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Review on Kernel Fabrication Processes

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SUMMARY

Within Work Package 4 (Fuel Fabrication) of the HTR-F Shared Cost Action (Fuel Technology) a project supported in the 5th European Union Framework Programme, the retrieval of past knowledge and deployment of kernel fabrication and coating facilities is foreseen. .

This document retrieves past information on kernel production and has been prepared by the Commissariat à l'Energie Atomique and the EC-JRC Institute for Transuranium Elements. It constitutes a significant contribution to Work Package 4 and is in fact deliverable number 15 of the HTR-F project.

This bibliographic review on kernel fabrication processes covers the beginning of the studies on HTR at the end of the 1950's and culminates in the latest studies at the end of the 1990's.

In a general approach, it covers the manufacturing of spherical particles of actinide compounds, not only in the HTR field, but also for other fuel forms such as for the consolidation of fuel by vibrocompaction.

For the industrial production of fuel kernels, the gel supported precipitation (GSP) is most favourable and was used by both General Atomics and NUKEM for the industrial production of kernels, but embarking on a programme to repeat previous achievements is fraught with difficulties, as key process parameters are not openly available.

EVALUATION, RECOMMENDATIONS AND OUTLOOK

At the heart of an HTR fuel element is the kernel containing fissile material, which is then enrobed in either two (BISO) or three (TRISO) coatings, which serve as a barrier to the release of fission products during and after irradiation. These coated particles are then assembled in a compact of spherical or cylindrical form, before being loaded in the reactor.

Since the beginning of HTR development a number of routes have been considered to produce such kernels containing the fissile material. One of the first methods used was powder agglomeration for the production of fuel for the DRAGON reactor. At General Atomics particle fusion involving the melting of and cooling of a fuel mixture was used to produce the kernels. Though both of these process were implemented with moderate success, they were later abandoned in favour of wet chemical processes.

The most important wet chemical processes had numerous variations, but were based around three common themes, which were

- the WAR (Weak Acidic Ion Exchange Resin) process developed at ORNL and CEA,
- the external gelation processes developed at KFA, Jülich, AERE-Aldermaston, Agip Nuclear in Italy, General Atomics in the USA and NUKEM in Germany, and
- the internal gelation process developed originally by KEMA, ORNL and KFA Jülich and subsequently at PSI in Switzerland.

Of these the WAR process is no longer considered. The internal gelation process could be feasible but has never been demonstrated at an industrial level. Here the metal (U,Th,Pu) nitrate feed solution is maintained at low temperature and contains urea and HMTA (Hexa-Methylene-TetrAmine) and is dispersed into droplets. Following their collection in a hot oil bath, gelation occurs due to reaction with ammonia released internally by the thermal decomposition HMTA. Washing, drying and sintering steps are required to obtain the final product. This process will probably be used in the Russian GT-MHR programme for the disposal of military plutonium. An interesting innovation, whereby heat to decompose the HMTA was supplied by microwaves rather than by a hot oil bath, was initiated, but not fully developed, by PSI. It deserves further attention if this process were ever to be considered at an industrial level.

For the industrial production of fuel kernels, an external gelation process known as gel supported precipitation (GSP) is most favourable. NUKEM and General Atomics used this process until the end of the 1980s. It is now used for the production of fuel for the Chinese HTR10 and Japanese HTTR reactors, and is planned in the South African PBMR programme.

The GSP process is based on the production of a metal (U, Th, Pu) nitrate feed solution, with the desired chemical and isotopic composition. This solution can be depleted in nitrate counter anion, and its viscosity is increased by the addition of polymers, e.g. polyvinyl alcohol (PVA), or Methocel. This solution is then dispersed into droplets, which are then gelled at the surface by contact with gaseous ammonia, before being collected in an ammonia bath, where bulk gelation occurs. Following ageing, and washing and drying steps, these particles are calcined and sintered to give the required dense final product.

Although the GSP processes are documented in the open literature and in published patents, the intrinsic process parameters are never mentioned. Denitration of the feed solution certainly should assist the droplet to particle conversion process, as surface gelation of the droplets by ammonia gas should occur more rapidly. In addition a more homogeneous gelation can be expected throughout the particle and possible shell formation avoided. Heating the feed solution not only facilitates the flow of the feed solution, but also droplet

formation. The metal concentration also has a significant influence on particle formation, and though not always specified, typical values are in the 150 – 250 g/l range. In the literature concentrations of PVA are often given, but this is a generic name covering many products. There is a considerable size reduction during the drying and calcination steps and this is influenced by the solution parameters as well as by the drying methods and thermal treatment steps. The SNAM process used an azeotropic distillation method, while NUKEM favoured drying with isopropanol, followed by thermal treatment at 80 °C under reduced pressure. Finally the calcination process must also be controlled and rotary kilns with stepwise temperature increase were constructed to keep the kernels moving, while maintaining high mass flow.

