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Kernel fabrication experience

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Summary

The HTR-F Shared Cost Action sets out to regain past knowledge HTR- type fuel, by accumulating as much past data as possible, initiating new irradiation tests on existing fuel elements, developing new irradiation behaviour code, and re-establishing a fabrication capacity in Europe. Work package 4 (WP4) is concerned with this later aspect. An assessment of the literature indicated that the kernel production is best achieved by a sol gel route known as external gelation. Indeed it is more appropriately described by the term "Gel Supported Precipitation (GSP)".

This document describes UO_2 kernel production investigations made from November 2000 to October 2002 at both the Commissariat à l'Energie Atomique Cadarache and the EC-JRC Institute for Transuranium Elements Karlsruhe. It constitutes the deliverable number 14 of the HTR-F project.

The CEA Cadarache and ITU Karlsruhe have followed two different variants of the GSP process, which are based on the polymer support used in the precipitation. Polyvinylalcohol and Methocel polymers have been investigated at the CEA and ITU laboratories, respectively.

Given the enormous parameter field, the results thus far are positive, even though they are still far from that achieved in the past, especially at NUKEM. Given the large manpower that the latter organisation had at its disposal in the 70's and 80's and the lack of accurate process data in the open literature, the achievements made at the CEA and ITU are very positive indeed.

UO_2 kernels have been produced in both laboratories, but substantial process improvements are required to fulfil specifications to be expected for irradiation experiments. This largely concerns the sphericity of the particles, as this needs further optimisation of the constitution of the feed solution. Accurate control of the size can be achieved by geometry of the dispersion devices and their operating frequency, along with selection of the flow rate of the feed solution.

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1 - INTRODUCTION

Within the 5th Framework programme (FP5) of the European Commission, the retention, reestablishment and development of HTR related key technology and innovation potential has been supported in a number of Shared Cost Action programmes. The HTR-F programme concentrates on the fuel for this type of reactor, and includes workpackages (WP's) on recuperation of past experience, irradiation testing of fuels still available from previous programmes, modelling of fuel performance, and finally re-establishment of fuel manufacturing technology.

Within the latter work package (WP4) the CEA laboratories at Cadarache and the laboratories of the ITU in Karlsruhe are performing tests to produce UO_2 kernels. The goals of this WP are :

(a) The review of existing technologies for fabrication of kernels and coated particles,

(b) The selection and optimisation of reference fabrication process(es) for kernels and coatings

(c) The study of these processes at a laboratory scale in a first step

The first of these tasks have been made in a detailed literature review issued as Deliverable 15 in this project. The choice of process to be followed was also made at this time and is discussed in chapter 2 of this report. The results obtained in each laboratory thus far are described in Chapters 3 and 4 and the main conclusions and prospects for the future are compiled in Chapter 5 of this report.

For the purpose of this work existing facilities at the CEA and ITU laboratories have been re-deployed and extensively upgraded. The work in each case is complementary. At the CEA it is planned to build in the forthcoming years a new facility for UO_2 kernel production. This should be considered as a pilot plant essential in the re-deployment of the technology at an industrial scale. The emphasis of the ITU research and development programmes is largely on the transuranium elements and correspondingly the goal of the ITU is the deployment of a laboratory facility for the production of Pu bearing kernels (MOX or inert matrix type).

2 - PROCESS CHOICE AND DESCRIPTION

2.1 HMTA and GSP Processes

Following the extensive literature review performed in the HTR-F project (deliverable 15), it is clear that the two main production procedures for kernels are

(i) external gelation (also known as gel supported precipitation -GSP)
(ii) internal gelation (also known as the HMTA process)

Only the GSP process has been validated at an industrial level both at NUKEM in Germany and General Atomics in the USA, where UO_2 and ThO_2 kernels were produced in large quantities. In contrast, the internal gelation process has never been put into industrial application, but is planned for the production of PuO_2 kernels for Pu destruction in the GTMHR project.

Both gelation processes have certain similarities: e. g. broth preparation, drop formation, ageing, washing, drying, calcination and sintering. Their fundamental difference lies in the source of ammonia for the gelation step (cf. figure 2.1). In the GSP process, ammonia is available in excess as a solution of Ammonium Hydroxide, into which the broth droplets fall. In this case the Ammonia diffuses into the droplet from the external ammonia in aqueous solution. In the internal gelation process a compound (Hexamethylenetetramine – HMTA) is added to the broth, which decomposes thermally to release ammonia internally within the droplet. Until now the heat source for the decomposition is hot silicon oil at 100°C, in which the droplets are collected. For the GTMHR production, the silicon oil is being replaced by Tetrachloroethylene. This is better than silicon oil in terms of the remaining process steps (*vis à vis* cleaning and also disposal). Nevertheless both versions of the process require the disposal of organic waste.

For all of these reasons, the gel supported precipitation (GSP) has been selected by both CEA and ITU as the process for UO_2 kernel production within work package 4 (WP4) of the HTR-F programme.

Despite the industrial proven experience gained in the past, little key information is available in the open literature, and has been discussed before in deliverable 15. Attempts to obtain data from NUKEM were unfruitful due to their involvement in a potential project in South Africa. A visit to China by a European delegation was also unsuccessful in gaining access to new data; probably due to the same reasons as NUKEM. In the following sections some aspects of the GSP process are described.

2.2 The GSP process

The GSP process is shown schematically in figure 2.2 and is discussed below.

2.2.1 "Broth" Preparation

The "Broth" is the feed solution in the GSP process. The uranium is dissolved either from Uranyl Nitrate or the Oxide (U_3O_8), in which the level of free Nitrate should be controlled. Normally the outgoing solution is highly concentrated (ca. 500 g/l). In the past two types of polymers (PVA and Methocel) have been used as "thickeners" for the solution. The viscosity can be selected by changing the polymer concentration (typically 1 %) and by changing the polymer chain length. Other additives include Tetrahydrofufuryl alcohol (THFA), which allegedly complexes Uranium, and a surface tense agent such as Triton. Depending on the process parameters, the solution is heated before dispersion.

The process has been modified at INET in China, whereby both UREA and HMTA are added to the broth, essentially to reduce the NO_3^-/U ratio.

2.2.2 Droplet Formation and Gelation

The solution (broth) can be heated prior to dispersion. This has the advantage that the viscosity is reduced as the liquid passes more easily through the dispersion device, which can have two forms. The most simple is a capillary. Otherwise a vibrating oriface can be used. Both have advantages, but for industrial production and control of size dispersion (and selection) the vibrating oriface is the preferred choice. Both devices break the liquid flow into droplets. A laminar flow of the liquid through a vibrating nozzle is preferable and can be achieved best via pressurisation rather than by a peristaltic pump.

The droplets are collected in an Ammonia bath with a concentration between 3 and 14 M, where the NH_3 induces the gelation process. It is preferable that the droplets first pass through Ammonia gas, which produces a shell on the droplet enhancing its stability as it collides with the surface of the Ammonia solution. In turn the severity of this collision can be reduced by the addition of a surfactant agent to the ammonia bath to reduce its surface tension.

2 2.3 Ageing/Washing

The gelled beads are aged for a suitable length of time to complete the reaction of the Ammonia with the Uranyl Nitrate ion to form the hydroxide. This step is necessary to ensure that the Ammonia has sufficient time to diffuse through the channels defined by the polymeric support in the original droplet. Ageing is generally an overnight process (or even longer). Ageing at elevated temperatures (60°C) has also been used.

The particles can be washed in water or dilute Ammonia solution to remove Ammonium Nitrate (NH_4NO_3) from the particles, as its decomposition during subsequent thermal treatments can cause undesired cracking or rupture of the beads (Ammonium Nitrate is explosive when dry and represents a safety issue in waste handling).

2.2.4 Bead Drying

The drying of the beads is a very sensitive step as it involves the first step in the shrinkage, and in this stage, the particles leave their support of the liquid phase and must be of sufficient mechanical stability that breakages or cracking do not occur. The NUKEM process involved washing the beads in Isopropanol, which extracts the H_2O. This was followed by mild temperature treatments (80 °C) under reduced pressure.

The original GSP process developed in Italy utilises an azeotropic distillation process, using Tetrachloroethylene. Recently, it appears that the Chinese fabrication uses a reduced pressure and mild thermal treatment possibly using IR as a means of heating and a controlled humidified atmosphere. This is claimed to reduce the phenomenon of "outside-in" drying, which can result in an outer shell and possible cracking of the beads as water is removed from the internal regions of the bead.

2.2.5 Calcination

Calcination of the beads removes remaining organic compounds by pyrolysis. Typically calcination temperatures are about 600°C. There is some indication that the particles should be kept in motion during this step. This could be achieved by rocking the beads on trays in a standard batch type furnace. Rotary furnaces could also be considered.

2.2.6 Reduction/Sintering

Reduction of the material is required to obtain UO_2 from the U_3O_8 following calcination. This is achieved at temperatures greater that 600°C in an Ar/H_2 atmosphere. Final sintering is usually achieved at temperatures of 1500°C or higher, under the same atmosphere.

2.3 Barriers to the Re-establishment of Kernel Fabrication

Despite the excellence achieved at NUKEM for kernel fabrication, little relevant data is available in the open literature. Despite individual efforts to gain access to this information, no success was achieved. The visit to China by a European delegation also did not yield access to necessary data. The development of the process in the past required considerable manpower over several years. This is caused by the multitude of independent but intricately connected parameters, which can be varied in the process. An inexhaustive list is given below.

Table 2.1 : GSP Process steps and parameters to be optimised

GSP Process Steps	Parameters to be optimised
Broth preparation	U_{conc}, NO_3/U Polymer Type (viscosity, concentration) THFA content Triton content
Drop formation	Temperature of broth Flow rate Vibrating oriface (ϕ, frequency) or needle Sheath air (N_2/Ar)
Gelation	NH_3 gasification (geometry, flow, residence time) [NH_4OH] in solution
Ageing	[NH_4OH] Time Temperature Static or in motion
Washing	H_2O or dilute NH_4OH Number of washing steps [NH_4NO_3] in wash solution Geometry of container
Drying	Isopropanol extraction Reduced pressure/mild heating Azeotropic distillation
Calcination	Temperature ramps Hold temperature/duration Cooling ramps
Reduction (Ar/H_2)	Temperature/duration
Sintering	Temperature ramps Hold temperature/duration

Given this extensive parametric field, the novice would undoubtedly be doomed to failure. Both at the CEA and ITU, there have been efforts made in the past on the use of the GSP process for the production of small polydispersed (20 – 150 mm) beads for direct pressing into pellets. This experience combined with intuition and snippets of information derived from other sources must be coupled to selective testing, to try to reach the desired result. An example is provided by the concentration of metal in the broth. Figure 2.3 shows the diameter of the precursor droplet, as a function of solution concentration of the metal, for a final UO_2 kernel with a diameter of 500µm. Clearly higher metal concentrations reduce the shrinkage.

