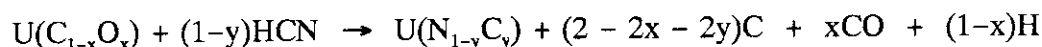
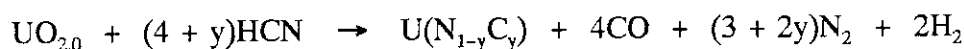
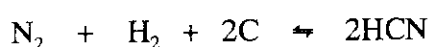
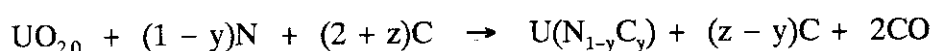
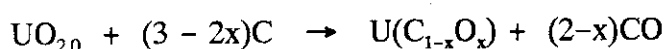
Uranium oxide microspheres in three different sizes have been fabricated for an irradiation experiment in a LWR power reactor[7], and similar spheres containing 5% plutonium for an experiment in an other LWR[28].

Uranium-plutonium nitride microspheres and pellets fabricated from microspheres have been developed and offered for the irradiation test "NIMPHE-3" in the Phenix reactor[37].

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Acknowledgements

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(Example 5% nominal (UPu)₂O₇ LWR fuel)

TITLE	POWDER BLEND (PELLET)	POWDER MASTER-BLEND (PELLET)	CO-PRECIPITATED MASTER BLEND (PELLET)	GEL-POWDER MASTER BLEND (PELLET)	GEL-POWDER INS-TANT BLEND (PELLET)	GEL-SPHERE INS-TANT BLEND (PELLET)	GEL-SPHERE-PAC
DESCRIPTION	TRADITIONAL METHOD 1	NEW POWDER METHOD BN/ALKEM 2	ALKEM PREFERRED FUTURE METHOD AUPuC 3	FIRST STEP TO TRUE GEL FUEL 4	INTERMEDIATE-1 5	INTERMEDIATE-II (DIPRESS, USA, CO-METHOD GEPEL BELGIUM) 6	ULTIMATE EIR METHOD 7
FEED	PuO ₂ -UO ₂ -powder	PuO ₂ -UO ₂ -powder	Pu-nitrate UO ₂ -nitrate powder	Pu-nitrate UO ₂ -nitrate powder	Pu-nitrate UO ₂ -nitrate powder	Pu-nitrate UO ₂ -nitrate powder	Pu-nitrate UO ₂ -nitrate powder
ROUTE			MIX	MIX	MIX	MIX	MIX
BLEND BY		BLEND	CO-PRECIPITATE	GEL (Co-precipitate)	GEL (Co-precipitate)	GEL (Co-precipitate)	GEL (Co-precipitate)
% Pu in U+Pu blend		30-50	40	~50	5	5	5
Form		Fine grain MASTER BLEND powder	Solid solution MASTER BLEND powder	Solid solution MASTER BLEND microspheres	Solid solution microspheres	Solid solution microspheres	Solid solution microspheres
Treatment of blend	Blend (mill)			CRUSH	CRUSH		
Enrichment Adjustment							
Final enrichment %Pu in U+Pu	5	5	5	5	5	5	5
Final form	Press pellets	Press pellets	Press pellets	Press pellets	Press pellets	Press pellets	
Heat treatment	Sinter	Sinter	Sinter	Sinter	Sinter	Sinter	Sinter
FUEL STRUCTURE	Large grains of 100% PuO ₂ in UO ₂ matrix	Fine grains of 30-50% PuO ₂ in UO ₂ matrix (some Pu diffusion during sintering)	Solid solution grains of 40% PuO ₂ in UO ₂ matrix	Solid solution grains of 50% PuO ₂ in UO ₂ matrix	Solid solution 5% Pu-95% UO ₂ matrix	Solid solution 5% Pu-95% UO ₂ matrix	Solid solution 5% Pu-95% UO ₂ matrix
CHARACTERISTICS	LARGELY INSOLUBLE IN NITRIC ACID	MORE EASILY SOLUBLE. THE MICRO-MILLING OR CO-MILLING TECHNIQUE IS NOT IDEAL FOR Pu POWDERS (DUST)	MORE EASILY SOLUBLE. LESS DUST. ONLY COMMERCIAL WHEN NITRATE (LIQUID) FEEDS AVAILABLE →	MORE EASILY SOLUBLE. LESS DUST. CRUSHING STEP NEEDED. COMPETITOR TO ALKEM ROUTE?	EASILY SOLUBLE. LITTLE DUST. CRUSHING STEP NEEDED. NO MECHANICAL BLENDING	EASILY SOLUBLE. LITTLE DUST. NO CRUSHING OR MECHANICAL BLENDING. PELLET STRUCTURE?	EASILY SOLUBLE. NO DUST. NO CRUSHING. BLENDING OR PELLET MANUFACTURE. IRRADIATION BEHAVIOUR?

Figure 1 Routes for mixed-oxide fuel fabrication from [7].

