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Development of Internal Gelation MOX Kernel Production

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Development of Internal Gelation MOX Kernel Production

H. Hein, A. Zentz, Y. Martin Alvarez, A. Fernandez, J. Somers

Summary

Within the reporting period of the HTR-F1 project, the work at the ITU concentrated on the development of internal gelation process in the inactive laboratories. In this time two versions of an internal gelation system were developed. Both use oil as the heat transfer mechanism. The internal gelation process has one explicit advantage against external gelation in that there are fewer process parameters and it should be easier to translate production results from one chemical system to another. Its disadvantage lies in the use of a (hot) silicone oil carrier, which must be removed from the kernels in the later steps of the process. In this work, moderately good kernels of yttria stabilised zirconia were produced.

In a second part of these studies, first attempts were made to produce MOX kernels using the external gelation method. For this purpose plutonium dioxide powder was dissolved in concentrated nitric acid, and once dissolved was denitrated using a distillation process. The mixed plutonium uranyl nitrate feed solution was prepared by adding an appropriate quantity of uranyl nitrate solution. Process modifications were made in the gelation step. Contrary to previous studies hexamethylenetetramine (HMTA) was added to the external gelation broth to give an additional ammonia source. In addition a further innovation was deployed. Carbon black was also added to the feed solution to improve the shape and hinder cracks in the kernels. Promising results for future applications were obtained.

Table of Contents **Page**

1. Introduction

This report covers the deliverable number 4.1 of the HTR-F1 project supported by DG RTD of the European Commission under contract number FIKI-CT-2001-00150. Within Workpackage 4, the ITU and CEA have investigated three tasks concerning the fabrication of kernels. These were:

Task 4.1: Production development methods and MOX kernel production (JRC-ITU)
Task 4.2: Innovative Coatings (CEA)
Task 4.3: QC Methods (CEA)

This report corresponds to the contractual deliverable of task 4.1 and was performed by the JRC-ITU.

The production of kernels for HTR fuels can be achieved by two main wet chemical routes. Other routes based on melting or powder agglomeration were abandoned in the early stages of HTR fuel development, as they were not able to meet the stringent HTR specifications without considerable rejection (and recycling) of scrap kernels, which did not conform to the specifications.

Of the wet chemical routes methods, the Weak Acid Resin approach did not prevail in industrial application. In the end, industry, and also the research laboratories, concentrated on two gelation methods. In Europe and US, the industrial focus at NUKEM and General Atomics, respectively, was on external gelation. In this process, a concentrated metal salt is prepared in aqueous solution. It is thickened, and dispersed into droplets, which are collected in an ammonia bath. Following washing and calcination steps, the product is then sintered at high temperature (1600°C) to give the final product kernels.

The external gelation process has a large number of process parameters, whose interrelation is often difficult to follow. Thus, it is not obvious that a set of process conditions optimised for one chemical system (e.g. UO_2) can be transferred to another (even related) system such as MOX ($(U,Pu)O_2$). Thus, a simplification would be desirable. Potentially, this can be achieved by using the alternative internal gelation route, which was developed originally by KEMA in the Netherlands, but was much more widely used at both Oak Ridge National Laboratory (ORNL) in the US and the Paul Scherrer Institute (PSI) in Switzerland.

The internal gelation process contrasts the external gelation process in that the ammonia is generated internally in the salt solution droplet. The number of process parameters is considerably less, particularly due to the lack of polymer. Though attractive, the process is handicapped to some extent by the means in which the ammonia is produced, i.e. by the thermal decomposition of hexamethylenetetraamine (HMTA). The heat source is traditionally silicone oil into which the droplets fall. Its disadvantage is that it results in a cleaning step and an undesirable organic waste stream.

Within the HTR-F1 programme, the original task 4.1 was meant to investigate the production of ThO_2 and $(U,Pu)O_2$ kernels. Following contract signature, it was decided not to pursue the ThO_2 production, rather to replace this part of the task with studies on internal gelation process development. The reasons were twofold. Currently, there is little interest in Th based fuel in Europe. Secondly, internal gelation has particular attractions, especially when many other fuel chemical compositions are considered. Thus the project partners all agreed that the establishment of a European competence in this area (especially with the impending closure of the PSI laboratories) would provided considerably more added value to the project.

2. Gelation Processes

2.1 External Gelation

Within the external gelation process (see Figure 2.1), a metal salt is dissolved in water or acid, its viscosity is adjusted by the addition of a polymer (usually methocel or polyvinyl alcohol (PVA)). The resulting solution, often referred to as a "broth", is dispersed into droplets using a simple needle or a vibrating orifice. The latter increases output and can be used to tailor the droplet size to some extent. The droplets are collected in an ammonia bath and gelation occurs due to ammonia diffusion from the bath into the droplet, hence the term external gelation. In this process a droplet to particle conversion occurs as the nitrate is precipitated in a controlled way to give the hydroxide. Thus this process often has an alternative name – Gel Supported Precipitation (GSP) as the hydroxide precipitates in a structure defined by the polymer.

The resulting particles are washed in water, or weak ammonia solution. Thereafter, they are dried using alcohol or azeotropic distillation, before being calcined and sintered to give the final product.