Although a vibrating oriface gives best performance in producing monodispersed droplets, the convenience of a simple needle is sufficient to test the production, and uniform shrinkage of the dried particle thermal treatment. Concerning the drying, safely relevant factors must be considered and these are always becoming more stringent. Thus the use of flammable liquids such as isopropanol should be avoided. This is an unconditional prerequisite at the ITU.

Following calcination of the kernels, their reduction to UO_2 should probably be performed before the onset of particle sintering (< 700°C). Many other parameters have to be tested in a systematic way to obtain the best result. Here inactive materials such as Hafnium and Cerium can be used as a stand in for Uranium. Even though the laboratory tests are easier to perform (particularly at ITU, where gloveboxes are a prerequisite to the handling of even depleted Uranium), they are limited as the chemistry of uranium and its mass are so widely different to the simulating elements.

3 - KERNEL FABRICATION AT CEA

3.1. Facilities description

Two UO_2 GSP particle production facilities were available at CEA/Cadarache. Most of the experiments were realized with a device using a fixed vertical capillary (double fluid nozzle). Indeed, this device can work with small quantities of broth solution so that most of the first parameters of the GSP process (cf. table II.1) could be studied and optimised, apart from the parameter "nozzle vibration" which mostly influences the drop size. The other equipment, restored and modified to current needs, was equipped with an horizontal vibrating nozzle. This second device was used to test the behaviour of a well defined broth with a vibrating nozzle, after having achieved good results with the same broth with the more simple vertical device. With the vibrating nozzle, control of the droplet size can be achieved more easily.

3.1.1. Vertical capillary GSP device

Figure 3.1. shows the vertical sol-gel device with its two-fluid nozzle. The broth solution was dropped through the central capillary while a fluid of N_2 or Air gas arrives all around the capillary to avoid the pre-gelation of the uranium nitrate by NH_3 . A chamber of about 10 cm is placed below the nozzle, in which there is a counter current of NH_3 gas. This NH_3 gas atmosphere is essential for the droplet surface solidification before it passes through the NH_4OH liquid phase. Under the NH_3 chamber, there is the ammonia liquid cylinder in which the droplet aging takes place. The possibility of creating foam at the surface of the aqueous ammonia solution was also available.

The broth solution (typically of 30 cm^3) is passed through the capillary by a peristaltic pump. With this device, the size of the droplet is controlled only by the capillary internal diameter because the nozzle is stationary.

3.1.2. Horizontal vibrating nozzle device

The horizontal vibrating equipment is an older CEA device, that has been restored for HTR-F project. This device can be compared to the GSP process apparatus developed at KFA/ICT with some modifications. It is based on an horizontal vibrating nozzle device with the use of a high voltage circle to avoid sticking of microspheres.

In contrast to the simple capillary, formation is no more accomplished by natural broth break-up, but really by imposed liquid break-up, itself controlled by the vibrating nozzle frequency. Therefore, the size of the droplet can be adjusted by the frequency.

Figure 3.2 shows the horizontal GSP vibrating nozzle device. In this case, one has a parabolic trajectory of the drops from the nozzle to the surface of the aqueous ammonia solution. This device has the same options than the vertical GSP device (i.e. flow of ammonia gas, foaming at the surface of the aqueous ammonia solution).

Another difference can be noticed with the vertical GSP device, and it concerns the aging NH_4OH solution, which was static with the first apparatus. In the horizontal device, the ammonia liquid solution (of about 8-9 l) was circulating from the bottom upward to the top of the gelation column.

The broth solution (typically of 150 cm3) was passed through the vibrating nozzle by a peristaltic pump.

3.2. Materials

3.2.1. Studied polymers

The polymer is of great importance in the GSP process since it supports the particle spherical shape while ammonia diffuses into the gel bead and precipitates the uranium by forming Ammonium Di-Uranate. This organic polymer must be water-soluble.

Most of the CEA experiments were made with polyvinyl alcohols (PVA) whereas, at ITU, cellulose ethers were studied.

From the PVA manufacturers (RHODIA Co., CLARIANT Co.,…) or PVA providers (Zschimmer & Schwartz GmbH,…), three kinds of PVA were tested ; two coming from CLARIANT (in the form of fine granules) and one coming from Zschimmer & Schwartz (in the form of a ready-to-use PVA solution).

The two PVAs manufactured by CLARIANT, called Mowiol 40-88 and Mowiol 56-98 are described in Table 3.1.

They are obtained by polymerisation of vinyl acetate and subsequent hydrolysis (saponification) of the polyvinyl acetate formed (cf. figure 3.3). By varying the degree of polymerisation of the polyvinyl acetate and its degree of hydrolysis, it is possible to adjust the residual acetyl group content, and finally, to obtain different grades of polyvinyl alcohols., either partially or fully hydrolysed. A simplified representation (structural formula) of both PVA grades can be found in Figure 3.4.

To simplify, it is possible to classify the PVA by two main characteristics that are :

- their viscosity in 4% aqueous solution at 20°C which is to related to polymeric chain length,
- their degree of hydrolysis (or ester value) which indicates roughly the ratio of polyvinyl acetate hydrolysed in PVA.

The two chosen Mowiol PVAs are different in their viscosity and in their degree of hydrolysis. Mowiol 40-88 (classified in the partially hydrolysed grade) is a little less viscous and less hydrolysed than the Mowiol 56-98 (belonging to the fully hydrolysed grade). Mowiol PVA-granules were dissolved in a stirring vessel of hot water (> 90°C) to reach a concentration of 80 to 150 g PVA/l.

Table 3.1 : Technical data of the two Mowiol PVAs studied

	Viscosity (4% in H_2O solution at 20°C) mPa.s	Degree of hydrolysis (saponification) mol %	Ester value mg KOH/g	Residual acetyl content wt/wt %
Mowiol 40-88	40 ± 2	87.7 ± 1	140 ± 10	10.8 ± 0.8
Mowiol 56-98	56 ± 4	98.4 ± 0.4	20 ± 5	1.5 ± 0.4

Poorer information is available for the PVA liquid supplied by Zschimmer & Schwartz called KB 2046, They are synthesized in Table 3.2. No data on the exact chemical composition and on eventual additives like preservatives were given.

Table 3.2 : Technical data of the KB 2046 (PVA solution)

	Weight concentration (g PVA/l)	Viscosity mPa.s	Density (20°C) $g.cm^{-3}$	pH
KB 2046 (liquid PVA)	About 250	About 3000	About 1.06	About 6

3.2.2. Preparation of uranyl nitrate solutions

Three kinds of uranyl nitrate solutions (300 to 450 g U/l) at various NO_3/U ratios have been prepared and tested.

One was prepared from U_3O_8 powder dissolved in hot concentrated HNO_3 and lead to a sub-stoechiometric uranyl nitrate with a NO_3/U ratio of 1.8. The chemical formulae of such a uranyl nitrate can be written as following : $UO_2^{2+}.(2-x)NO_3^-,xOH^-$ where each lost NO_3^- anions is substituted by an hydroxyl OH^-.

The second uranyl nitrate solution was realised by adding a known amount of HNO_3 to the latter solution in order to obtain a NO_3/U ratio slightly above 2 (i.e. there is a little excess free acid).

The third uranyl nitrate was prepared from UO_3 powder dissolved in hot concentrated HNO_3 and lead to the more denitrated uranium solution ($NO_3/U=1.6$). The UO_3 powder was prepared in CEA laboratories.

The objective of these solutions was to test the influence of NO_3/U ratio, in other words the influence of the free acidity, of the 3 uranyl nitrate (2 sub-stoechiometric and 1 over-stoechiometric) on the Ammonium Di-Uranate precipitation (which is believed to have repercussions on sol-gel bead formation and on the bead shape). Reducing the NO_3/U ratio is also of interest as less NH_4NO_3 is created during gelation, thereby decreasing risks of cracking in later thermal treatments.

3.2.3. Other additives or chemical products

The other materials used in the GSP process at CEA/Cadarache were a 99% TetraHydroFurfuryl Alcohol - THFA (PROLABO) and a surfactant liquid Triton X 100 (PROLABO) to form a foam on the surface of the NH_4OH gelation bath to cushion the impact of beads on this liquid surface. For the washing steps, commercial isopropanol (PROLABO) was employed.

3.3. Thermal treatments : from drying to sintering

After washing in isopropanol, several tests were made with different drying procedures including using vacuum drying at different temperatures (25°C, 45°C, 75°C), air drying at 110°C, azeotropic distillation (in CCl4) or wet drying at 110°C. The latter seems to be the reference method and gives the best results. As it was often mentioned in literature, air drying is considered as a necessary step, and must take place in a sufficiently wet atmosphere, to avoid the outer shell of the beads becoming impermeable to water vapour, and then increasing vapour pressure inside the spheres and possible crackings.

Calcination was made in a metallic batch type furnace, under air up to 650°C, and sintering was realised in standard UO_2 pellet sintering furnace (batch type) under wet $Ar/5\%H_2$ at 1600°C.

3.4. Experimental investigations

All the CEA experiments were realized with the same general process, described in Part 2 of the present document. It consisted of the following steps:

- preparation of the feed solution by mixing uranyl nitrate, PVA and THFA (measure of the viscosity),
- dispersion of this solution via one of two devices (vertical capillary or vibrating horizontal nozzle), an NH_3 counter-flow was always present between the nozzle and the surface of aging solution,
- aging of the droplets produced in NH_4OH solution (7M or 14M),with a surfactant TRITON,
- washing (1-2 times) of the gelled beads in NH_4OH solution (1M) and in isopropanol,
- drying, calcination and sintering

At first a search was made to define the best proportion of the 3 components of the feed solution, i.e. ratio of $UO_2(NO_3)_2$, PVA and THFA. Then, the effect of NO_3/U ratio or Uranium concentration on the shape of sintered beads was studied. Finally, different thermal treatments (from the drying step to the sintering step) were tested.

Most of the tests were made with the simple vertical capillary, the section 3.4.6 describes the experiments realized with the vibrating nozzle.