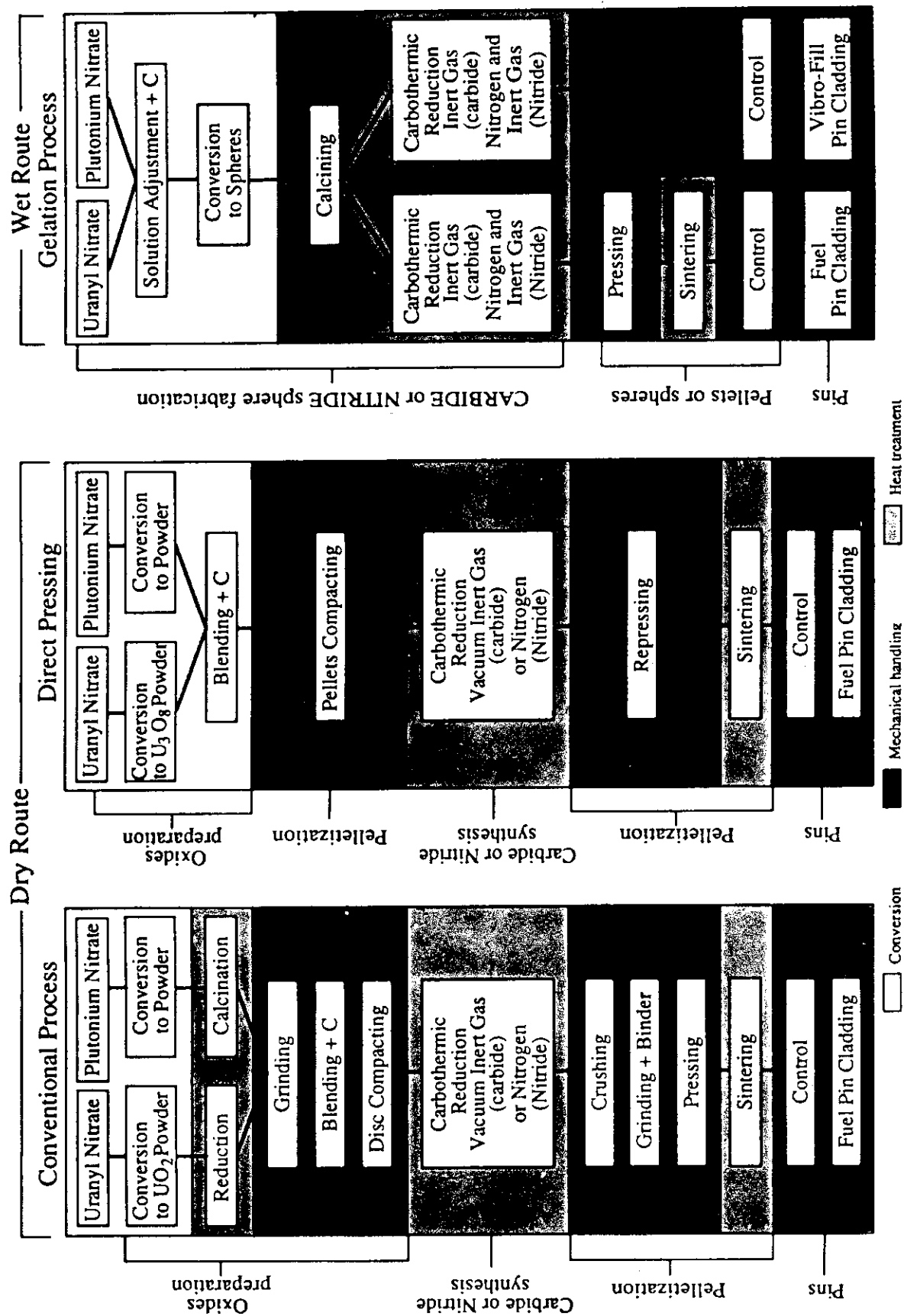


Figure 2 Nitride and carbide fabrication flow sheets from [8].