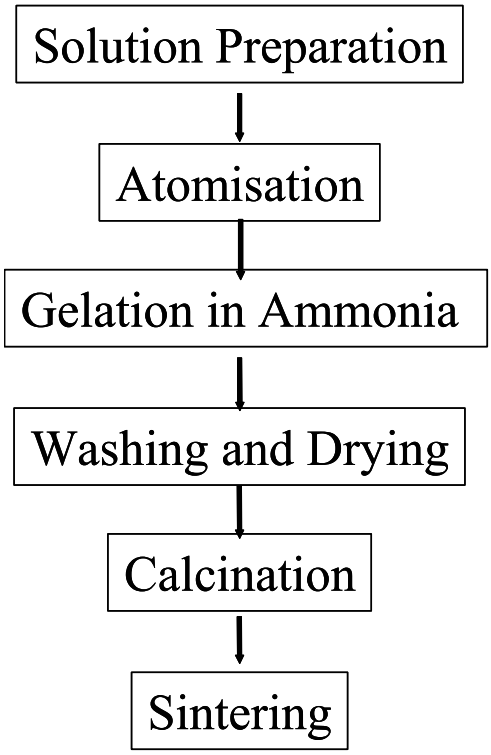

Figure 2.1: External Gelation process

2.2 Internal Gelation

The internal gelation process (see Figure 2.2) differs from the external gelation process in that the ammonia for the precipitation is generated internally in the droplet. This is achieved by the thermal decomposition of an organic precursor molecule – hexamethylenetetramine, or HMTA for short. There are variations of this process, some of which also require the addition of urea as a complexing agent.

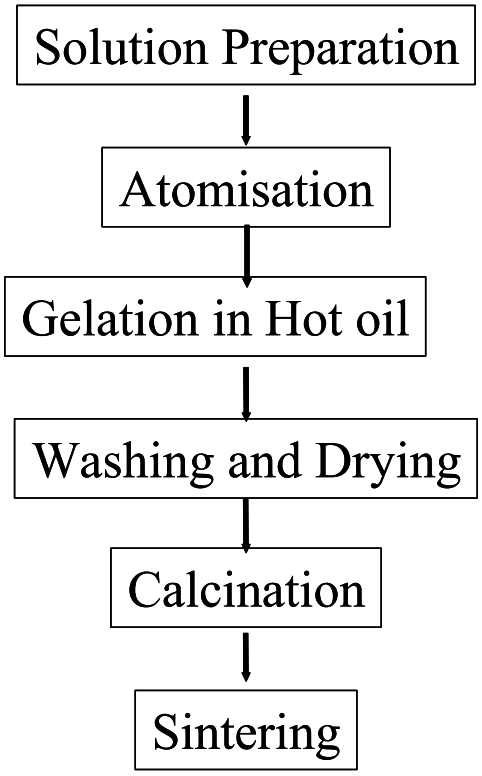

Figure 2.2: Internal gelation process

The process requires the production of a feed solution of the metal nitrate or chloride solution. To this, HMTA is added in the desired amount, taking account of the molar equivalent (or excess) of ammonia to be released. This solution should be made at relatively low temperature (ca. 5°C) to avoid thermal decomposition, even though its rate is far slower at room temperature than at 100°C.

The solution is then dispersed into droplets which are collected in hot silicone oil (ca. 100°C) which provides the heat to decompose the HMTA. The kernels are allowed rest in the hot oil to make sure the conversion is complete. Thereafter the kernels are removed from the oil, after it is cooled. An industrial installation might benefit from a continuous process, whereby the hot oil (with a lower viscosity) could be separated from the kernels.

The resulting kernels should be washed in water or perhaps dilute ammonia solution, after which they should be dried, either by thermal treatment, alcohol washing or azeotropic distillation. The particles are then calcined to remove organic residues and convert the hydroxide to oxide. Thereafter they are sintered to give the final product.

The main advantage of the internal gelation route lies in its simplicity compared to the external gelation route. This simplicity is due to the limited number of constituents. The main adjustment parameters are the metal concentration and HMTA / metal ratio in the feed solution. In addition it is a two phase system, whereby the sphericity of the particle is guaranteed. The generation of ammonia internally gives a homogeneous distribution of the metal hydroxide throughout the particle. In the external gelation process the attainment of a (relatively) homogenous material distribution is by no means straightforward, and eventually governs the quality of the kernel.

For the HTR-F1 programme, the tests were made in a relatively simple device shown in Figure 2.3. Oil was heated in a round bottom flask and from another reservoir it was added into an extension to increase the time in which the droplet falls to the bottom of the vessel. In addition tests were also made in alternative heat transfer media such as hot ammonia solution, and hot tertrachlorethylene.