The standards have been firmly set by the achievements of NUKEM production campaigns in the 1980's, and will probably not be reproduced easily. Nevertheless, there may still be scope for process innovation. It could be advisable to avoid the use of isopropanol in the drying step, due to fire risk. This might be achievable, for instance, by using microwaves, a method sometimes used in ceramic industries.

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1 - INTRODUCTION

Presently, at the international level, there is a clear renewal of interest in High Temperature Reactors (HTR) moderated by graphite and using the helium as coolant. This resurgence is partly due to the technological progress achieved in the gas turbine domain, and for the possibility offered by HTRs to construct small modular units (100-300 MW_e). This allows the development of economically competitive concepts with inherent safety characteristics.

In this context, several partners within Europe have joined together to regain knowledge on HTR Fuel Technology. This is the purpose of the Shared Cost Action called HTR-F in the 5th European Framework Program.

The first stage in the manufacture of the fuel is the production of kernels, i.e. particles of fissile matter (or fertile, if such a cycle is considered) coated with different protective layers, which ensure tightness during irradiation.

The object of this document is the bibliographic synthesis of fabrication processes for HTR kernels, to make a balanced review of work performed, and to make proposal for future (industrial) developments.

This document is the contribution of the Commissariat à l'Energie Atomique and the EC-JRC Institute for Transuranium Elements to the Work Package 4 numbered as deliverable number 15 of the project.

In the first part of this document, the main features of the HTR fuel are recalled and certain definitions are provided. The following chapter reviews the historical progress of the processes since the beginning in the 1960's, which gives not only an evolution of the work, but also identifies ties between them. Thereafter each of the processes are classified and described by category. Finally, possible choice for future realisation of research and development or industrial facilities is concluded.

NB: For simplification, mixed compounds are noted without indication of the stoichiometry e.g. $ThUO_2$.

2 - FEATURES OF HTR KERNELS / DEFINITIONS

The HTR acronym is used in a general way to designate reactors based on particle fuel, moderated by graphite, cooled by helium and functioning at high temperature. The temperature at the centre of the fuel kernel is the order of 1100 to 1300°C and the exit temperature of the coolant gas is 750 to 950 °C [BEC77, MOR83, BAS93, IAEA97]. Other abbreviations often used include HTGR for High Temperature Gas Reactor or GT-MHR for Gas Turbine Modularised Helium - Cooled Reactor. A list of terms, abbreviations and acronyms is given at the end of the document.

Generally, the fuel for the HTR is constituted of fissile (and/or fertile) particles about 1 mm in size, dispersed in a graphite matrix through which the gas coolant circulates. The gas coolant used is nearly exclusively helium, due to its neutronic transparency, chemical inertia and its good thermal properties.

Two types of fuel were developed to the industrial prototype stage [BEC77, MOR83, BAS93, IAEA97]:

- **Compact Fuel**, developed mainly by General Atomics (GA) for the Fort-Saint-Vrain (FSV) reactor in the USA;

- **Pebble Fuel**, developed notably by the HOBEG (Hochtemperatur-Reactor-Brennelement G.m.b.H.) company in Germany for the THTR reactor in Schmehausen.

In the GA concept, the fuel is formed of hexagonal prismatic blocks of about 800 mm in height and 360 mm in (face to face) section (cf. **appendix 1**). These blocks are manufactured from graphite. Channels are pierced parallel to the major axis, either for the circulation of the helium coolant, or for insertion of the compact with the fissile material. The compacts themselves are small cylinders of graphite about 50 mm in height and with a diameter of about 10 mm. In these compacts, the fissile (or fertile) matter is dispersed in the form of spherical particles about 1 mm in diameter. Each compact contains about 7 000 such particles.

In the second case (German concept), the kernel is formed of graphite pebbles containing the fissile matter loaded directly in the reactor. The helium coolant circulates in the porosity between the pebbles. Pebbles are spherical in shape and have a diameter of the order of 60 mm (cf. **appendix 2**). They are composed of a matrix in graphite in which particles, similar to the compact concept, are dispersed. A pebble contains about 12 000 particles.

Each of these technologies presents advantages and disadvantages (e.g. [BEC77, MOR83, BAS93, IAEA97]). Briefly, the pebbles permit a continuous loading and discharge of the fuel, whereas the prisms and compact concept permits a better management of the reactor core [IAEA97].

Whatever the reactor design, the fuel is based on particles dispersed in graphite (cf. **appendix 3**). These particles are constituted of a kernel coated with several protective layers based on pyrocarbons (PyC) or silicon carbide (SiC).

The first type of particle was developed for the experimental reactor Peach Bottom in the USA, but tested also in the experimental European reactors: DRAGON [DRP78, IAEA97] and AVR [IAEA97]. This BISO particle is composed of the fuel kernel with a diameter of a few hundred of microns, coated in two layers of pyrocarbon, each a few tens of microns thick. The inner layer is porous and gives a free volume for the fission gases and creates a buffer zone for the outer pyrocarbon layer, which has a high density (close to the theoretical 2.26 $g.cm^{-3}$) and hinders fission gas release.