3.4.1. Effect of concentration of PVA and THFA on the spherical shape of gelled beads.

To define best feed solution characteristics, the effect of PVA and THFA concentrations on the shape of gelled beads (cf. Table 3.3) was studied for a given uranyl nitrate (NO_3/U ratio = 1.8 and Uranium concentration = 150 g/l). The kind of PVA was Mowiol 56-98 and the concentration of NH_4OH solution was above 10M. Some tests made with an ageing NH_4OH solution of 7M concentration led to less good results.

Table 3.3 : Influence of the concentration of PVA and THFA on shape of gelled beads

Batch denomination	**A**	**B**	**C**	**D**	**E**
THFA (%vol)	10	30	20	10	30
PVA (%wt)	1	1	1	3	3
Viscosity (mPa.s)	11	23	30	62	135
Spherical shape	very bad hollow bead	bad	bad	rather good	good

It was found that for a given uranium concentration (here 150 g/l), a minimum amount of both PVA and THFA is necessary to assure the spherical shape of the droplets. Gelled beads corresponding to the compositions of tests A and E are given in Figure 3.5. This result seems to confirm literature data, i.e. the polymer (here polyvinyl alcohol) thickens the feed solution and provides a structure strong enough to support the heavy uranium metal in the spherical shape whereas the modifier THFA assures, at least, the protection of the polymer from acid attack. The best combination of polymer and modifier agent found was 3%wt PVA and 30%vol THFA. The other parameters of the feed solution like NO_3/U ratio and uranium concentration were then varied to see influence on sintered beads.

3.4.2. Effect of NO_3/U ratio on the calcined beads.

Table 3.4 shows the effect of the uranyl nitrate NO_3/U ratio - for a given uranium concentration (150 g/l) in the feed solution on the shape of sintered UO_2 beads. The other parameters of the feed solution were fixed : 3%wt PVA 56-98 and 30%vol THFA. The concentration of the NH_4OH solution has to be above 10M.

Table 3.4 : Influence of NO_3/U ratio on the shape of calcined beads

Batch denomination	**F**	**E**	**G**
NO_3/U ratio	1.6	1.8	2.1
viscosity (mPa.s)	166	135	-
Shape of calcined beads	bad	medium	good

The more the NO_3/U ratio increases, the more the gelled beads are spherical and no cracks appear after drying (110°C, 12h under moist air) and calcination (500°C, 4h under air). Observations of calcined beads corresponding to compositions F and G are presented in Figure 3.6. In the literature, denitration of $Th(NO_3)_4$ or thorium-uranium nitrate is insistently recommended, whereas divergences have been noticed in the case of uranium. For instance, in the SNAM Italian process, it is reported that excess acid and salts are tolerated. Here, it seems preferable to be in such a condition.

3.4.3. Effect of uranium concentration of the feed solution on the shape of beads

Increasing uranium concentration of the feed solution, for a given UO_2 bead diameter, should decrease the diameter of the initial sol-gel droplet (cf. chapter 2). That means that the further shrinkage of the U-based beads should be reduced, consequently, the hazard of cracking should be lessened. Such experimental investigations were attempted at CEA Cadarache on two kinds of feed solution, one with a NO_3/U ratio of 1.8 and another with the same ratio of 2.1. All tests are resumed in Table 3.5. The concentration of the NH_4OH solution was above 10M.

Table 3.5 : Effect of U concentration on the shape of beads (for given NO_3/U ratios =1.8 and 2.1)

	NO_3/U ratio of the uranyl nitrate =1.8			**NO_3/U ratio of the uranyl nitrate =2.1**		
Batch denomination	H	E	I	G	J	K
Uranium concentration (g/l)	50	150	225	150	200	225
PVA (%wt)	2.5	3	3	3	3	3
THFA (%vol)	37	30	30	30	30	30
Viscosity (mPa.s)	20	135	-	-	133	128
Shape of beads	bad (hollow gelled beads)	medium	bad (cracked beads)	good sintered beads	very good sintered beads	bad (cracked beads)

Best results were obtained, once more, with the presence of free nitric acid in the uranyl nitrate. In this case, increasing the uranium concentration up to 200 gU/l in the feed solution gives good spherical sintered beads (cf figure 3.7.). This value of uranium concentration seems to be the upper limit since the sintered beads obtained with 225 gU/l show significant damage and cracks. The diameter of sintered kernels (of batch J) is around 720-730 µm.

3.4.4. Tests with other polyvinyl alcohols

All the previous experiments were realized with the PVA Mowiol 56-98. A shorter series of tests were made with the liquid PVA solution – KB 2046 – the other Mowiol 40-88.

All attempts to fabricate sol-gel beads with the KB 2046 were unsuccessful. Either the gelation step resulted in hollow gelled beads, or the calcination steps led to exploded kernels. Because of these poor results and of the lack of precise information of the real composition of this liquid PVA, further tests with it were abandoned.

One isolated but successful dropping test was made with the PVA Mowiol 40-88, whose experimental conditions are summarised in Table 3.6. Tests of aging in NH_4OH of different concentration have shown the necessity of using an ammonia hydroxide solution of molarity at least above 10M. Figure 3.8. illustrates sintered UO_2 kernels produced with PVA Mowiol 40-88. Improvements have still to be done to make more spherical beads, but no surface cracks can be noticed. Even though the present results are not as good as with the other polymer, it must be remembered that the nitrate ratio was less than 2.0 and that optimisation with this polymer could eventually lead to best results. This is an option that remains open.

Table 3.6 : Experimental conditions of the feed solution made with the PVA Mowiol 40-88

Batch denomination	**L**
Uranium concentration (g/l)	150
NO_3/U ratio	1.8
PVA 40-88 (%wt)	2.5
THFA (%vol)	37
Viscosity (mPa.s)	76
Aging NH4OH solution concentration (M)	14
Shape of sintered beads	good, slightly deformed

3.4.5. Investigations made with horizontal vibrating nozzle

In all three tests were made with this device. Their feed solution and dropping conditions are given in Table 3.7. The apparatus (pump + injector), used for older projects in the laboratory and modified for these new objectives, has reached its working limits. Indeed, it seems very difficult to disperse liquid whose the viscosity is more than 150-170 mPa.s. The whole concept will be rebuilt and transformed in a vertical vibrating nozzle, in order to handle viscous solution. Heating of the feed solution may also be necessary to reduce the viscosity.

Nevertheless, one batch (M) gave encouraging results with a production of few good sintered kernels without cracks (cf. figure 3.9). The diameter of the beads produced is smaller than with vertical capillary and is between 250 µm to 450 µm after sintering. The particles produced had a rather polydisperse size, which can be eliminated in future tests by further optimisation of the vibrational frequency, and the flow rate and viscosity of the feed solution. The other tests were unsuccessful due to the too viscous feed solution, and have to be retried either in a new configuration of the vibrating device, or by decreasing the viscosity of the feed solution.

Table 3.7 : Experimental conditions for GSP beads produced by horizontal vibrating device

Batch denomination	**M**	**N**	**O**
Uranium concentration (g/l)	150	200	150
NO_3/U ratio	1.8	2.1	2.1
PVA 56-98 (%wt)	2.5	2	3
THFA (%vol)	37	30	30
Viscosity (mPa.s)	117	208	175
Frequency (Hz)	50-100	50-100	50-100
Aging NH_4OH solution concentration (M)	14	14	14
Shape of sintered beads	some good beads	no beads, failure of dispersion	rare good beads, large difficulties to do dispersion

3.5. Conclusion and Perspectives

Among the extensive number of experimental parameters that had to be optimised in the GSP process, many have been tested, after having fixed the kind of polymer that would be studied as the PolyVinyl Alcohol. Even if we still don't manage to produce, in great quantities, high quality UO_2 beads, nevertheless we have progressed and learnt a number of things:

- apparently a good combination of PVA and THFA quantities has been found in order to obtain spherical gelled beads for a given uranium concentration,

- the best results in terms of sintered particles have been obtained with a slightly excess free acid in the feed solution, even with a NH_3 flow for surface gelation of the droplets,

- the concentration of ammonia hydroxide (aging liquid) has to above 10M. At lower concentration, the spheres tend to be deformed during subsequent handling or transport,

- the uranium concentration should be around 200 gU/l,

- the drying step appears to be definitively the crucial step in the GSP process, mainly with the control of the humidity level when air drying is performed,

- the horizontal vibrating nozzle leads to smaller particles diameter but in a broader range of diameter (250 µm - 450 µm) than the vertical non-vibrating device (620 µm - 730 µm), but this can be improved by optimising the feed solution viscosity and flow rate as well as the vibrational frequency to eliminate satellite droplets.

All the efforts and experiments done until now show the real difficulties of the GSP process applied to UO_2 kernel fabrication, without precise information or industrial key data. First encouraging results have been obtained, but confirmation (and improvement) need to be realized. The main outlook can be summarised as follows :

- the best tests obtained with the vertical simple capillary have to be repeated using the vibrating nozzle,

- further investigations with the PVA Mowiol 40-88 need to be done, but initially this should be treated as a second option,

- the horizontal vibrating nozzle needs to be transformed to the vertical to control better the droplet diameter and to achieve dispersion of higher viscosity liquids,

- others parameters need to be tested like heating the feed solution to decrease viscosity, heating the first washing solution of NH_4OH 1 M to enhance the elimination of ammonium nitrate.

4 - KERNEL FABRICATION AT ITU

4.1 Installations

The ITU is dedicated to the study of the physics and chemistry of the transuranium elements, (Pu, Np, Am,). Many of the installations are designed to handle these isotopes, with appropriate radiological protection for the personnel. Apart from the cold laboratories, where inactive materials are handled, all laboratories are categorised as contamination zones. In these zones, all activities are performed in closed glove boxes, including the handling of depleted and natural uranium, which usually do not require such precautions in other institutions. This limits the flexibility and causes more lengthy working steps. For this reason initial tests can be considered on inactive simulant materials, such as Hafnium.

4.1.1 Droplet Dispersion Units

Two types of dispersion units have been used. The most simple is based on a simple needle (cf. Fig. 4.1) through which the feed solution is pumped slowly. The droplets produced are collected in NH_4OH solution (4M). The simplicity in construction and operation of this device is its main advantage. It is incapable, however, of producing (sintered) particles less than 600 μm.

The other device is in principle similar, but a vibration is applied to the oriface, through which the liquid passes (cf. Fig. 4.2). A laminar flow of the solution is required. The frequency of vibration, the oriface diameter and the flow rate can be used to vary the particle size in the 100 – 500 μm range. Care must be taken that satellite droplets with different diameter are not produced.

Within this programme a new dispersion unit is being constructed for implantation in a glove box. The design is now complete (cf. Fig. 4.3) and the construction begun (cf. Fig. 4.4).