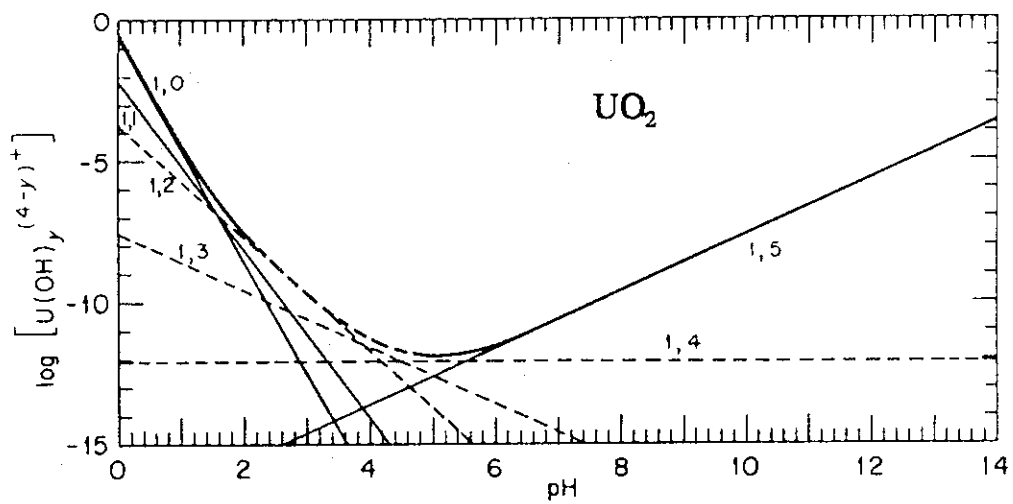
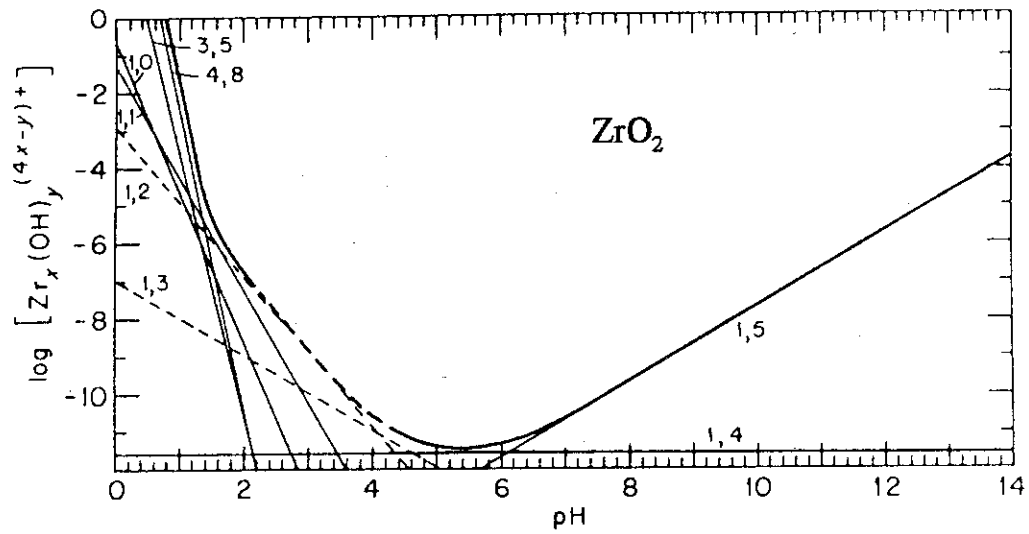


Figure 3 Distribution of hydrolysis products (x,y) at a concentration of 1m and 25°C for zirconium and uranium in comparison [17].