In order to improve the tightness of the coating, a second type of particle was developed, first for the DRAGON project. This **TRISO particle** is composed of an internal porous layer of PyC, a dense PyC layer, a SiC layer and finally a dense PyC layer. The thickness of the layers is always of the order of a few tens of microns.

The fuel was originally constituted by UC_2 kernels. Oxy-carbide (UCO) was also considered. These products may have an interesting behaviour in the reactor, but they pose severe problems due to their pyrophoric nature. **Today, mainly oxides are considered**.

The choice of the fuel kernel also depends on the considered fuel cycle.

In the DRAGON project, although different configurations were tested, the reference fuel was lightly enriched uranium (LEU) with a ^{235}U content between 6 and 10%. The particle was of the TRISO type, with a UO_2 kernel about 800 µm in diameter.

In the case of Peach Bottom (experimental reactor) and Fort-Saint-Vrain (industrial prototype), the heterogeneous thorium cycle was implemented. The fuel was formed of fissile TRISO kernels and fertile BISO kernels. The TRISO kernels were small (200 µm for Peach Bottom and 350 µm for Fort Saint Vrain) and composed of highly enriched uranium (HEU) (93% ^{235}U). The BISO kernels were larger (500 µm) and composed of thorium. Uranium and thorium were in carbide, oxy-carbide or oxide forms.

In the case of the German projects AVR (experimental reactor) and THTR (industrial prototype), the homogeneous thorium and uranium cycles were considered. The fuel was mixed oxide kernels of uranium and thorium ($ThUO_2$). The particles were initially of the BISO type and had a kernel size of 400 µm. The uranium enrichment was high (93%) and the $Th/^{235}U$ ratio was 5 for the AVR and 10,76 for the THTR [HUS73]. Eventually in the final German concept at the beginning of the 1980's, HEU and Thorium cycles were abandoned, and only LEU (<20% ^{235}U) TRISO particles with a kernel diameter of about 500 µm were used.

The different fuel types studied show the spread of possibilities for HTRs. The principle of the TRISO particles is well established, and it presents a very good resistance to fission gas release. The coating principle using the fluidised bed technique is also well established, even though further optimisation and development may remain, e.g. use of ZrC instead of SiC, for higher temperature and burn-up of the fuel.

The porosity of the kernel can be adjusted to create a complementary free volume to the inner PyC to accommodate fission gases (e.g. DRAGON fuel has a porosity between 5 and 20%). Nevertheless, this operation is not specific to the development process. It can be achieved while adding a pore former or adjusting the kernel's sintering cycle. The difficulty is rather to get kernels whose density is close to the theoretical density.

Today, the thorium and HEU cycles are abandoned. In recent projects [IAEA97, MCE01], the reference kernel is essentially a **dense spherical particle of uranium or plutonium dioxide**. This report is concerned with processes to produce such materials.

Also within the HTR-F programme past information has been drawn together to establish specifications, which should be achieved for new fuel production campaigns either for R&D or industrial purposes [GUI01].

3 - HISTORIC OF DEVELOPMENT PROCESSES

The beginning of particle fuel development is difficult to define, because preliminary work were not always published in the open literature and the laboratories were often involved in many fuel projects (HTR, vibropacked fuel…). For the HTR fuel, it appears to be around 1957 both in the UK and USA [DPR78].

3.1 Period 1957-1970: Survey of processes

In England, work on the development of the HTR kernels started at the **AERE-Harwell** (Atomic Energy Research Establishment) in the frame of the **DRAGON** project [DRP78], which ran between 1959 and 1976. This was a European wide, but piloted by the UKAEA (United Kingdom Atomic Energy Authority). An experimental reactor and an installation for fuel manufacture were constructed at Winfrith in England. The HTR technology was an evolution on that initiated for the Magnox reactor and was continued with the AGR (Advanced Gas - Cooled Reactor) [SAU65]. AERE concentrated on the coating process [CAR63], whereas Springfields laboratories (RFL: Reactor Fuel-Element Laboratories) worked on the development of kernels, initially intended for the AGR reactor and, then later for the HTR programme [ALL77]. The fabrication process was based on **Powder Agglomeration** of uranium dioxide and carbon to form kernels of uranium carbide (cf. § 5). At the same time, the DRAGON project also financed studies on this same type of process at the MOL research centre in Belgium [GOR63].

In the USA, HTR development work began in the laboratories of General Atomics (GA), a company created in 1955 for the development of the HTR, and in Oak Ridge National Laboratory (ORNL).

Studies made by **GA** were published mainly in internal reports, and are not easily accessible. The process initially involved a heat treatment at high temperature (superior to 2500°C) of a powder mixture of carbon and oxides of thorium or uranium and a fusion of the dicarbide formed [RAG63]. This **Fusion process**, otherwise called V.S.M. for Vanek-Smith-Miertschin [MOR83], was used for the manufacture of kernels for the Peach Bottom reactor (cf. § 6.1).