4.1.2 Gelation, Washing and Drying

Collection of the beads was made in ammonia solution (4M) with addition of Triton to decrease the surface tension and thereby lessen the effect of impact of the gelling droplets on the surface of the ammonia bath.

Washing is achieved either in cold laboratory or glove box using standard laboratory glassware. No control was made on the pH or conductivity of the wash solution. Typically the beads are washed 4 (– 6) times with an equivalent volume of water to the volume of the beads.

Several tests were made with different drying procedures using direct thermal energy, or washing with isopropanol or ethanol. The technique of choice, however, remains azeotropic distillation (cf. Fig. 4.5).

4.1.3 Calcination and Sintering

Calcination is made in standard batch type furnaces in inactive laboratories and glove boxes in the active zones. Calcination is made under air for UO_2. A reduction using Ar/H_2 is required before sintering, which for UO_2 is also performed under Ar/H_2. Inactive samples such as CeO_2 or HfO_2, can be sintered under air.

4.2 Solution Preparation

Solutions of Hf are prepared by the dissolution of $HfOCl_2.5H_2O$ in water. Following concentration, this can be analysed to give the Hf content. Uranyl Nitrate solutions are prepared by dissolving $UO_2(NO_3)_2$ in water with gentle heating. The solution is then concentrated to about 500 g/l and analysed by titration.

The external gelation process requires the addition of polymers to the solution typically with a concentration of 2 %. In order to facilitate this step a stock dispersion of the polymer is made. The required quantity is dispersed in water according to the method provided by the manufacturer. In these investigations three types of Methocel (DOW) were used: A4C, K4M and J75M, which increase in viscosity (for a 2 % solution) from 100 to 4000 to 75000 cPs, respectively.

Other solutions required are THFA and Triton, which are added along with Methocel, just before the production.

4.3 Tests on HfO_2 kernel production

Tests have been made with a Hf solution to test the influence of the Cl/M ratio and drying procedure on the integrity and form of the beads. The denitration was achieved by taking 50 cc from the Hf mother solution (190 g/l), which was extracted in two steps using 80 cc of an equal volume mixture of xylol and trioctylamine. Two types of methocel were tested: A4C and J75MS. The solution conditions for two such tests are given in Table 4.1 below

Table 4.1 Solution conditions for the HfO_2 kernel production

Batch Number	Dropper 4	Dropper 5
Concentration of mother Hf solution (g/l)	190	190
Volume of feed solution taken (cc)	50	50
Dechlorination of solution by extraction	yes	no
Methocel Type	J75MS	J75MS
Methocel 3% solution added (g)	15	15
THFA added (cc)	5	5
Triton added (cc)	1	1
Water added	25	25
Metal concentration in feed solution (g/l)	99	99
Methocel concentration (wt%)	0.5	0.5
Viscosity (cPs)	85	87
Drying in air	yes	yes
Drying in ethanol	yes	yes
Drying by azeotropic distillation	yes	yes

Dispersion was made using the simple cold laboratory dropper. Following ageing overnight, the beads were washed in water and divided into different lots, which were then dried by various means. The results are shown in Figure 4.6. After their collection, the gelled hydroxide particles were relatively large (ca. 2.5 mm), which is a consequence of the form of the dispersion device. This size was independent of the Cl/Hf ratio investigated. Following drying an enormous shrinkage (a factor of 3) is observed.

The drying methods tested indicate that best results were obtained by washing in ethanol. Drying in air at low temperature results in at least one “flat” side of the particle, where it was resting on the solid surface during drying. The azeotropic distillation resulted in more cracked particles.

Generally, better beads were found after drying, when the chloride had been extracted form the solution. This is particularly evident for the kernels dried by azeotropic distillation, where, without anion extraction, many were completely in pieces, so that any diameter evaluation is impossible.

Other tests were also performed on Hafnium, but were less successful than those presented above. Given the difference in the chemistry of Hf and Uranyl species, it was decided to abandon these investigations on simulant materials and continue with tests on the production of UO_2 kernels.

4.4 Tests on UO_2 kernel production

Several tests have been performed on UO_2 kernel production. The results of the first quasi successful test and that of the best achieved tests are presented in detail here. The solution parameters of the relevant tests are shown in Table 4.2.

The first tests (Dropper 6) were largely unsuccessful with a paste and no particles formed. A number of tests ensued, whereby addition of urea and of HMTA and an alternative polymer (PVA), albeit in small amounts were tested.

The first real beads were eventually found but by reverting to the original polymer used in the first studies made in Italy – Ressina HG90 4000.The resulting particles are shown following the drying step in Figure 4.7 (Tests 02SG002 and 0008). Although they are of good form, they are mainly hollow inside. Another aspect of these tests was the addition of a small amount of free nitric acid, where normally a denitration step would be expected to give best results. This was performed to decrease the gelation at the needle, as in a glovebox the ammonia vapour above the collection vessel is not controlled and despite a protective sheath air at the dropping needle, it can reach this point and cause blockages. It would appear that this is an advantageous step, even if it is counter to normal logic and the results obtained above for Hafnium oxide.

Table 4.2 Solution conditions for the UO_2 kernel production

Batch Number	Dropper 6	02SG002	02SG008	02SG031 (A and B)	02SG066	02SG067	02SG068
Concentration of mother U solution (g/l)	523	512.84	512.84	523	505	505	505
Volume of feed solution taken (cc)	20	25	25	25	25	25	25
Methocel Type	J75MS	Hg90 4000	Hg90 4000	K4M	K4M	K4M	K4M
Methocel solution added (g)	19.5 (3%)	22.37 (2%)	22.37 (2%)	22.15 (2%)	22.15 (2%)	11.8 (2%)	14.8 (2%)
THFA added (cc)	5	16.1	16.1	16.1	16.1	8.1	10.9
Triton added (cc)	1	0.12	0.12	0.12	0.12	0.07	0.08
Water added (cc)	60			5	5	0	0
HNO3 added (cc) [14M]	-	0.63	0.63	0.63	0.63	0.3	0.42
Metal concentration in feed solution (g/l)	99	199	199	190	190	282	247
Methocel concentration (wt%)	0.6	1.04	1.04	0.96	0.96	0.78	0.86
Viscosity (cPs)	85	-	-	-	-	-	-
Ageing with heat treatment				Test B			
Drying in air	yes	-	-	-	-	-	-
Drying in ethanol	yes	-	-	-	-	-	-
Drying by azeotropic distillation	yes	yes	yes	yes	yes	yes	yes

The effect of ageing has also been investigated in the tests 02SG031A and 02SG031B. The U hydroxide beads were prepared using the recipe in given in Table 4.2. Afterwards, the batch was divided in two portions, with portion A being aged, washed and dried (azeotropic distillation) in the normal way, while portion B was heated in dilute (1M) ammonia solution for 1 hour before being washed and dried (azeotropic distillation) in the standard way. The methocel used was K4M, which is similar in viscosity for a given concentration to HG90 4000.

The beads from each of these batches have been subjected to a series of thermal treatments, the results of which are shown in Figures 4.8 to 4.12. Ageing in warm ammonia does not lead to any advantage. On the contrary, after heating to 400°C, these particles had a worse shape than those aged and dried in the standard way. No recovery of the shape during the remaining heat treatments was observed. Perhaps this is not surprising, as it was a step originally invoked to decrease the mechanical strength of the particles for pelletisation purposes.

The results obtained for batch 02SG031A are by far the best achieved so far. The particles are not perfectly spherical, but they are intact and exhibit a near spherical form without cracks or voids. One reason for this positive result could be the relatively high U content in the feed solution (190 g/l). As discussed in §2 one would expect that the higher the concentration in the feed solution, the smaller the shrinkage of the kernel during drying and subsequent thermal treatments. The only attempt to repeat this result (02SG066) was not so successful, as the particles had an oriface after drying. This problem is linked to the dropping and possible slight deviations in the solution viscosity. Nevertheless, as the best result so far, this test will be repeated.

In two further test (02SG067 and 068), an attempt was made to increase the metal concentration further in the feed solution. This was achieved by maintaining the U solution, but decreasing all the organics (methocel and THFA) proportionally. Metal concentrations in the feed solution of 280 and 247 g/l were obtained, but the tests were unsuccessful. All the particles were broken after drying and in fact the damage showed that only shells were present. This could be a consequence of the higher Metal/polymer ratio. Further tests will be made but increasing the methocel content in the mother dispersion from 2 to 4%, to permit higher metal content, while at least maintaining the same methocel content in the feed solution, or even the same metal to polymer ratio as in the most successful tests thus far.

4.4 Conclusions and Outlook

4.4.1 Lessons learned

Given the multitude of parameters that can be adjusted in the sol gel external gelation process, it is very difficult to produce high quality particles in a short time frame. Nevertheless significant progress has been made. The investigations made thus far lead to the following conclusions as follows :

- alcohol drying seems to be better than thermal or azeotropic distillation. This is problematic for ITU as the quantities permitted for glovebox use are very small, so that azeotropic distillation must be pursued,

- anion removal (or pre-neutralisation), gave better results for Hf. In contrast, the UO_2 tests gave best results when a small amount of excess acid was available. This mainly improved the flow through the needle and hindered premature gelation and blocking thereof. In a better designed system, where ammonia can be kept away from the oriface, it can be expected that the process is better with lower anion/metal ratio,

- given the different chemistries of simulant metals (e.g. Hf) to UO_2, little knowledge can be transferred from one chemical system to another. This will have implications for mixed oxide or even PuO_2 production,

- for UO_2 kernel production the metal concentration should be of the order of 200 g/l,

- methocel of the type K4M (4000 cPs for a 2% solution) seems to give best results. Lower viscosity (A4C) appears to give shells rather than full particles, while higher viscosity (J75MS) is too difficult to pump.

4.4.2. Perspectives and outlook

The achievements made by NUKEM and other organisations cannot be attained in short time frames. Nevertheless, promising results have been obtained and can be built upon in the future, but a production fulfilling former reactor specifications is still far away.

The following points need to be investigated further:

- the best results obtained until now need to be repeated,

- additional tests are required at higher metal concentrations but still respecting the metal/organic additive content ratio,

- the feed solution should probably be heated to reduce the viscosity and ease the flow through the nozzle and improved droplet shape on cooling,

- the pre-gelation of the droplet surface by ammonia gasification is probably essential to maintaining stability of the particle on collision with the surface of the ammonia solution.

Many of these parameters will be tested further using the existing dropper device, but the new installation now nearing completion will permit ammonia gasification and most importantly the production of smaller particles, which should benefit the gelation process.