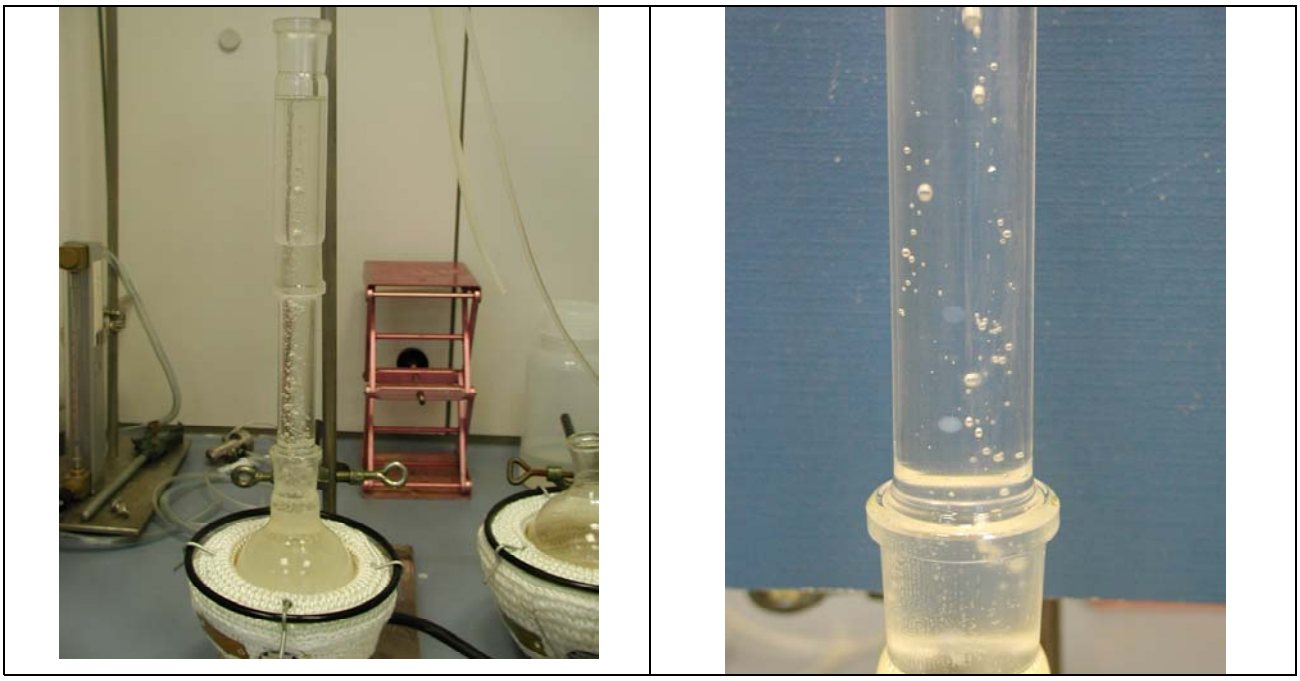

Figure 2.3: Basic internal gelation device

This simple device had a number of limitations. This included gas bubbles which continuously evolved as the oil is “boiled”. A much bigger problem was encountered due to the cooling of the oil by the solution as it was added. These observations led to the modification shown in Fig. 2.4. Here the oil is heated in a reservoir which is pumped from top to the bottom of the installation. In addition, the uppermost part of the installation is surrounded with a water jacket (90°C). These developments greatly assist in the generation of uniform particles throughout a given experimental run.

Figure 2.4: Modified internal gelation device

3. Results

3.1 Internal Gelation

3.1.1 Installation development

At present, two types of dispersion units are available in our cold laboratories (see Figures 2.3 and 2.4). The most uncomplicated dropper is a simple needle through which the feed solution is pumped slowly. The droplets produced are collected in a column of hot silicone oil. The simplicity and flexibility in construction and operation of this device are its main advantages. It is incapable, however, of producing particles with diameters less than 600 μm after sintering. The other device is in principle similar, but a vibration is applied to the orifice, through which the liquid passes. The frequency of vibration, the orifice diameter and the flow rate can be used to vary the particle size in the 100 – 500 μm range. Care must be taken, however, so that satellite droplets with different diameter are not produced. All results presented in this work have been obtained with the dropper unit.

A new installation has been designed and constructed (see Figure 2.4). The main modification is related to the column dimensions and the silicone oil heating. The new design guarantees a continuous flow of hot silicone oil, i.e. the temperature should be constant along the whole oil column length during the experiment. Moreover, the diameter of the column has been increased to avoid sphere agglomeration therein. The system can be adapted to both dropper and vibrating nozzle devices.

3.1.2 Selection of the HMTA/metal ratio

In these investigations the internal gelation process was tested for the production of yttria stabilised zirconia (YSZ) kernels. This is an alternative host material considered for the incineration of plutonium and minor actinides in thermal and fast neutron reactors.

First tests were performed with a high HMTA/Metal ratio (1.212). Independent of the heat transfer medium, no spherical particles were obtained. Moreover, the feed solution gelled spontaneously before dispersion, due to thermal decomposition of the HMTA even at and below room temperature. Secondly, tests with a lower HMTA/Metal ratio were performed (~0.604). Although no spontaneous gelation occurred before it was dispersed, the quality of the particles was poor, no spherical particles were obtained. Figure 3.1 shows YSZ particles obtained using both HMTA/M ratios (hot ammonia was used as heat transfer medium). Several tests were performed to improve the quality of the particles**.** The most promising results were obtained with a HMTA/Metal ratio of about 0.9. (All further tests use this value). Thus, the tests performed to optimise all other process parameters, such as heat transfer medium, drying, thermal treatment, were carried out with this HMTA/Metal ratio.

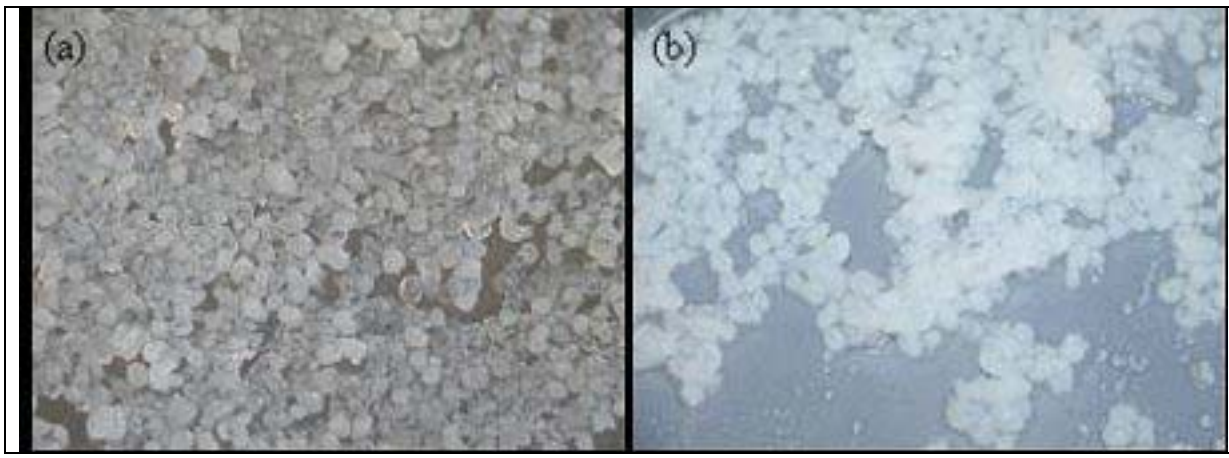

Figure 3.1:- YSZ gel particles after washing. Heat transfer medium:
NH_4OH 4M (a) HMTA/M= 1.20 (b)HMTA/M= 0.599

3.1.3 Effect of heat transfer medium

A key process parameter is the heat transfer source for the decomposition of the HMTA. Therefore, several tests have been performed to identify the best medium. Pictures depicting YSZ kernels synthesised by using warm ammonia, C_2Cl_4 vapour and silicone oil as heat transfer medium are shown in Figure 3.2.