Studies published in the beginning of the 1960's by **ORNL** concern spherical particle development for vibropacked fuels [FER61]. The first studies concerned the development of thorium oxide and uranium/thorium mixed oxide spheres by a **sol-gel process** (cf. § 4.3).

Also, at the beginning of the 1960's, work on the development of spheres using sol gel were published by W.R. GRACE & Co. in the USA and by the **KEMA** research centre (Keuring sieve Electrotechnische Materialen Arnhem) in the Netherlands (cf. § 4.3).

The W.R. GRACE & Co. published its findings exclusively in the form of patents [BAR60, HUR61, FIT62, FIT69]. They were concerned with the development of particles for vibropacked fuels and stable sols for aqueous homogeneous reactors. Nevertheless, this work was not pursued, and the aqueous homogeneous reactor technology was abandoned [SAU65].

KEMA studied the development of thorium, uranium (and other actinide) sols, in the 50's and 60's for a research reactor at Arnhem also operating using the aqueous homogeneous reactor technology [DEB55, HER58, HER64]. Even though this technology was abandoned, the work of KEMA continued during 1960's in the frame of an agreement with the DRAGON project. KEMA's objective was the manufacture of HTR uranium and thorium oxide kernels by a sol gel process [DRP78]. The KEMA work was important, as it was the origin of the internal gelation process using HMTA (Hexa-Methylene-TetrAmine), subsequently used by many other laboratories (cf. § 4.5).

During the 1960's, the DRAGON project made agreements with other European laboratories to study the development of HTR kernels, in particular with the Italian nuclear research organisation CNEN (Comitato Nazionale per the Nucleare Energia) and the Belgonucléaire society. **CNEN** was assigned the study of fuel reprocessing aspects in parallel with fuel manufacture, while Belgonucléaire concentrated on the development the plutonium based particles [DRP78, PRI68]. In France, **SFEC** (Society French of the Catalytic Elements) and the **CEA/DMG** (Department of Metallurgy at Grenoble) manufactured kernels for the DRAGON reactor, using the Powder Agglomeration process developed at Winfrith.

3.2 Period 1970 -1980: Industrial development of reference processes

At the end of the 1960's, many investigations had been made on sol gel processes (cf. § 4.3). These investigations were presented notably in the international symposia mentioned in the references [CNE67, IAEA68]. Nevertheless, even though a pilot installation had been constructed by ORNL, no installation had been developed at an industrial scale. One of obstacles to this development was the sol preparation, which is difficult and complex (cf. § 4.3.1).

At the beginning of the 1970's, the **pseudo sol-gel processes GSP** (Gel Supported Precipitation) appeared in international publications (cf. § 4.4). These processes were studied and patented toward the middle of the 1960's [BRA64, DRE67], but diffusion in the open literature occurred at the beginning of the 1970's, notably at the IAEA symposium of Gatlinburg [IAEA70].

The best known of these processes (cf. § 4.4.1) is that patented by the Italian **SNAM** organisation, a subsidiary of the ENI group [BRA64]. This process was next developed, in the 1970's, by the affiliated **AGIP-Nuclear** society of the ENI group. Pilot and laboratory scale installations were built, by AGIP and CNEN, in Italy and also in England for BNFL (British Nuclear Fuels Limited) [TAY73]. These investigations presumably inspired NUKEM and GA for the development of their industrial facilities (cf. **appendix 4**).

Some time later, but still in the middle of the 1960's, the English military research centre **AWRE-Aldermaston** (Atomic Weapons Research Establishment) filed a patent concerning a process of the GSP type [DRE67]. These investigations were pursued for the civilian activities at **AERE-Harwell** [HAR68, HAR70]. Studies conducted in England concerned the use of different polymer supports for the precipitation process and different reagent injection systems (cf. § 4.4.2). Even though the AERE - Harwell process was not pursued as intensely as the SNAM process, investigations published by them could also have influenced NUKEM and GA in the realisation of their industrial facilities (cf. § 4.4.3).

In the 1970's, other processes than GSP continued to be developed, either for political or historical reasons (they were already in use by the laboratories concerned) or because they presented alternatives to the GSP process.

The Powder Agglomeration process was used for the DRAGON project until manufacture studies were stopped in about 1972 (cf. § 5). Around this time, the CEA constructed and commissioned an installation for the manufacture of ThO_2 kernels, in the frame of an agreement with GA. This installation operated until 1979, corresponding to the end of the GA-CEA agreement, the stop of the Fort Saint-Vrain reactor development, and HTR manufacturing activities both in the USA and in France.

In the beginning of the 1970's, ORNL developed an original process for the manufacture of HTR uranium carbide and oxy-carbide kernels. This process, called **Resin process** or WAR process (Weak Acidic ion Resin exchange), consists of the impregnation an organic resin formed of particles by a solution of uranyl nitrate (cf. 6.2). Different variations were tested by GA and CEA/DMG for the manufacture of kernels for the Fort Saint - Vrain reactor project. Again for the reasons mentioned above, these activities concerning this process were stopped at the end of the 1970's.