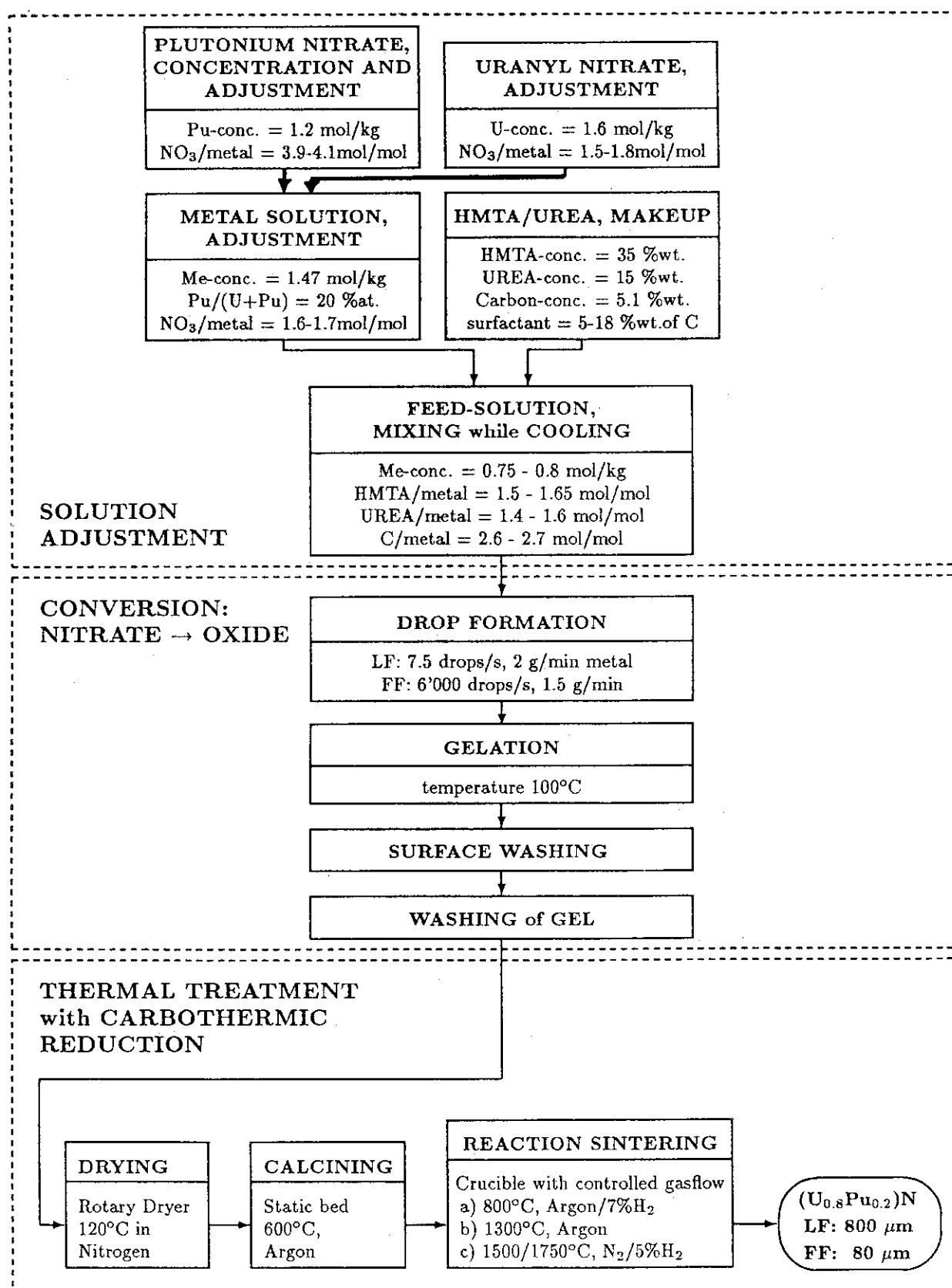


Figure 4 Preparation of uranium plutonium microsphere by Internal Gelation.