5 - CONCLUSIONS

Within Work Package 4 (WP4) of the HTR-F Shared Cost Action, the laboratories of the CEA Cadarache and ITU Karlsruhe have initiated laboratory scale experiments to rebuild a European capability to produce kernels for HTR applications. The chosen production process is the external gelation route, also known as the "Gel Supported Precipitation" process, as recommended by the conclusions of the literature review made on kernel fabrication (deliverable 15).

The results so far are perhaps more positive than could have been expected, given the large number of parameters to be optimised in the GSP process. In addition, no support in the form of process parameters was forthcoming from the few organisations remaining, who had performed this type of work in the past.

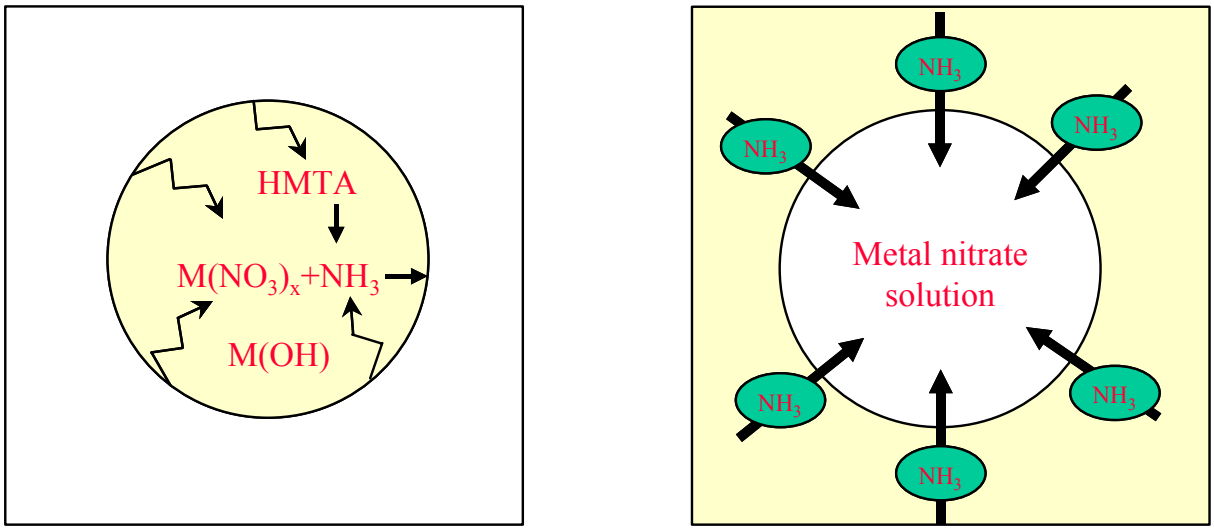
At both research institutes, where experimental tasks were independent with each laboratory working with a defined kind of polymer (PVA and cellulose ether polymers at CEA and ITU, respectively), UO_2 kernels have been produced. Nevertheless, these kernels are still far from fulfilling the specifications required for an experimental HTR irradiation. Within the next years, further tests will be pursued :

- to improve the particle sphericity,
- to control the kernel diameter at the required dimension,
- to increase the capacity of the experimental devices.

BIBLIOGRAPHIC REFERENCES

All the bibliographic references can be found is the deliverable 15 which is the literature review made on kernel fabrication

FIGURES



Internal Gelation
→Diffusion of heat

External Gelation
→Diffusion of ammonia

Figure 2.1 : Schematic diagram of ammonia generation in the internal and external gelation processes

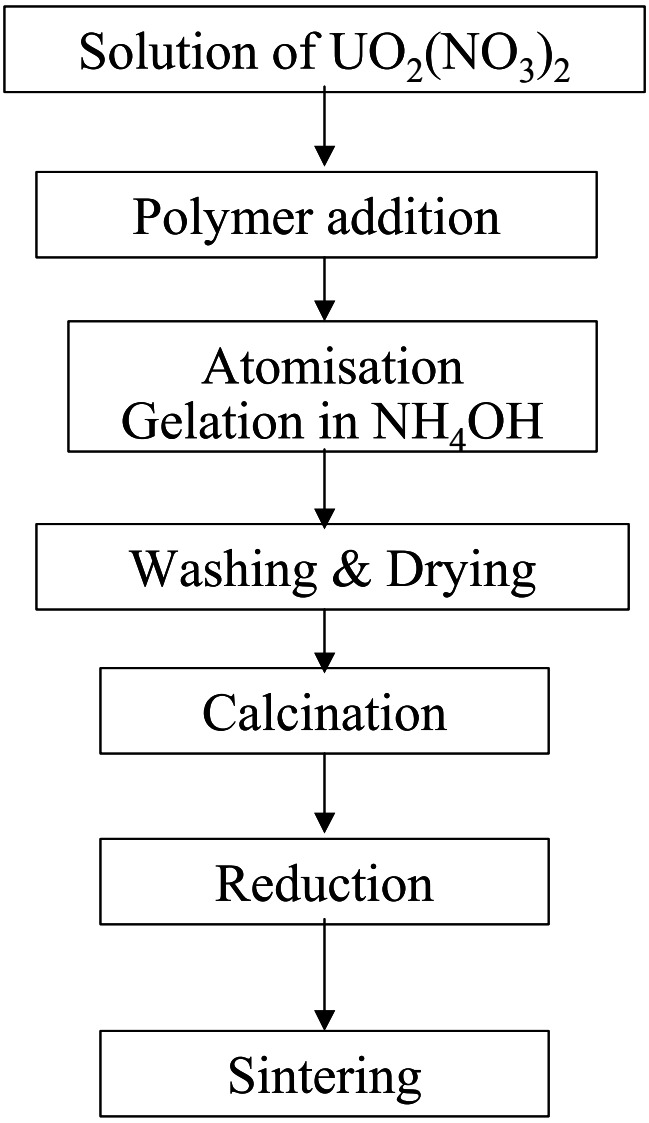


Figure 2.2 : Flow scheme of the external gelation (GSP) process

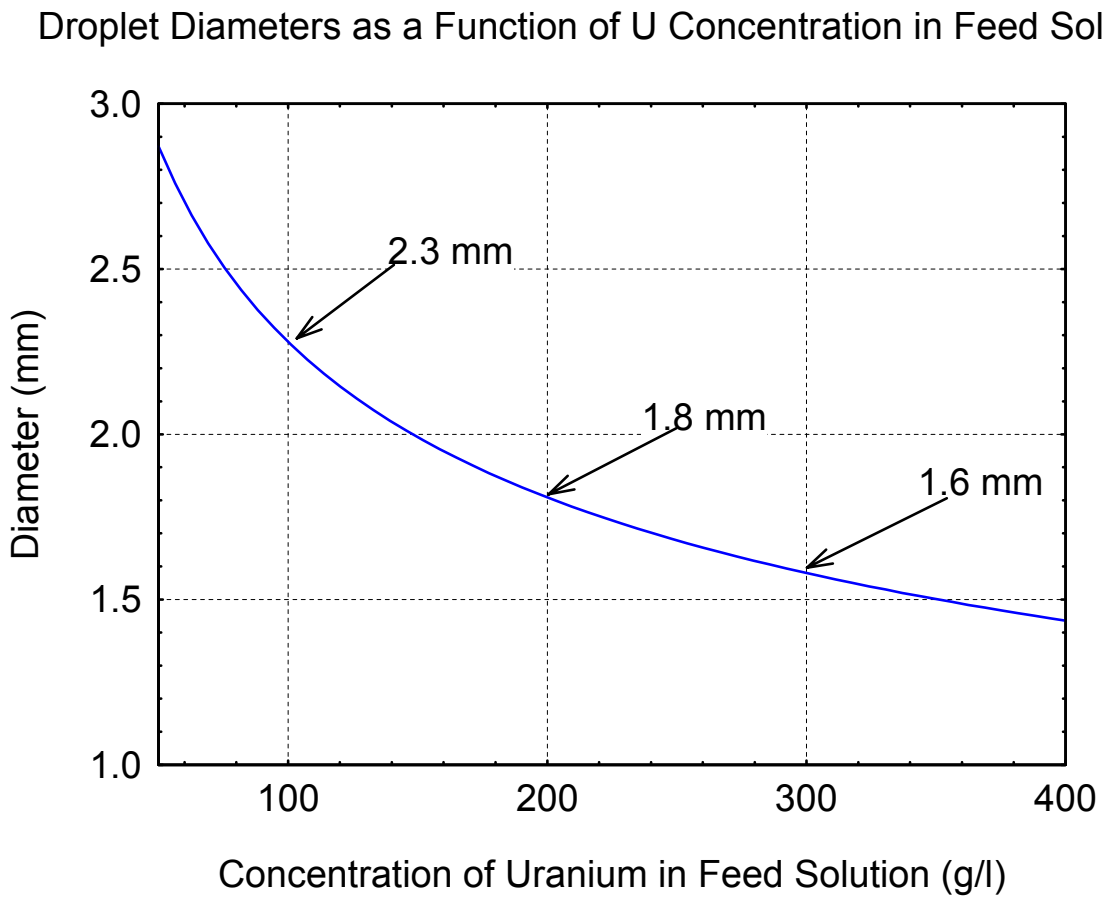


Figure 2.3 : Droplet size as a function of the metal concentration in the feed solution for the production of a sintered UO_2 kernel with a diameter of 500 µm.