Figure 3.2: Kernels and agglomerates obtained with different heat transfer medium: (a) warm ammonia 4M, (b) C_2Cl_4 vapour and (c) silicone oil.

Kernels obtained by dropping into an ammonia bath were not spherical and most of them were broken even before the washing and drying steps. Major problems were encountered by dropping into a hot C_2Cl_4 bath, as the kernels agglomerated[1]. Best results were achieved using silicone oil where spherical particles were obtained. Despite the good quality of the kernels obtained in the preliminary tests, two other silicone oils were tested. The physical characteristics are given in Table 1.

Table 1: Silicone oils used as heat transfer medium

Commercial Silicone Oil	Density ($g \cdot cm^{-3}$)	Viscosity* (cPs)
FLUKA	**0.973**	**320**
ALFA AESAR	0.963	50
MERCK	0.940	3703

*at room temperature

From the fabrication point of view the viscosity of the oils was the most important parameter. Low viscosity oils provoke lower residence times in the gelation column (column height 55cm) and some agglomerates were obtained in the collecting bath. This limitation could be solved by increasing the length of the column (which would be limited eventually by the glovebox dimensions). Kernels synthesised by dropping into high viscosity oils were difficult to wash even with hot distilled water. Best results were achieved with FLUKA Silicone Oil with a viscosity of 320cPs which allows enough residence time in the gelation column and the resulting kernels can be completely washed with hot water. Kernel quality is also highly dependent on the silicone oil used as is shown in Figure 3.3, which shows YSZ kernels fabricated with different silicone oils after sintering. Those kernels fabricated with the highest viscosity oil were cracked or broken.

[1] Planned installations in Russia use tetrachloroethylene as heat transfer agent for PuO_2 kernel production. In addition this method also is used in the US.

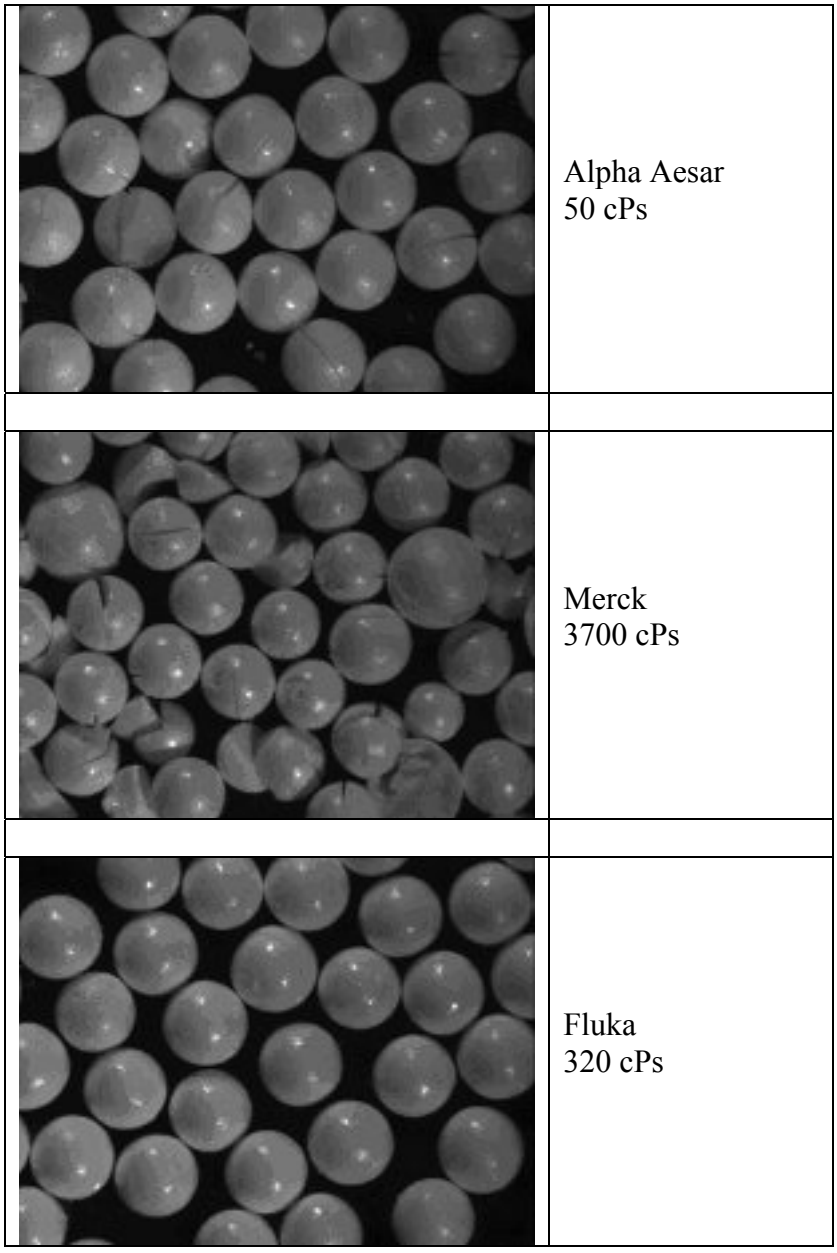

Figure 3.3: Sintered YSZ kernels collected in different heat transport oils

Considering all these factors (final quality kernels, difficulties on washing, etc) the FLUKA silicone oil was selected as heat transfer medium for the internal gelation process.

The effect of the drying step was also investigated. The results using ethanol and azeotropic distillation drying are shown in Figure 3.4. Both are very poor. In addition microwave drying was also investigated. A standards kitchen type device form Siemens was used. The results shown in Figure 3.5 demonstrate that this method is very favourable.