A variation of the GSP process is the KFA **External Gelation process** (EG) developed at the institute of Chemical Technology (ICT) of the **KFA** Centre in Jülich (cf. § 4.6). The principle is similar to the GSP process. The modifications consist in the reduction of the organic polymer quantity in the initial solution and the modification of the reagent injection configuration. This process was tested by the KFA on a pilot scale (cf. **appendix** 5). Studies on the manufacture of HTR kernels were stopped presumably in the beginning of the 1980's.

Another alternative to the GSP process is **internal gelation by HMTA** (cf. § 4.5). This process is derived from the investigations of **KEMA**. It was tested on a pilot scale by the **INTERFUEL** company in partnership with KEMA at the Petten research centre in the Netherlands, for the manufacture of vibropacked fuels [SEN75]. These activities were interrupted at the end of the 1970's.

At the end of the 1970's ORNL investigated the HMTA internal gelation process for the manufacture of vibropacked fuels (cf. § 4.5). Even though these investigations didn't result in the realisation of a large capacity installation, they are interesting as they performed a comparative assessment of the GSP and HMTA processes [BEA79]. In this setting, ORNL indicates that the HMTA process is more interesting than the GSP process for the manufacture of fine (< 100 µm) and large (800-1200 µm) spheres, and that both processes are convenient for the manufacture of medium sized (200-350 µm) spheres. ORNL also indicated that the choice of the process must be based on its appropriateness for each scale (laboratory, pilot or industrial).

During the 1970's, other organisations studied the HMTA process (cf. 5.5), e.g. the Russians [MAR73], Czechs [URB77], Swiss at the research institute of EIR at Würenlingen, which thereafter became a part of the Paul Scherrer Institute (PSI) [BIS73], and in Germany at the ITU [LOU74] and at the Institute of Reactor Research (IRW) at KFA, Jülich [FÖR77].

The overview of the investigations made by these organisations in the 1970's is difficult to achieve (cf. 4.5). More than likely Russian scientist continued to work on the internal gelation process as it is being planned for the GT-MHR project. The Czechs worked on fundamental aspects of the process and no publication was found apart from the end of the 1970's. At the ITU the internal gelation was abandoned and GSP process developed with AGIP - Nuclear and CNEN (by then ENEA) [COG79, GER91].

KFA/IRW researchers at Jülich participated in the spread of the HMTA process and applied it to the manufacture of UO_2 kernels for HTR fuel. Nevertheless, after some tests on the manufacture of mixed oxide $UPuO_2$ kernels, in the facilities of EIR-Würenlingen [FÖR77], activities of KFA/IRW-Jülich in this domain stopped toward the end of the 1970's.

In Switzerland at EIR-Würenlingen investigations started at the end of the 1960's, with the objective of manufacturing mixed carbides of uranium and plutonium for vibropacked fuel [BIS73]. The laboratory installation appears to draw on the investigations by KEMA and KFA/IRW-Jülich, while adapting them to the specific safety requirements to handle plutonium. Thereafter, their studies pursued

with the development of plutonium oxide, carbide or nitride fuels. Nevertheless, in the 1980's, their studies moved toward the development of sintered pellets derived form the sol gel route.

3.3 Period 1980-1995: Processes reorientation

At the end of the 1970's, practically all development on the manufacture of spherical particles for HTR fuels or vibrocompaction ceased [GER91, BAS93]. The main reference reactors became PWR, BWR and FBR (Pressurised Water Reactor, Boiling Water Reactor, and Fast Breeder Reactor) that use pellet type fuel produced by powder metallurgy. In the case of the HTRs, some technological problems were encountered in the starting of the industrial prototypes at Fort St-Vrain and Schmehausen [BEC77, BAS93].

At the beginning of the 1980's, a number of the industrial or pilot facilities (cf. **appendix 4**) for HTR fuel production were closed and laboratories maintaining their activity in this domain essentially moved toward the development of sintered pellets produced from sol gel type powders. Italian research at AGIP - nuclear and ENEA was essentially pursued in collaboration with ITU, at the end of the 1970's [COG79], and also with the CEA, during the period 1980-1986. The objective of this collaboration was the development of $UPuO_2$ particles for pellet fabrication for FBR's. Investigations were in the main performed at ITU, for tests on plutonium and for tests on uranium at CEA/Grenoble, who still had a laboratory scale GSP installation from General Atomics. In this setting, the Italian knowledge played an important role in adapting GSP to the new needs. At that time, the CEA objective was to construct a pilot installation to fabricate Pu fuels at CEA/Cadarache. This action was stopped toward 1986-1988, both for logistical reasons, and also, the industrial powder metallurgy processes became the standard for this type of fuel at least (cf. 4.4.4). Beyond this period the nuclear fuel fabrication activities in Italy were stopped completely. The Italian specialists continued to promote the GSP technology, notably in the non nuclear domains [GER91].