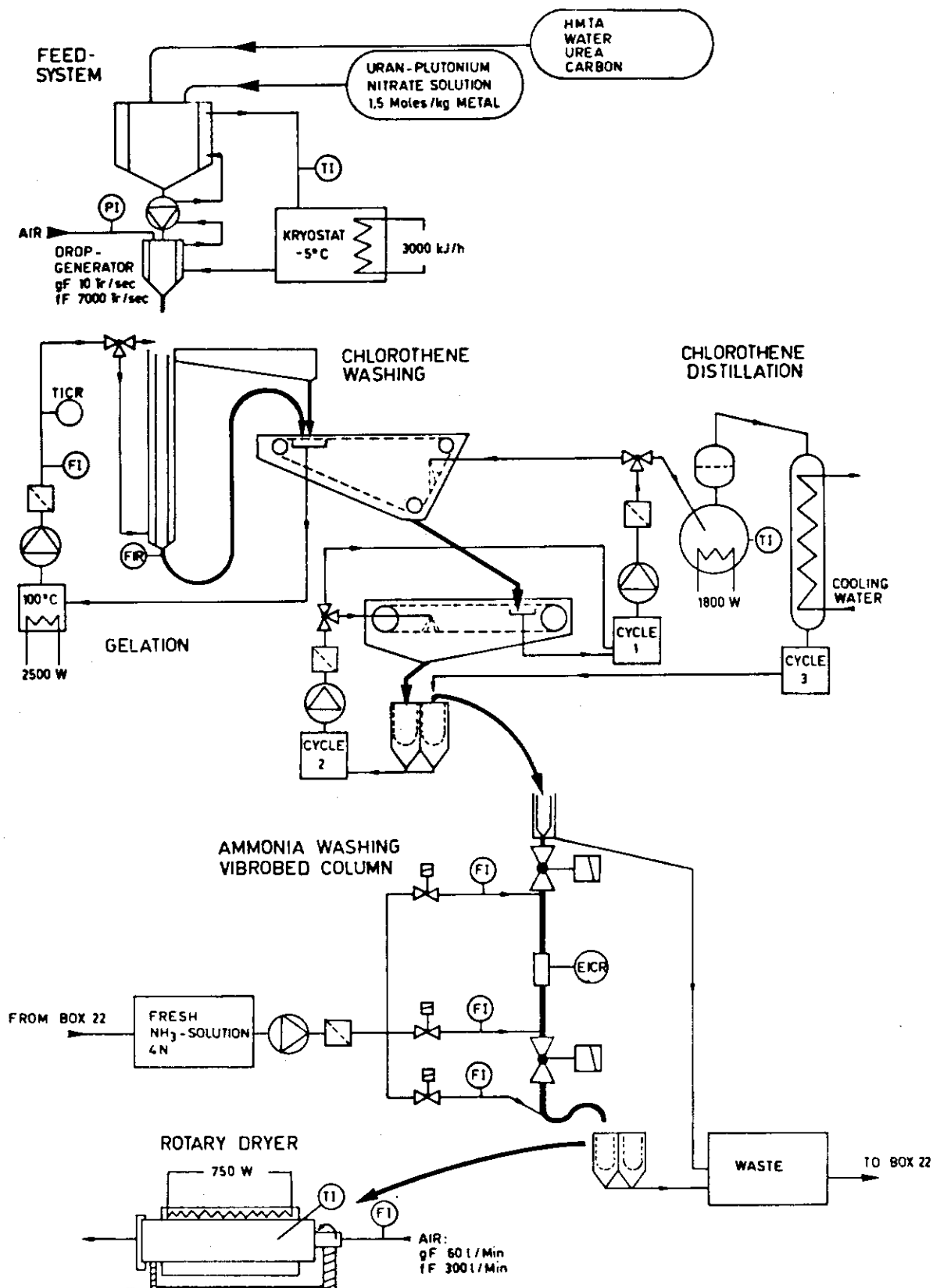


Figure 5 Diagram of gelation equipment built in a glove box (see [22]).

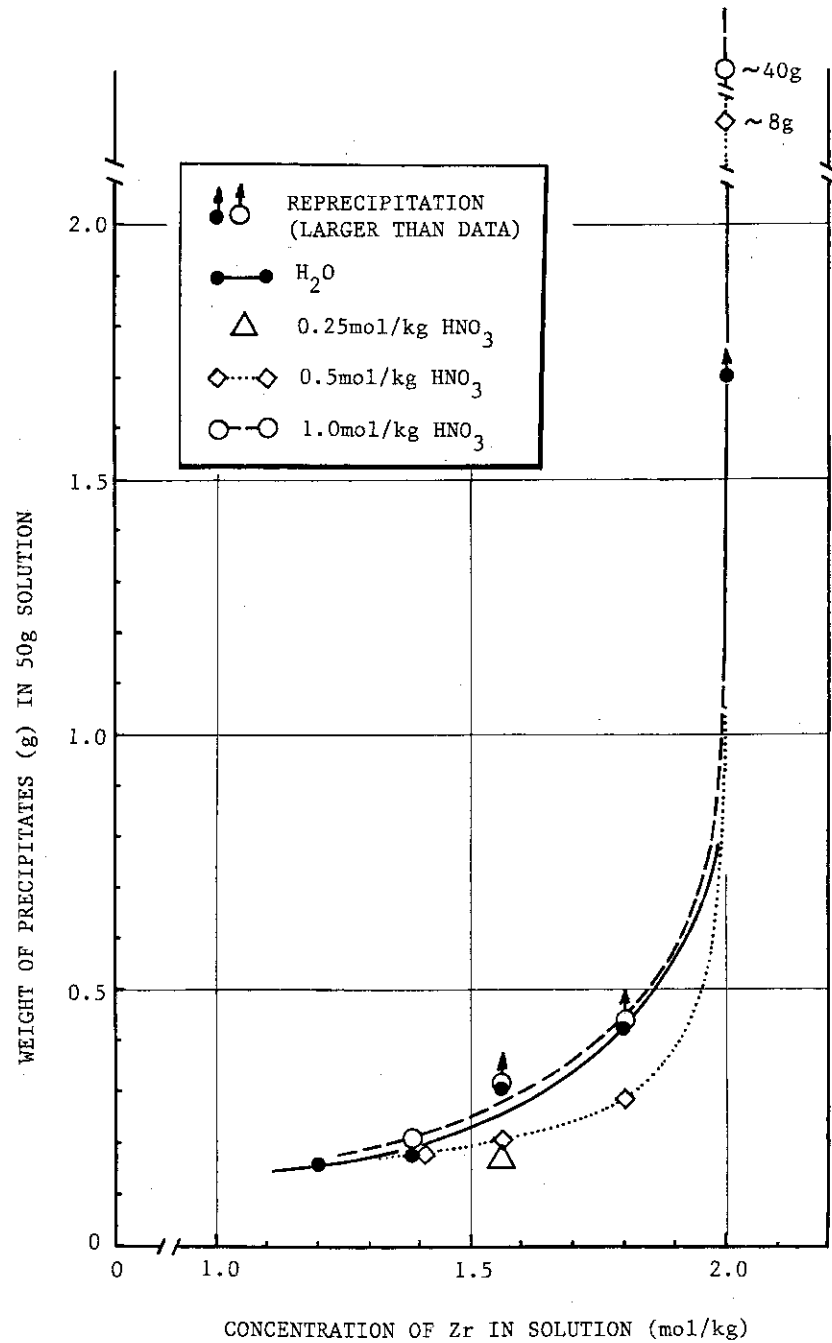


Figure 6 Solubility and precipitates of zirconyl nitrate dissolved in water and low concentration nitric acid [21].