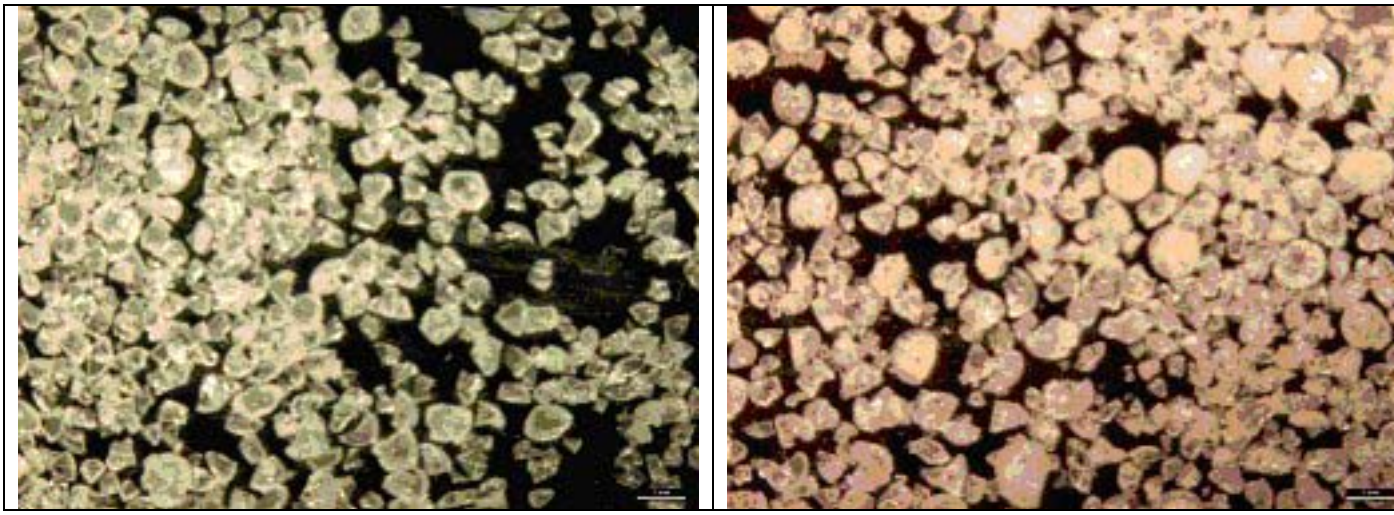

Figure3.4: YSZ kernels dried by azeotropic distillation (left) and by washing with alcohol (right)

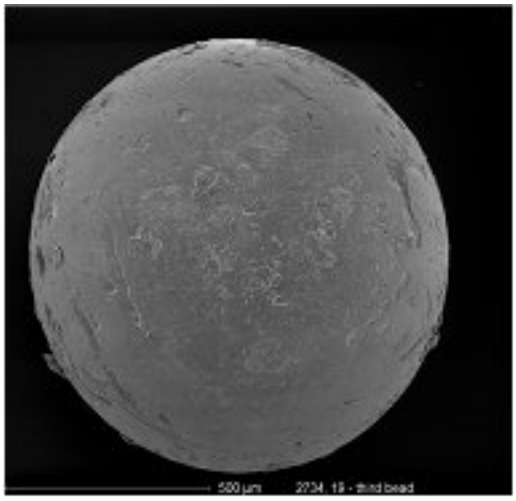

Figure 3.5: YSZ kernel after drying with microwaves

In the initial microwave drying studies, no cracks were observed in the dried kernels. Nevertheless, continued heating of the kernels dried in the microwave to 800°C results in cracks, most likely because the kernels were not totally dried before their calcination. A control test was made to determine the optimum microwave drying time. Therefore the kernels were dried for 1, 1.5 and 2 hours in the microwave. Afterwards a TG analysis was carried out to measure their weight loss when the temperature increases. The kernels dried for only 1 h shown an enormous weight loss of about 70%. This was reduced to less than 20% if the kernels were dried for 2 h (see figure 3.6). After calcining the latter kernels had no cracks. A longer drying period is not advisable, as it has been observed some remaining humidity is recommendable prior to their calcination. The drying methods tested in these studies indicate that best results were obtained by using the microwave. Azeotropic distillation and washing with ethanol resulted in completely broken kernels.

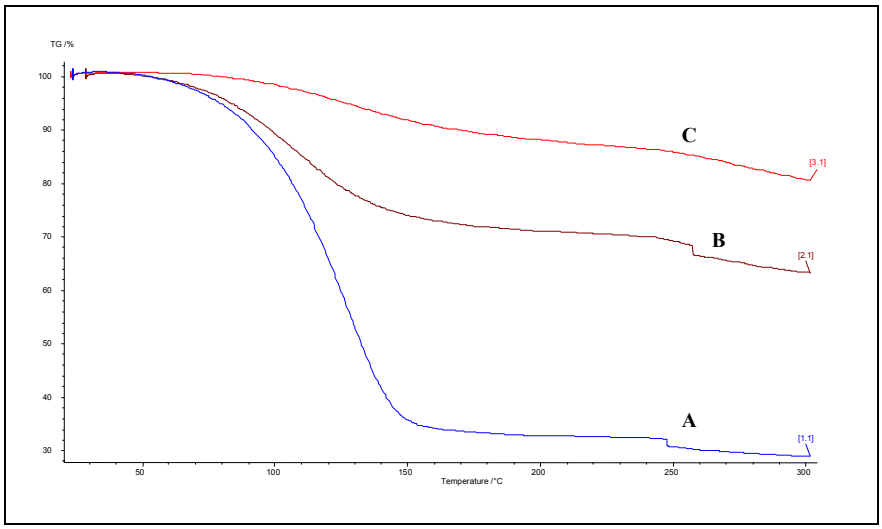

Figure 3.6: TG analysis of YSZ kernels (IG46) after (a) 1 h (b) 1.5 h and (c) 2 h heating in the microwave

3.1.4 Thermal treatments

A systematic investigation using TG/DTA analysis has been carried out on the "wet" kernels to determine the appropriate thermal treatment conditions. As an example a TG/DTA analysis is shown in Figure 3.7. The weight loss from room temperature to 120°C is attributed to desorption of absorbed water, which corresponds to an endothermic peak around 120°C. The further weight loss from 250° to 400°C is ascribed to the removal of hydroxide which correlates with the endothermic peak about 300°C. A strong exothermic peak around 420°C is consistent with the beginning of the formation of the YSZ phase. Considering these results the following calcination programme has been established (see Table 2).