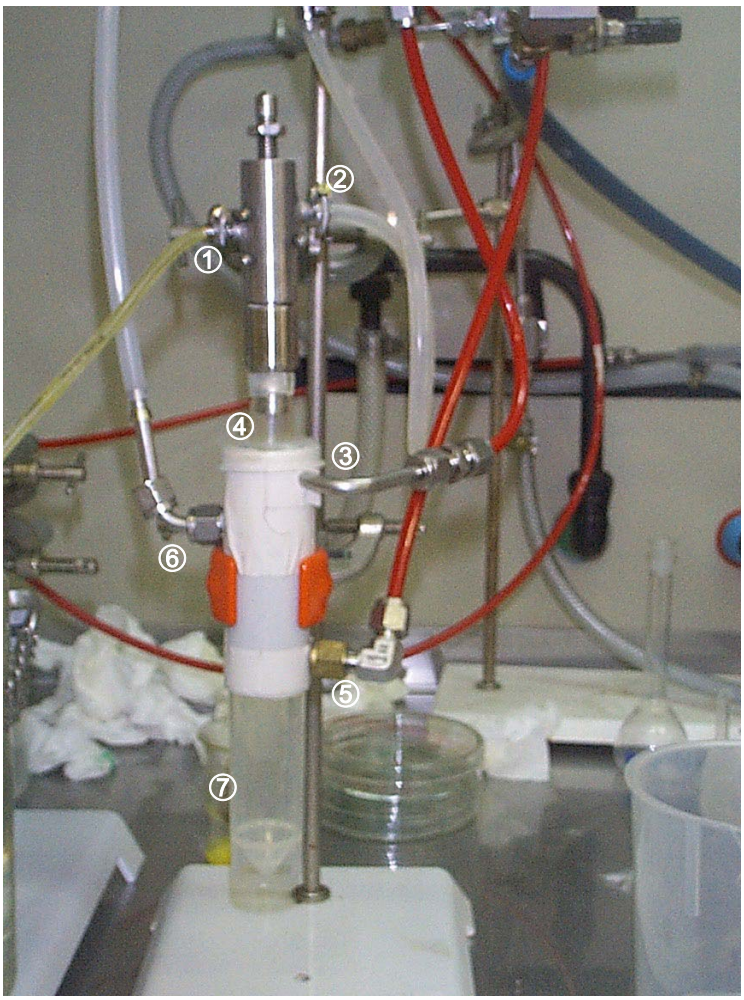


Figure 3.1 : Vertical capillary GSP device (non-vibrating dropper dispersion)

1	→	Broth arrival
2 and 3	→	Air gas inlet
4	→	Vertical capillary
5	→	NH_3 gas inlet
6	→	Gas exhaust pipe
7	→	NH_4OH aging tube

Figure 3.2 : Horizontal vibrating nozzle device

1	→	Peristaltic pump
2	→	Broth arrival
3	→	Vibrating nozzle
4	→	NH_4OH aging tank and tube
5	→	NH_3 gas inlet
6	→	Gas exhaust pipe
7	→	Power supplier, Frequency controller

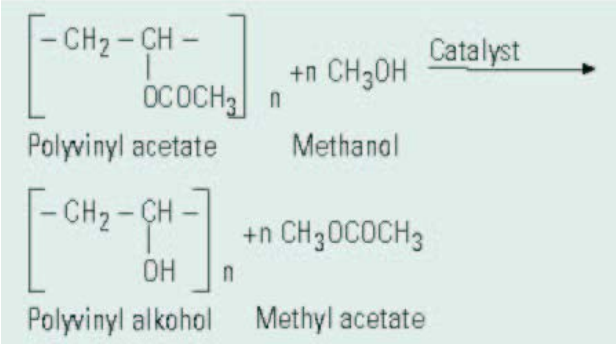


Figure 3.3 : Hydrolysis reaction of Polyvinyl acetate in PVA

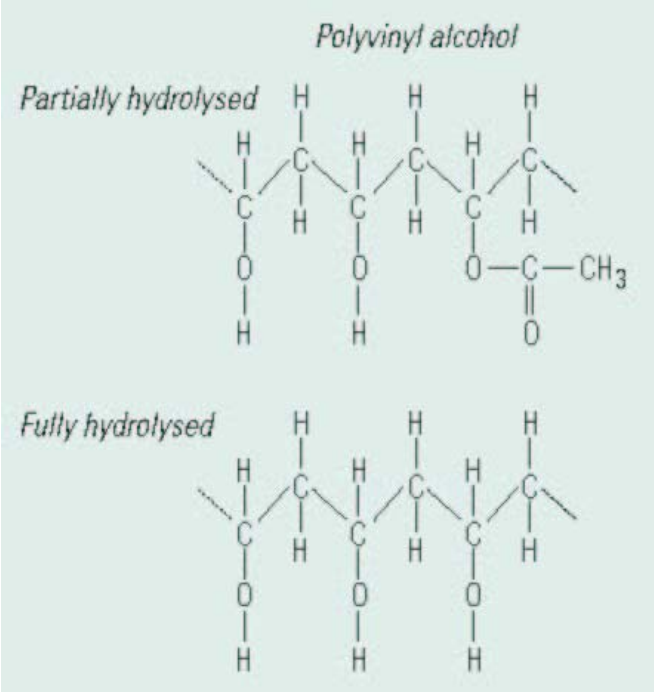


Figure 3.4 : Simplified structural formulae of partially and fully hydrolysed PVA

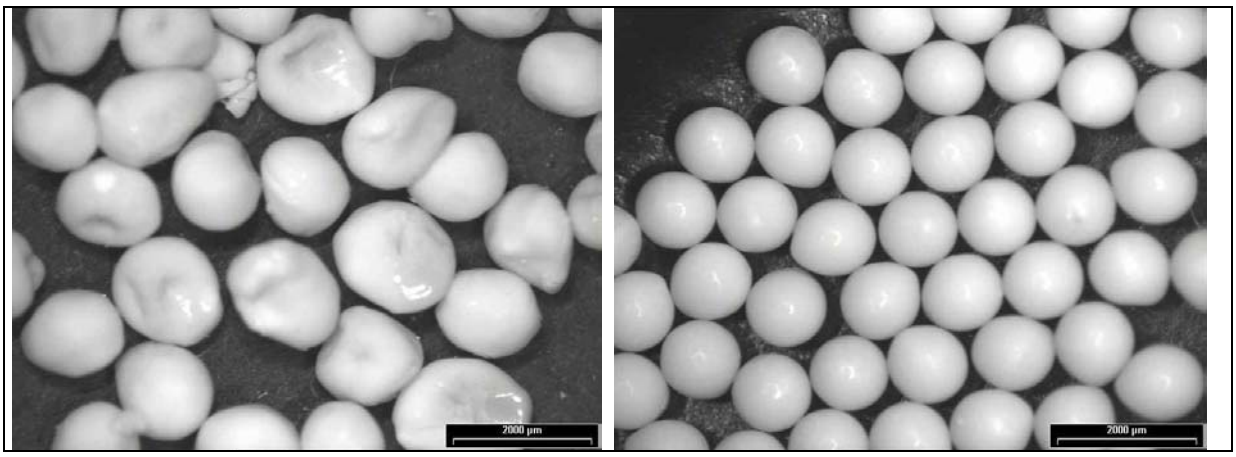


Figure 3.5 : U-based kernels after gelation step, batch A (right image)
and batch E (left image)

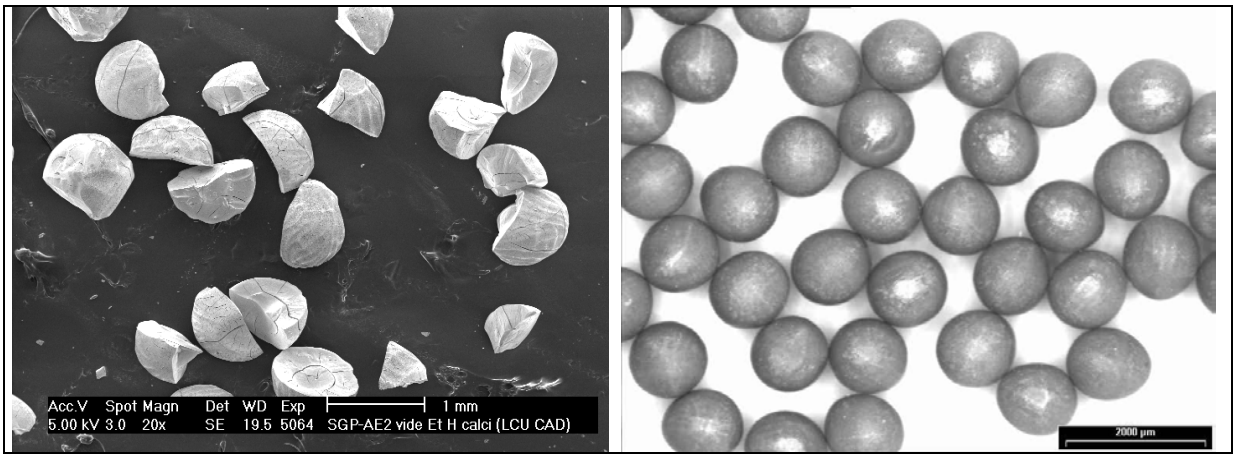


Figure 3.6 : U_3O_8 kernels after calcination step, batch F (right image) and batch G (left image)

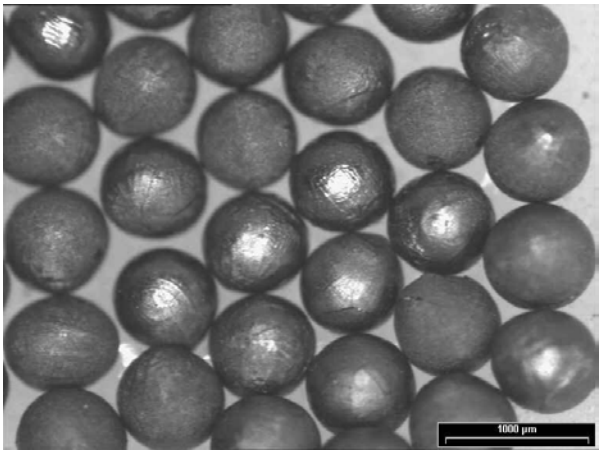


Figure 3.7 : UO_2 kernels after sintering step obtained with batch J

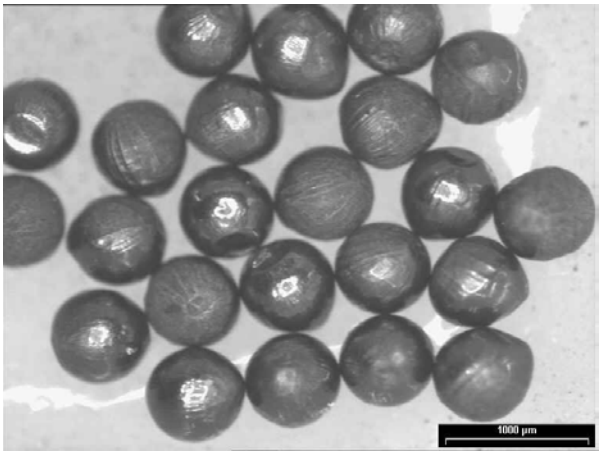


Figure 3.8 : UO_2 kernels after sintering step obtained with batch L (Mowiol 40-88)