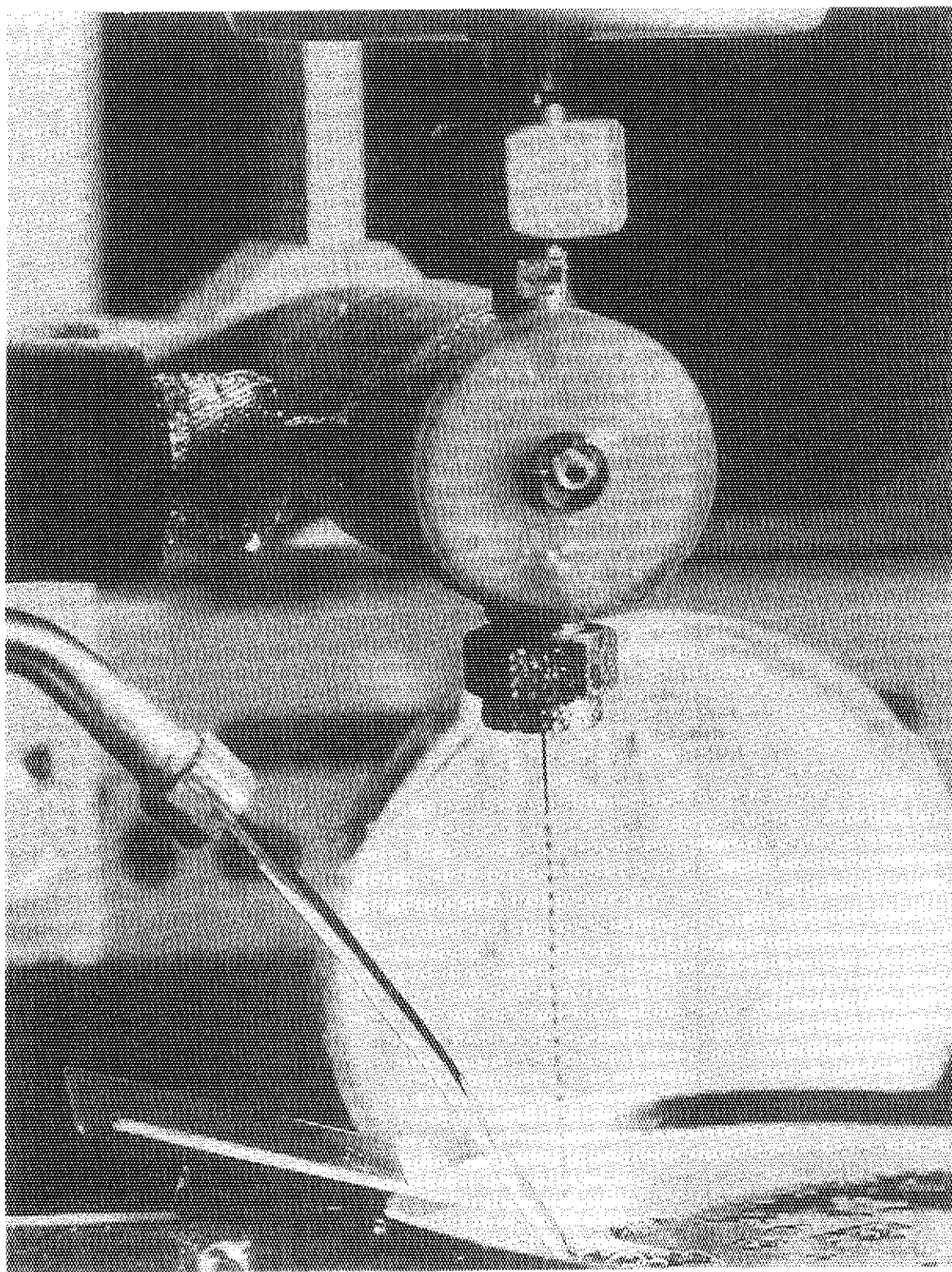


Figure 7 Arrangement for medium size spheres.