In France at the beginning of the 1990's, tests were made at the UO_2 Laboratory of the CEA/Cadarache to develop macromasses by the GSP process. In particular, Gd_2O_3 and UO_2 macromasses were intended for incorporation in inert matrix heterogeneous fuel pellets (of the Ceramic – Ceramic CERCER type). Nevertheless, these tests were not pursued beyond 1995, as mechanical granulation of powders was used for these studies (cf. 4.4.4).

At ORNL [TIE79, HAA88] and KFA/ICT-Jülich (cf. 4.6), the manufacture of pellets of ThO_2, UO_2, $UThO_2$ and $UPuO_2$ from sol gel powders was studied during the 1980's. These investigations were not pursued, because powder blending became the industrial standard and there was a loss in interest in the Thorium cycle.

At the beginning of the 1990's, apart from the tests in the UO_2 Laboratory at CEA/Cadarache, the two sol gel facilities still in operation in Europe were those of ITU and PSI. These laboratory scale facilities are used for the development of innovative materials for targets for the incineration of actinides or pellets of alternative fuels for PWR and FBR (nitrides, carbides, heterogeneous fuels...) [LED90, LED92, DAU97, ITU95, HAA99].

Outside Europe, at the BARC (Bhabha Atomic Research Centre) research centre in India the development of pellet fabrication from sol gel was studied under the acronym SGMP (Sol gel Microspheres Pelletisation) [GAN91]. Their investigations started with researchers of KFA/ICT-Jülich, on compounds based on thorium, uranium and cerium [ZIM85, ZIM88] and were pursued at BARC, on compounds based on plutonium [GAN87, GAN91]. The initially used sol gel process was the KFA/ICT variant of the GSP process (cf. § 4.6), but later a HMTA type process was also investigated for the development of pellets based on plutonium. Reasons of the method change are not very clear. It would seem that they are bound to problems of microspheres pressing [GAN91]. The installation in India is laboratory size and seems similar to that in PSI. BARC maintain their know how in this area, and despite its potential advantages in the reduction of personnel exposure, powder metallurgy routes appear to have become the standard procedure for fuel production in India [CHI96].

In Europe the SGMP process was also pursued within a co-operation between Empresas Nucleareas Brasileiras S.A: (NUCLBRAS), the KFA Jülich Siemens- KWU and NUKEM [PIN88] in an investigation of the utilisation of thorium in PWRs. The HOBEG/NUKEM sol gel external gelation route was modified to optimise the kernels for direct pressing. Apart from changes in the solution chemistry, this was achieved by the addition of carbon pore formers to the feed solution to make the kernels less dense and thus "softer" to press. In this way the well-known "blackberry" structure often observed in SGMP can be avoided. The BARC process also used carbon addition for the same purposes.

Japanese, Russians and Chinese researchers presumably pursued an activity on the spherical particle development by sol gel during the 1980's, but little information is available in the open literature.

In Japan, PNC (Power reactor and Nuclear fuel development Corporation) published an article at the IAEA symposium in Gatlinburg in 1970 [IAEA70], on the development of the sol gel route for particles in vibropacked fuel [NAK70]. Processes described for UO_2 and $UPuO_2$ are similar to those proposed by ORNL in the 1960's (cf. § 4.3). They don't present particular interest in comparison to the GSP and HMTA methods. Specifically, their precursor is in the form of an uranium chloride, which is a chemical form that is not easy to handle and is not used in the classical fuel cycle. Thereafter, JAERI (Japan Atomic Energy Research Institute) and NFI (Nuclear Fuel Institute) published articles concerning the development of their HTR reactor program (called VHTR initially, then HTTR, i.e. High Temperature Test Reactor) [IKA74, IWA76, NOM77, KIT97]. These articles essentially describe features of the fuel considered, a few on methods of particle coating, but nearly nothing on the process used for the manufacture of kernels.

The Russian investigations were mentioned previously (cf. § 3.2) and on the Chinese side no article was found before 1988 [BAO88]. This article, unfortunately in Chinese (summary in English) presents a process of sol gel type developed in the frame of their HTR-10 reactor program (cf. § 3.4).

3.4 Period 1995-2000: Resumption of investigations for HTR

From about 1995 there has been a renewal of interest at the international level for the HTR concept.

In Japan the HTTR program even though it has delayed a little is being steadfastly pursued. [JAE00]. The first fuel core was manufactured by NFI in the period 1995-1997, and the first criticality was obtained in 1998 [SAW99a, SAW99b]. The technology employed is the prism type, with the annular compact arranged in a pin before insertion in the prisms (cf. **appendix 5**). The fissile matter is UO_2 with an enrichment between 3 and 10%. A patent was filed by NFI in 1995 on the process of kernel production [WAT95]. This patent and other information [SUZ92] indicates that NFI use a GSP process similar to that of General Atomics or NUKEM. The capacity of the installation for kernel manufacture is the order of 10 kg/day in UO_2 [KIT97].