Table 2: Derived calcination programme

	Preliminary tests	Optimised test
Heating ramp (°C/h)	20	50
Dwell temperature (°C)	80	350
Dwell time (h)	2	0.1
Heating ramp (°C/h)	50	20
Dwell temperature (°C)	800	600
Dwell time (h)	2	2

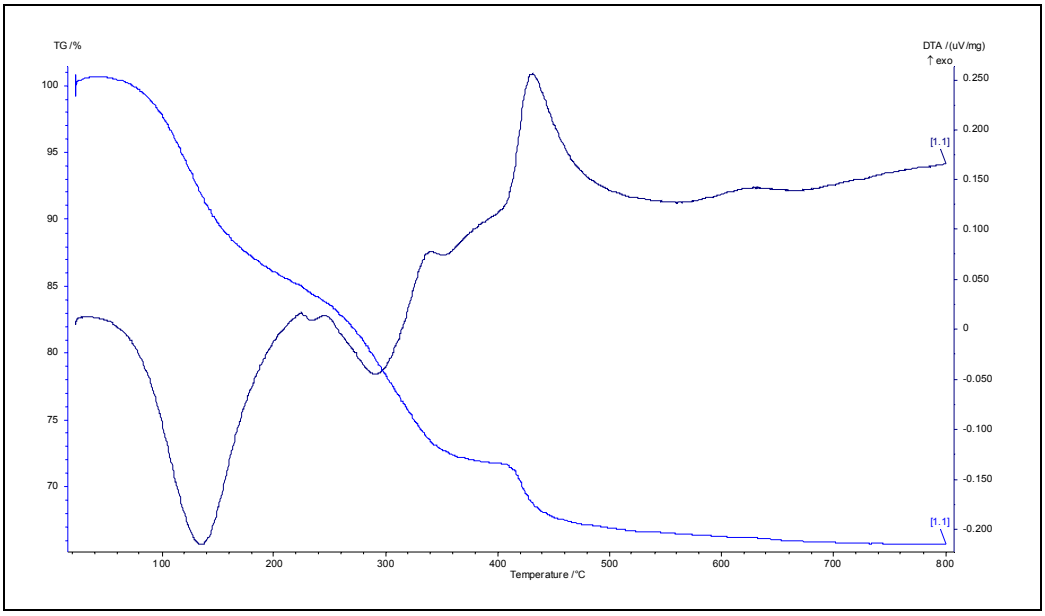

Figure 3.7: TG/DTA analysis on dried YSZ kernels

The typical (not optimised) heating conditions were used and pictures of YSZ kernels after drying with microwave for 1.5 hours, calcination at 800°C and sintering at 1650° under air are shown in Figure 3.8. The calcination step drastically affects the kernel quality. In this case kernels with no cracks following drying in the microwave were calcined at 800°C for 2 hours and a diameter reduction of about 20% was observed and although the kernels kept their spherical shape almost all kernels were full of cracks. These kernels were sintered at 1650°C for 2 h under air. This final thermal treatment had a beneficial effect on the kernel microstructure and an unexpected result was observed: most of the cracks were cured. Nevertheless they show slight cracks along quadrants of the spherical kernel.

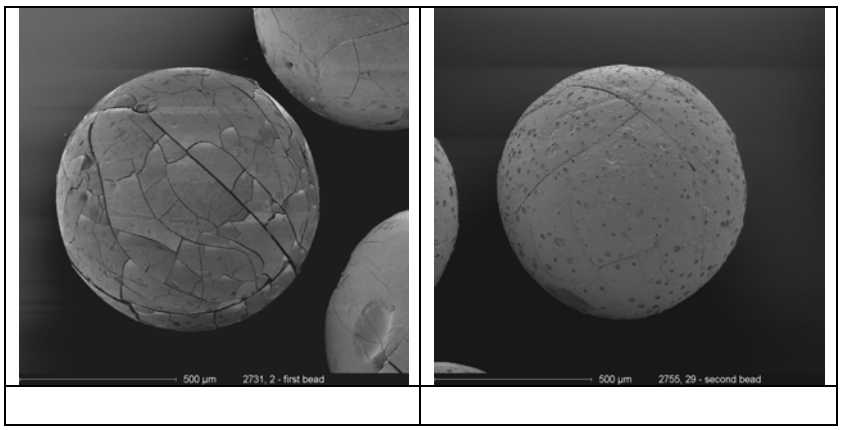

Figure 3.8: SEM photographs of YSZ kernels (IG46) after calcinations (left) and sintering (right)

3.1.5 Internal Gelation Outlook

The investigations made thus far lead to the following conclusions

- Good quality spherical YSZ kernels have been fabricated by the internal gelation process.

- The HMTA/Metal ratio is a crucial parameter. A value of about 0.9 was found to be optimal. Higher values provoke the spontaneous gelation of the broth solution and lower values produce non spherical kernels.

- Silicone oil is the best heat transfer source. The optimum silicone oil depends on the required residence in the gelation column. For the ITU installation, FLUKA Silicone Oil (320cPs) is the best.

- Gentle thermal treatments are required to avoid cracks on the kernels.