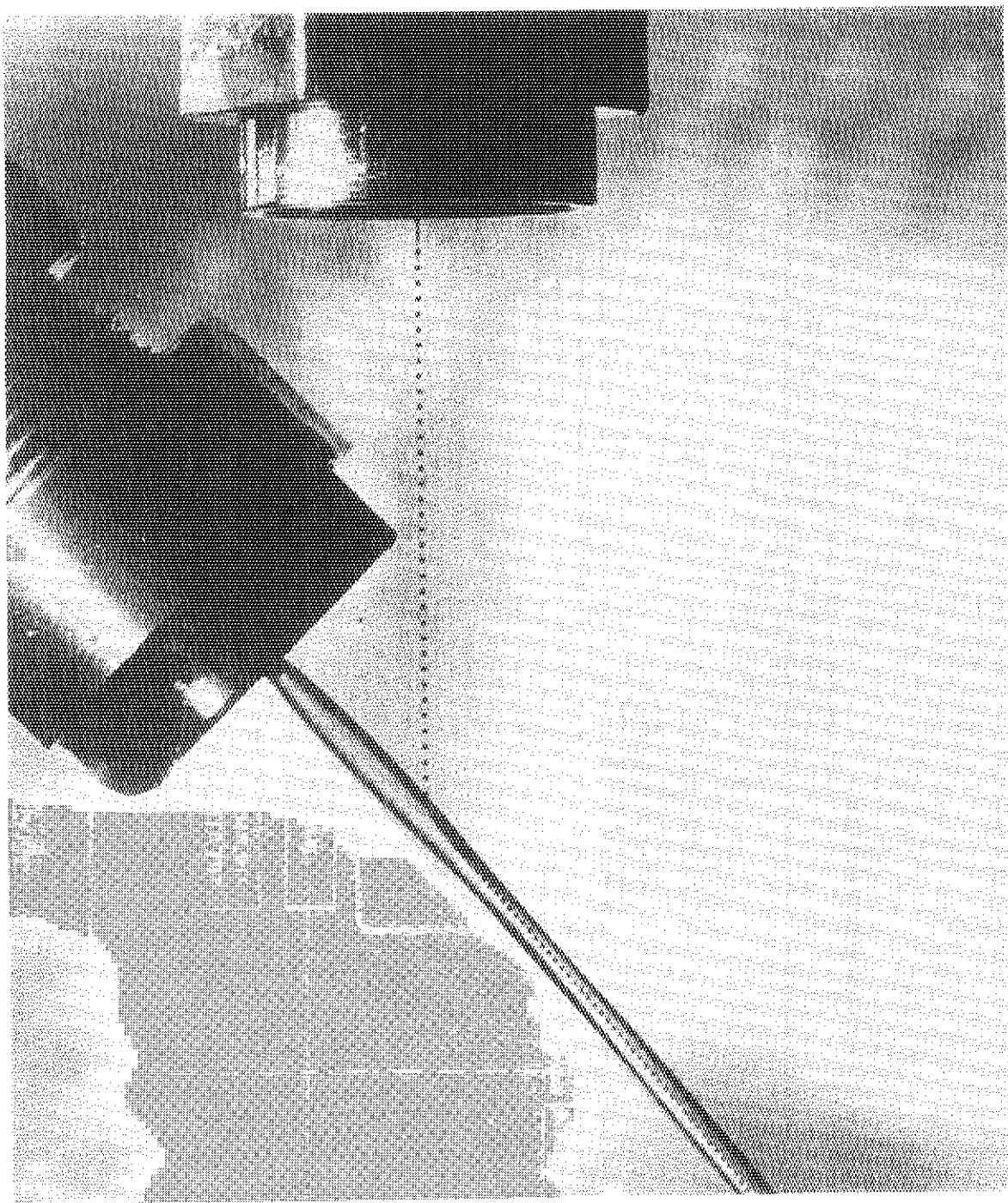


Figure 8 Formation of small droplets with agitation by a vibrator and gelation of droplets in a jet of silicon oil.