In Russia, within in the frame of the GT-MHR program, a HMTA process for the manufacture of PuO_{2-x} kernels will be used. The first demonstration is of laboratory size for the production of tens of grams of plutonium kernels [MCE01].

The Chinese had started their HTR-10 program in 1992 [BAS93]. The objective of this program is the operation of a 10 MW_{th} HTR. The pebble fuel compact technology is employed. The fissile matter is UO_2 with an average enrichment of 17% [AIE97]. The process used for kernel production is the so-called TGU-process (Total Gelation Uranium process), a combination of GSP and HMTA processes (but nearer to the GSP one). According to the Chinese this technique unifies the advantages of each two processes without the inconveniences of either [BAO88, XU94, TAN95, TAN97].

To finish this historical review on kernels processes, the PBMR program in South-Africa must be mentioned. The purpose of this program is to build a pebble reactor of about 100 MW electrical output. In this case the NUKEM GSP process will probably be used for kernel manufacturing. Indeed, this work is being pursued within a contact involving BNFL and NUKEM.

4 - SOL GEL PROCESSES

4.1 Definitions

By definition a sol is a colloidal suspension of small particles, which remain suspended by Brownian motion. [TUR91]. The colloidal particle size is generally between 1 and 300 nm [ZIF68].

By definition a gel is a tridimensional network of particles or macromolecules (or of particles) interconnected in such a way that represents a solid expanse through a liquid phase.

The sol-gel processes represents the transition from the sol to the gel.

4.2 Principles

The transition between a sol and a gel is achieved by destabilising the sol by modification of a controlling parameter maintaining the particles in suspension, e.g. the particle concentration, the presence of a gelation agent, the temperature or the pH of sol.

The sol gel processes were developed notably for the manufacture of catalysts in the petrochemical industry [HER64]. In this case, one maintains the gel structure while eliminating the solvent by drying. The obtained tridimensional structures have a very high specific surface, which is very favourable for catalytic applications.

For the synthesis of powders with well defined particle shape, droplet formation is necessary component of the gelation phenomenon. The spherical shape of these sol drops permits the production, after thermal treatment, of the well calibrated spherical particles.

The sol gel process, for the manufacture of spherical particles, requires the following operations:

1) Constitution of a sol (or of a pseudo sol ; cf. 4.4), from an aqueous metal salt solution;

2) Dispersion of the sol into calibrated spherical drops;

3) Gelation of the drops, maintaining initial spherical shape;

4) Separation of particles from the solvent;

5) Drying of the particles;

6) Thermal treatment of particles (if one doesn't want to keep the gel structure), to obtain denser particles and possibly to transform them chemically.

In the case of nuclear materials, such as oxides or carbides of thorium, uranium, plutonium or mixed compounds thereof, several processes were developed. These processes differ, sometimes by the type of product required (thorium, uranium or plutonium), but especially by the method used in the sol gel transition (stages 1, 2 and 3). The following stages (4, 5 and 6) are generally not specific to the process and can be selected as required.

In certain cases the process doesn't involve a true sol gel transition. One speaks then of a pseudo sol gel process. As they are closely related, they are classified nevertheless in the same category. In the following sections true sol gel processes and the subsequently developed pseudo sol gel processes are presented and discussed.

Processes are described for the manufacture of oxides (ThO_2, UO_2, PuO_2...). For the production of carbides or nitrides, process modifications are required, in particular ,the addition of carbon to the sol or initial solution and subsequent carbothermal reduction of the particles, under neutral or nitrogen atmospheres for carbide and nitrides, respectively.

Generally, the different sol gel processes yield, spherical particles after sintering with a density close to the theoretical value (96-98% TD). Their size can be adjusted between 200 and 800 µm (or even smaller or larger), with a size deviation (2σ) of 1 to 10% [KAN73, BRA70a, RIN77, RIN79] and a

sphericity factor (Φ_{max} / Φ_{min}) of the order of 1.05 [VAN70, RIN79]. Product yield meeting these requirements can be of the order of 95 to 98% of the actinide quantity present in the initial solution [BRA70b, HUS73, NAE79, BEA79].

Particles with these characteristics are suitable for HTR application [GUI01]. The assessment of sol gel processes presented here is not based on features of the final product, which should be independent of the process, but on operational conditions.

4.3 True sol gel processes

As described previously, these processes were studied mainly in the beginning of the 1960's, by ORNL, KEMA and CNEN. They differ in the sol preparation and the gelation method.

4.3.1 Sol preparation

4.3.1.1 Thorium (ThO_2) sols

Thorium sols were the first studied because they are simpler to prepare than sols of uranium or plutonium. Also they constitute the first stage of the preparation of a mixed sol of uranium and thorium.