3.2 Tests on $(U,Pu)O_2$ Production by External Gelation

3.2.1 Plutonium Dioxide Dissolution

The plutonium used in these was taken from ITU reserves in the form of an oxide powder. The Pu isotopic vector is given in Table 3 below. The powder was placed in a teflon container and concentrated nitric acid (13M) was added along with a small quantity of HF. The plutonium oxide was dissolved by refluxing the solution in an installation shown in Figure 3.9. This process takes a long time[2] (several weeks – as it cannot be heated overnight for security reasons). It is particularly slow for this powder as its isotopic vector is high in ^{239}Pu and low in ^{238}Pu. The latter is present at a level of ca. 1.5% in reactor grade plutonium and it assists the dissolution by means of heat produced and to its α activity.

Table 3: Pu vector as analysed 31.12.2001 (1 GEN)

Isotope	Weight %
^{228}Pu	0.01
^{239}Pu	90.63
^{240}Pu	9.10
^{241}Pu	0.19
^{242}Pu	0.07
$^{241}Am/Pu$	0.82

[2] An industrial HTR MOX application would not require a Pu dissolution step. The Pu feed would be taken from the reprocessing plant, where it is already in solution form.

Figure 3.9: Pu dissolution (left) and denitration (right) facilities

Once the Pu was dissolved it was filtered and the supernatant liquid collected. At this stage the nitric acid concentration is very high, so that even by dilution with uranyl nitrate, it would remain too high. High acid content in the sol gel solution results in substantial formation of NH_4NO_3 in the kernels, which may not be adequately removed in the washing steps. Thus, should appreciable quantities be removed in the pyrolysis steps, cracking of the kernels could occur. To eliminate this undesirable effect, a denitration step was employed to decrease the level of free nitrate in the Pu solution. The solution was concentrated to circa 600 g/l and then water added to return the concentration to 200 g/l. This denitration step must be made with a certain care and diligence, otherwise the Pu nitrate has a tendency to polymerise and precipitate out of solution, when its concentration exceeds 250 g/l. This process was made over five days, with one denitration cycle performed per day. Simple titration of the Pu nitrate solution against ammonia solution was made. Eventually, the free nitrate was about 3M.

The solution was then analysed for its Pu content and then mixed with uranyl nitrate solution, which was prepared in parallel and whose concentration was already known. The Pu content was 18 mole%, i.e. Pu/(U+Pu) = 0.18.

3.2.2 Broth preparation

The "broth" is the feed solution in the external gelation process. The broth solution is prepared by mixing the metal/acid solution and the organics (methocel, THFA, triton, HMTA) just before drop atomisation. In some experiments a further production variant was chosen. HMTA was added to the broth solution to act as a further ammonia source through its decomposition as described above. Therefore when HMTA is added, two gelation sources are present, the ammonia bath where the droplets are collected (external gelation) and the ammonia produced by the decomposition of HMTA. The latter process modification should result in a more uniform gelation is expected. The HMTA is used in the internal gelation process, but in that case an external heat source (hot silicone oil bath) was provided for the decomposition of the HMTA. In this work the effect of the HMTA content (without a collection heat source), type and content of methocel, and the effect of carbon addition to the broth have been investigated.

3.2.3 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 at the ITU currently can have two forms. The most simple capillary was used here to break the liquid flow into droplets.

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 an ammonia gas column[3], which produces a shell on the droplet enhancing its stability as it collides with the surface of the ammonia solution. Furthermore, the severity of this collision can be reduced by the addition of a tenside agent to the ammonia bath to reduce its surface tension.

3.2.4 Ageing/Washing/Drying

The gelled kernels were aged for a suitable length of time to complete the reaction to form the hydroxide. This step is necessary to ensure that the kernels have sufficient time to complete their gelation. The kernels were kept in the ammonia bath overnight, before they are washed in distilled water to remove residual and ammonium nitrate (NH_4NO_3) from the particles, as its decomposition during subsequent thermal treatments can cause undesired cracking or rupture of the kernels.

The drying of the kernels 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 breakage or cracking does not occur. In this work different drying methods have been tested:

- washing the kernels in ethanol, which extracts water.
- an azeotropic distillation process, using tetrachloroethylene.
- simply allowing them stand in the air atmosphere of the glovebox.

[3] There was no deliberate addition of ammonia gas in these tests, but they were performed in a glove box. Thus there is always a considerable partial pressure of ammonia present in the glovebox.

3.2.5 Calcination and Sintering

Calcination of the kernels removes remaining organic compounds by pyrolysis. Typical calcination temperatures are between 600 and 800°C. This step is performed first under air and then under Ar/H_2 to reduce the uranium to U(IV), i.e. O/M =2.00.

Final sintering is achieved at 1600°C under an Ar/H_2 atmosphere. Slow heating ramps are required to avoid undue cracking of the kernels.

3.2.6 Effect of HMTA/Metal ratio

The ideal "broth" solution requires a careful adjustment of the metal and HMTA content in the solution. First the optimum ratio between metal and HMTA solution was determined. Indeed to obtain good quality spheres with a short residence time it is important to have a broth solution as close to the gelation point as possible. Table 4 lists the different tests performed to determine the best HMTA/Metal ratio. Process parameters investigated for each ratio are also indicated.

Table 4: Process parameters investigated at different HMTA/Metal ratios

Test N°	**HMTA** (%weight total solution)	Results
04SG029	0	*Kernels redissolve in the ammonia bath*
04SG028	1	Good kernels after dropping, Broken after drying
04SG030	2,5	Good spherical kernels
04SG031	5	*Good kernels some hollow kernels*

Independent of the HMTA content, spherical kernels were obtained during the dropping step. Nevertheless, kernels produced from a broth solution without HMTA where redissolved (or collapsed) in the ammonia bath. Figure 3.10 shows kernels obtained using an HMTA content of 1%wt. Although good quality kernels were obtained after washing with distilled water, some kernels broke during the drying step. Several tests were performed to improve the quality of the particles. The most promising results were obtained with a HMTA of about 2,5 %in weight . Thus, the tests performed to optimise all other process parameters, such as, drying, thermal treatment, were carried out with this HMTA content.