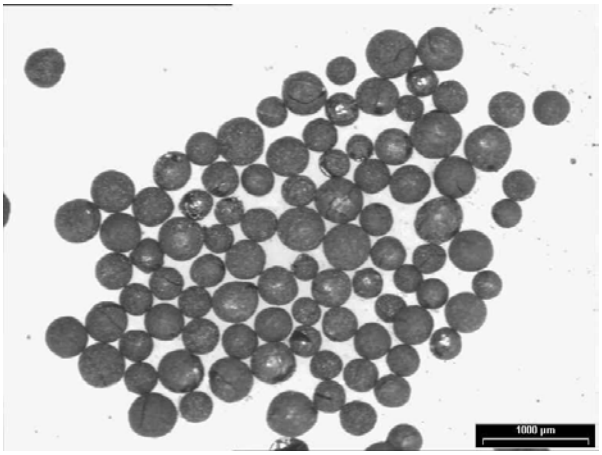


Figure 3.9 : UO_2 kernels after sintering step obtained with batch M (with vibrating device)

Figure 4.1 : Simple dropper dispersion unit in a glove box (left) and cold laboratory (right)

Figure 4.2 : Vibrating oriface dispersion unit

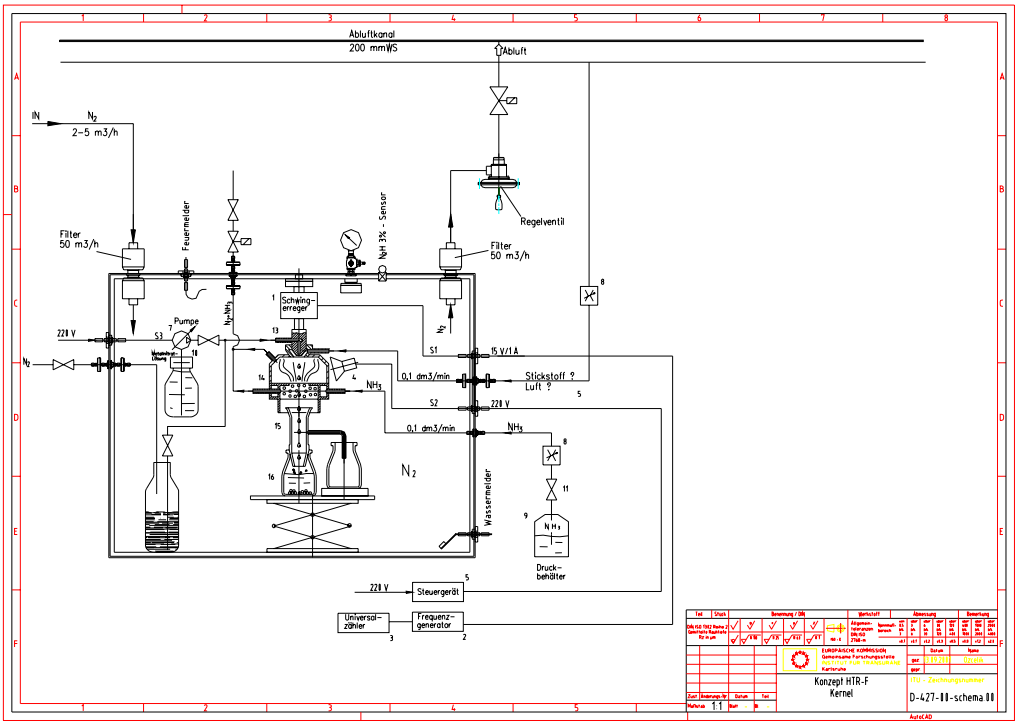


Figure 4.3 : Design of a vibrating oriface for glovebox applications

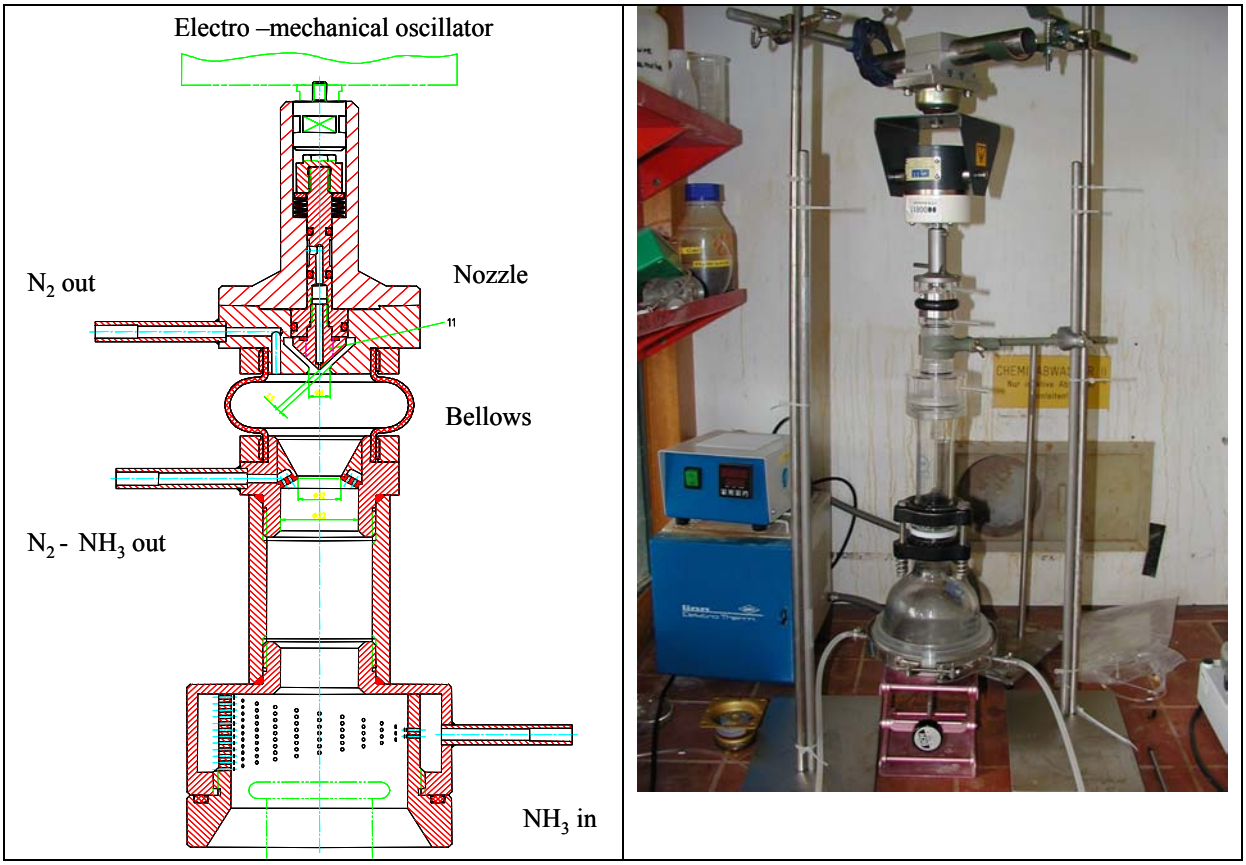


Figure 4.4 : Construction of a vibrating oriface for glovebox applications

Figure 4.5 : Azeotropic distillation unit

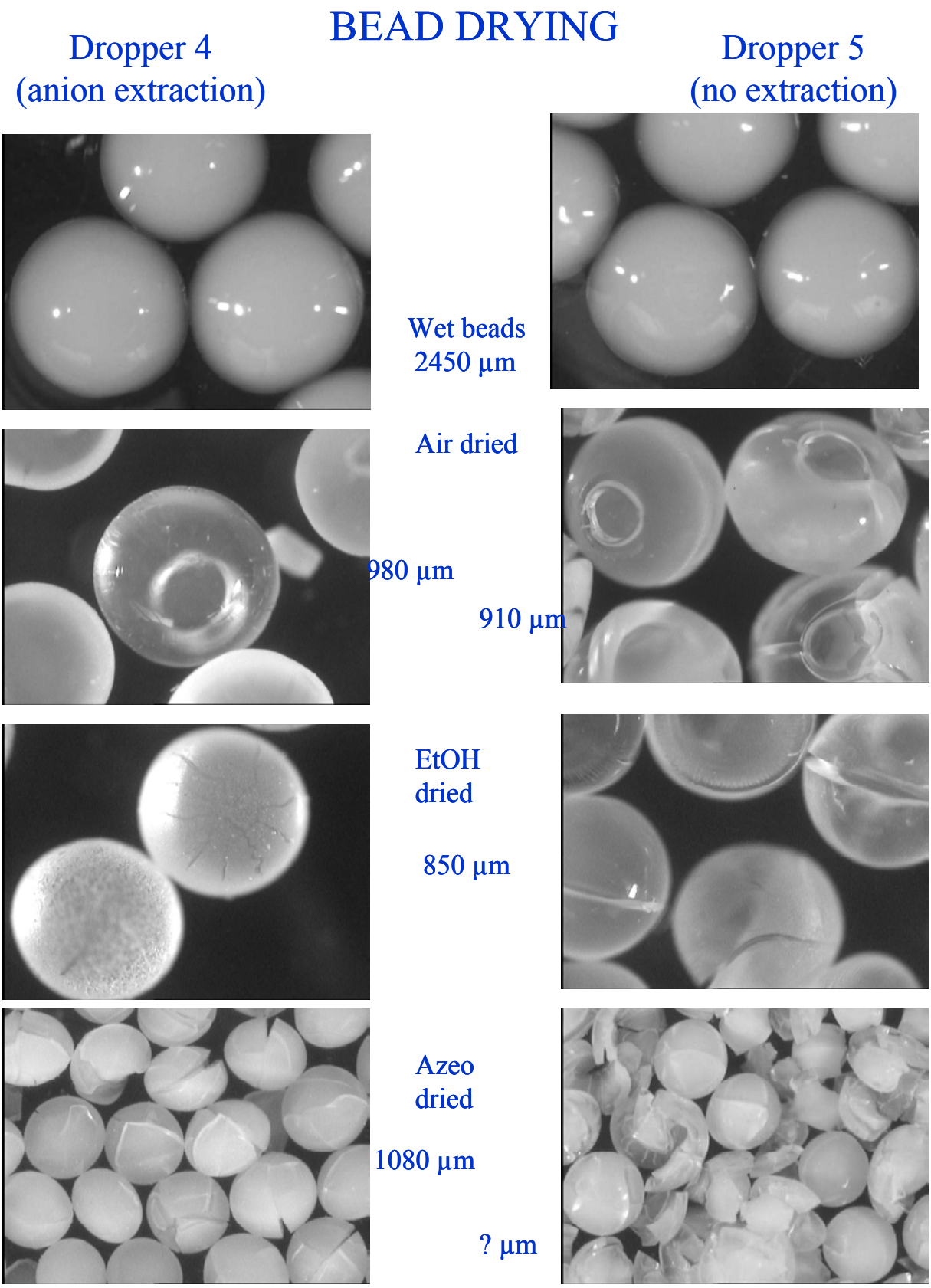


Figure 4.6 : HfO_2 kernel production

Figure 4.7 : UO_2 particles after azeotropic drying

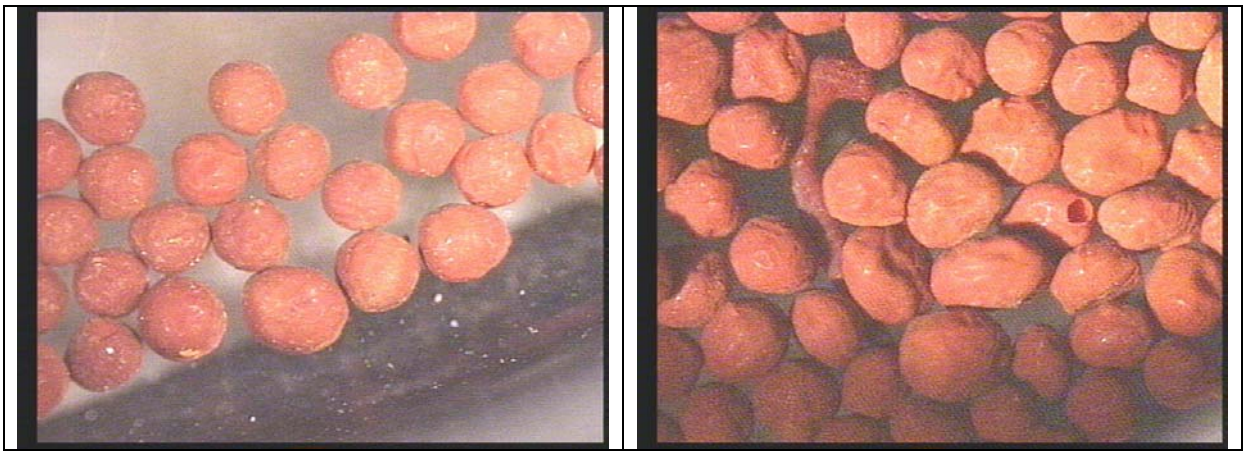