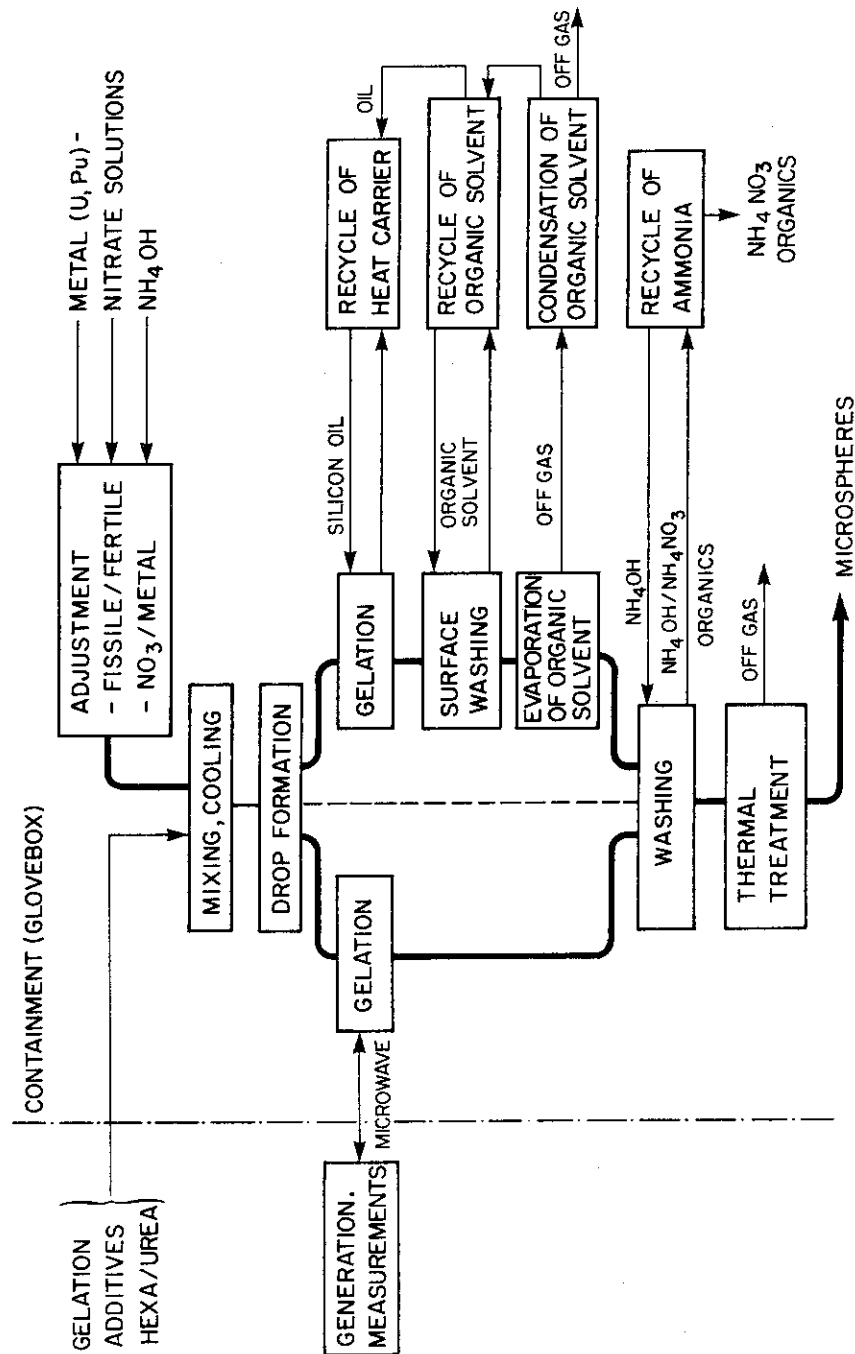


Figure 9 Comparison of the gelation methods.

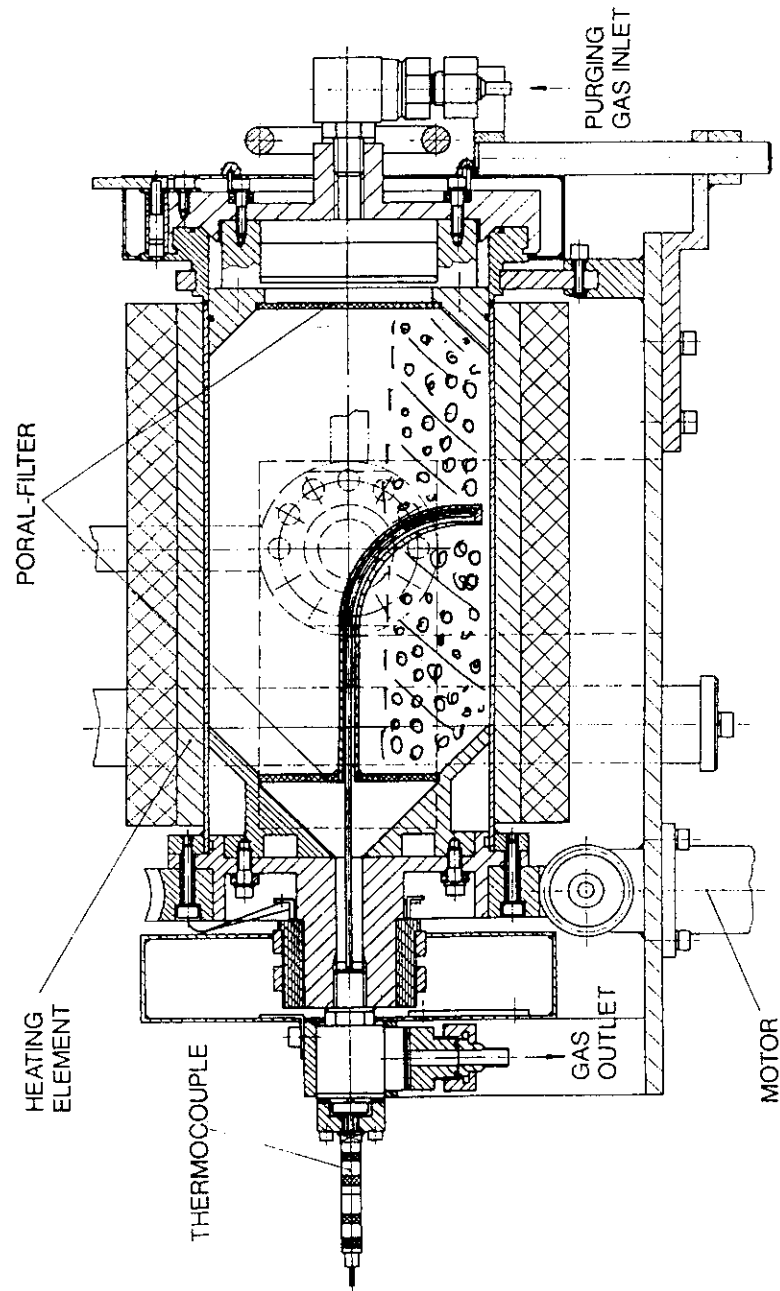


Figure 10 Rotary dryer for particles.