Figure 3.10: - Kernels after dropping (right) and after washing with distilled water (left).

3.2.7 Effect of carbon addition

The influence of the carbon addition to the broth solution has been also investigated. Normally carbon is added to the sol gel feed solution for the preparation of carbides or nitrides, where a little more than 2 times the molar content of the metal is required. At the ITU, processes are also being developed to control the porosity of the sol gel particles. The carbon addition gives good results in the production of PuO_2 kernels with the rotating cup device (small kernels with a polydisperse (50-150 μm) size distribution). In a chance observation, it was found that carbon addition not only increased the porosity of the kernels, but also improved their form (sphericity and significant decrease in the number of cracks). A key process parameter is the carbon content. Therefore, several tests (see Table 5) were performed to identify the best carbon content. Pictures depicting MOX kernels synthesised by using a broth solution with 80gC/l are shown in Figure 3.11. Though not yet meeting the HTR specification, significant advances have been made.

Table 5: Kernels produced with addition of carbon powder to the broth solution

Batch N°	Carbon content (gC/l)
04SG043	10
04SG044	80
04SG045	40
04SG051	10
04SG052	20

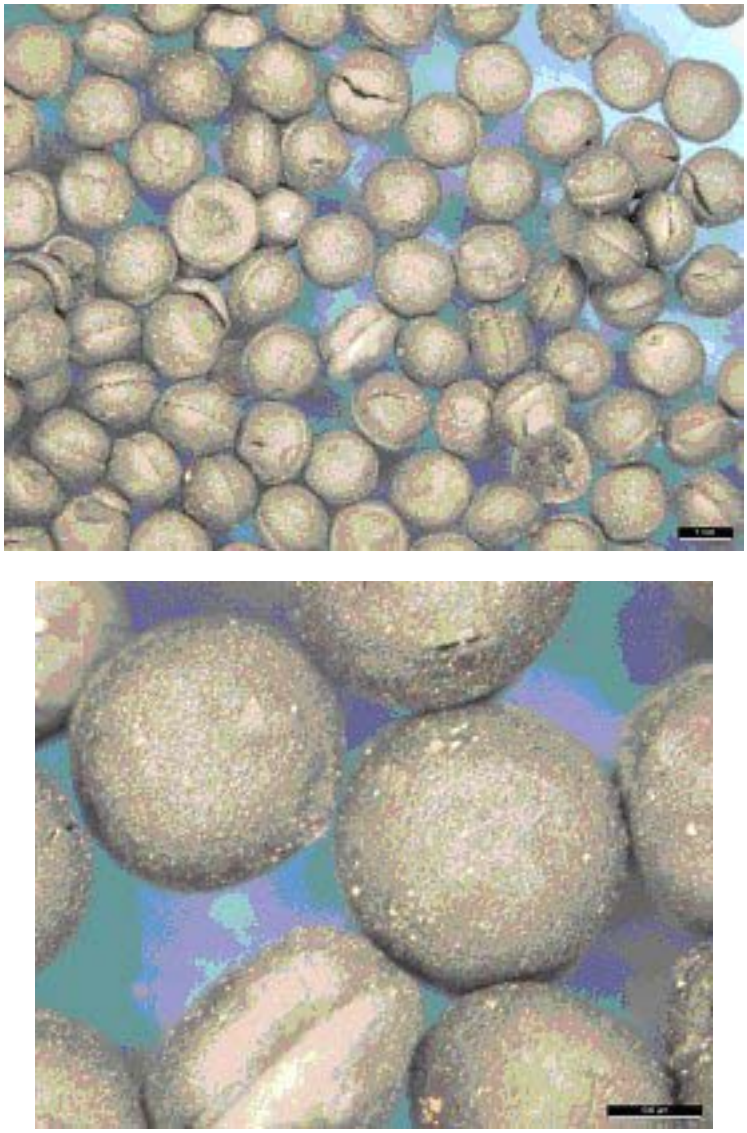

Figure 3.11: Kernels produced from a broth solution with 80gC/l.

3.2.8 Effect of the drying method

The aim of this set of studies was to determine whether or not there is a significant difference in kernel quality depending on the drying method. In this study different drying methods has been tested: azeotropic distillation, washing with ethanol and drying under air. Conventional (ITU) drying by azeotropic distillation (C_2Cl_4) or by washing in alcohol results in broken kernels. Drying under air improves the kernels quality but some holes were still present. Best results were obtained by drying by azeotropic distillation with a very slow heating ramp, also during boiling a gentle heating is recommendable. The kernels in Figure 3.11 were produced in this way.

3.2.9 Outlook for MOX kernel production

The investigations made thus far lead to the following conclusions

- The HMTA/Me ratio is a crucial parameter. A value of about 2.5%in weight was found to be optimal. Higher values provoke spontaneous gelation of the broth solution and lower values produce non spherical kernels.
- Gentle heating during the azeotropic distillation is required to avoid cracks.
- Gentle thermal treatments are required to avoid cracks on the kernels.
- Further R&D is still needed to produce kernels meeting HTR specifications.

4. Conclusions

Internal gelation offers several advantages for the production of kernels. In particular there is a restricted number of chemical process parameters to be adjusted. Good quality yttria stabilised zirconia spheres were produced. The major drawback of the process is the use of the silicone oil as a heat transfer medium. Although this was mastered at PSI for MOX production (albeit for kernels meeting SPHEREPAC fuel specifications), the process application within a glove box environment is by no means straight forward. Alternative approaches such as the use of microwaves as a heat transfer medium are worthy of a more detailed investigation.

Significant progress has been made in the production of MOX kernels. Addition of HMTA to the feed solution can assist in the gelation process. The drying steps need much care and attention. The azeotropic distillation process works best, but the heating rates must be slow and boiling gentle to avoid collisions between kernels that result in their destruction.