Figure 4.8 : UO_2 kernels following thermal treatment at 400 °C in air with normal ageing (left) and ageing with heat treatment (right)

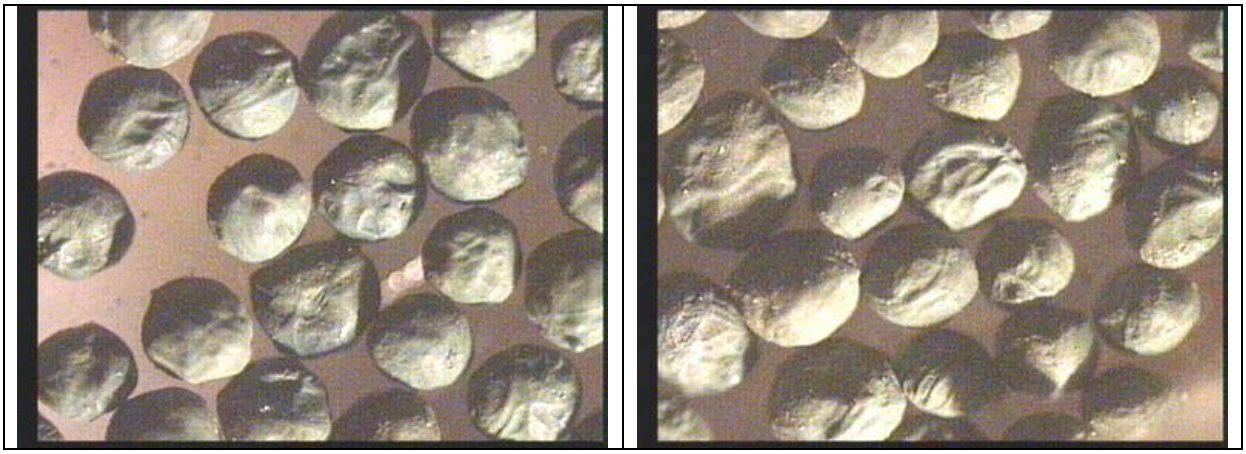


Figure 4.9 : UO_2 kernels following thermal treatment at 650 °C in air with normal ageing (left) and ageing with heat treatment (right)

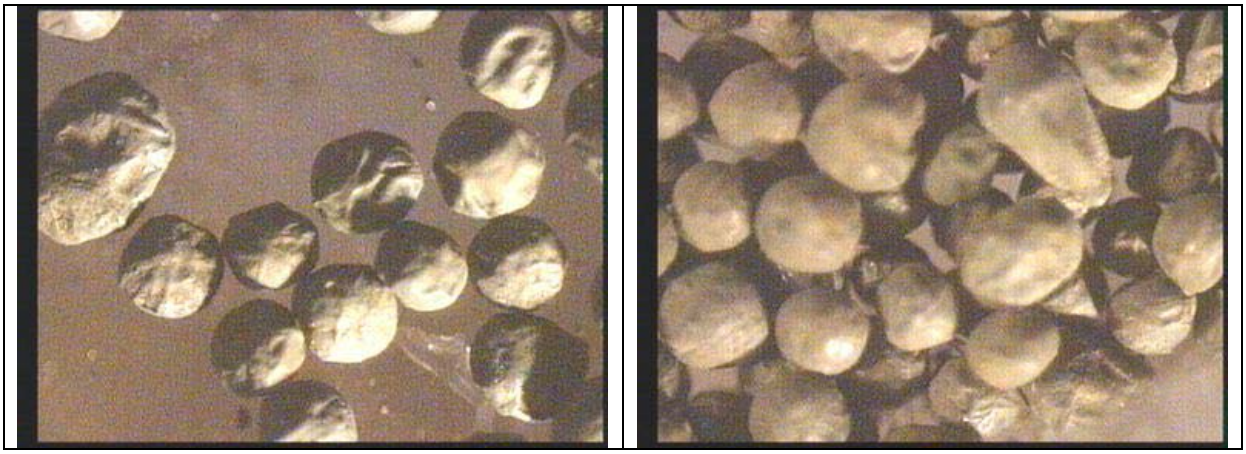


Figure 4.10 : UO_2 kernels following thermal treatment at 650 °C in Ar/H2 with normal ageing (left) and ageing with heat treatment (right)

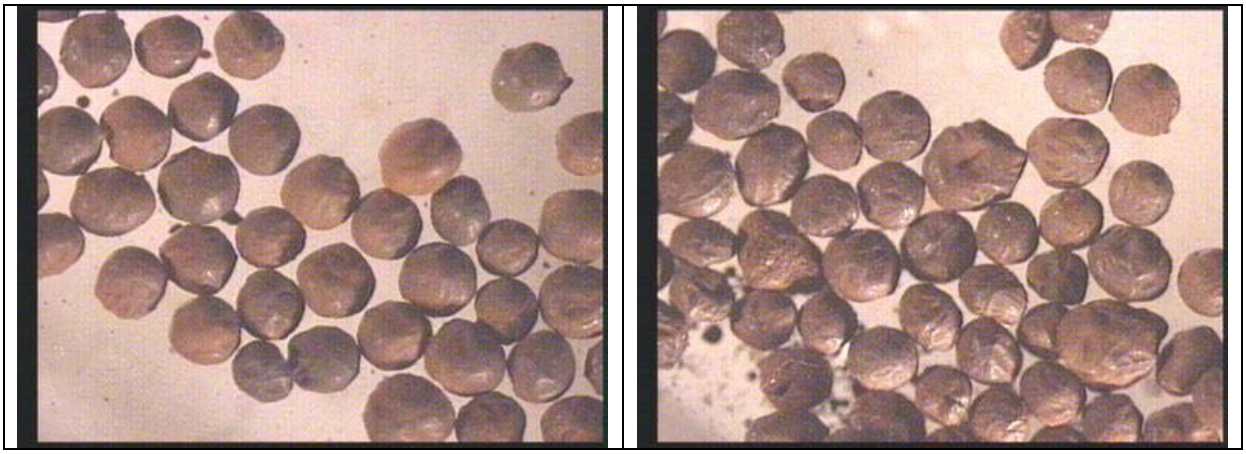


Figure 4.11 : UO_2 kernels following thermal treatment at 800 °C in Ar/H2 with normal ageing (left) and ageing with heat treatment (right)

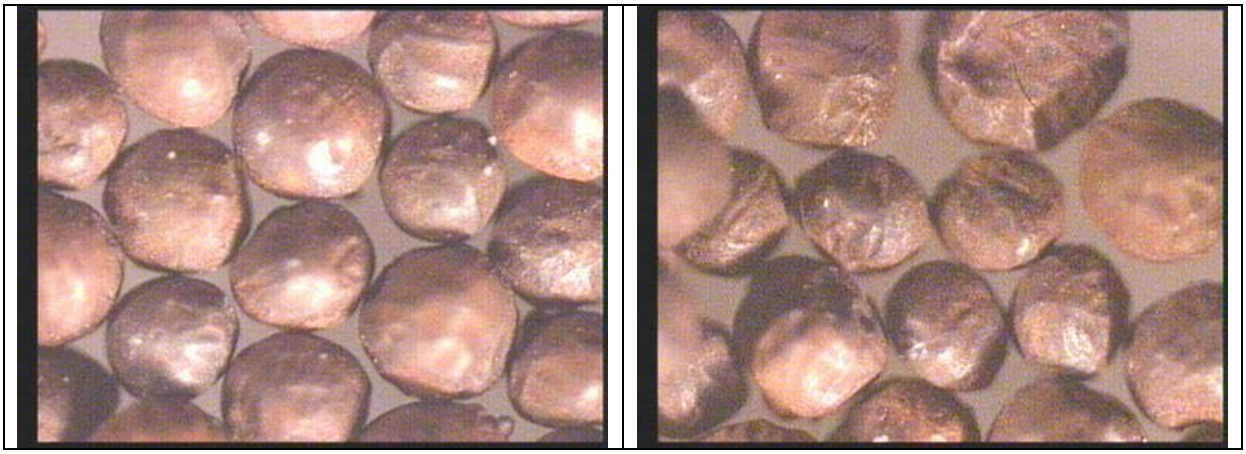


Figure 4.12 : UO_2 kernels following thermal treatment at 1500 °C in Ar/H2 with normal ageing (left) and ageing with heat treatment (right)