A method developed by **KEMA** [HER59, HER64, HER67, KAN67], but known since 1906, considers the precipitation of a thorium hydroxide from an aqueous solution of thorium nitrate, which is then peptised by heating in nitric acid. The **peptisation** operation creates a stable sol by peptide-like links. In this process, the thorium hydroxide is obtained by the reaction of ammonia with thorium nitrate (1 M). The precipitate formed is washed by an ammonia solution (to eliminate the remaining nitrates) then by water (to eliminate the ammonia solution). Peptisation is achieved by heating the precipitate to boiling point in an aqueous nitric acid solution. The concentration and the acidity of sol depend on the water evaporation rate and on the initial nitric acid concentration. Increased nitric acid concentration enhances the kinetics of peptisation but reduces the stability of sol. This technique can yield stable thorium sols with a concentration of 4 M [HER64]. According to various authors the process is well suited to laboratory scale operations [KAN67].

In the same way, **ORNL** developed an alternative **hydrothermal denitration** process of a thorium salt [FER61, FER64, MCB67, WYM68]. This process involves the extraction of nitrates from a thorium nitrate solution, or a precipitate of thorium nitrate, by action of superheated steam at about 350-450 °C. The powder thus obtained contains few nitrates (NO_3/Th (0.025) and water (< 1%). When it is mixed with dilute nitric acid, it gives a stable thoria sol with a crystallite size of 7 to 8 nm and a maximum thorium concentration of 7 M. This process was used by ORNL in a semi - pilot scale in the 1960's, for the manufacture of ThO_2 particles (cf. **appendix 6**).

4.3.1.2 Thorium - uranium (ThO_2-UO_3) sols

The first studies on uranium-thorium processes are derived naturally from the thorium processes.

Within the process developed by KEMA, the thorium hydroxide is not peptised by the nitric acid but by a solution of uranyl nitrate. In these conditions the maximum uranium content (U/Th) is 0.25. To increase the uranium content a variation of the process was studied. This variation called hydroxide coprecipitation, involves peptising a Thorium-uranium coprecipitate by a solution of nitric acid and uranylnitrate. This technique permitted U contents (U/Th) of 1. [HER64, KAN67].

ORNL studied the production of uranium and thorium sols using steam to denitrate. The thorium sol is mixed with a solution of uranyl nitrate. The resulting mixture is maintained at 80 °C for several hours and the pH is adjusted in a very precise way to avoid the precipitation of the sol. This technique did not succeed in obtaining an U/Th ratio greater than 0.1 [FER61, FER64, HAA67].

To significantly increase the content in uranium and to simplify aspects of industrialisation of the process **ORNL** studied another sol production process by solvent extraction [MCB67, HAA67, WYM68]. The process developed by ORNL was inspired by CNEN investigations in Italy [COG64]. In the process a thorium and uranium sol is formed from initial thorium and uranium solutions by extraction of nitrates with the help of a long chained amine. ORNL used the amino with the commercial name: **AMBERLITE LA2**™, which was dissolved in an organic solvent (n paraffins). This SOLEX process (**SOLvent EXtractaction**) used a three stages extraction unit (cf. **appendix 7**). The resulting sol had an adjustable uranium content for U/Th ≤ 1, with a NO_3/(U+Th) ratio of the order of 0.1. After evaporation the sol can be concentrated to about 2 M. ORNL developed this process to a semi pilot plant scale with a capacity of 1 kg/h in oxide mixed ThO_2-UO_3 [WYM68, WYM73].

At **CNEN** [COG64, COG67, ZIF68], the amino used was **PRIMENE JMT**™ (Rohm & Haas Co.) with the chemical formula $C_{18}H_{37}NH_2$. It was diluted to 50% in a hydrocarbon solvent (SOLVESSO 100™). The process principle is similar to ORNL and CNEN obtained sols with a metal concentration (U+Th) of about 3 to 4 M, with NO_3/(U+Th) = 0.5 and U/Th = 1/7. For U/Th > 1/7, CNEN developed a mixed sol of uranium and thorium starting from a uranium sol.

4.3.1.3 Uranium (UO_2) sols

The generation of uranium sols is more delicate than for either thorium or thorium - uranium, because uranium in the VI valence state derived from a solution of uranyl nitrate doesn't permit the production of a stable UO_3 sol. It must be therefore reduced to the IV valence state to give a stable UO_2 sol [KAN67].

KEMA studied the generation of uranium sols but didn't develop a specific process. They used processes proposed by ORNL and CNEN [KAN67, HER68].

The first process practised by **ORNL** [MCB66, HAA67], was filed in several patents [MOR64, MOR66]. It consists of the **reduction** to the IV valence of the uranyl nitrate solution and subsequent **precipitation** in concentrated ammonia solution – the so-called **nitrate method**. The precipitate is then **peptised** by heating to a temperature of 60 - 65 °C (cf. **appendix 8**). The reduction of uranium is achieved by hydrogen in presence of a Pt catalyst and urea to avoid the formation of nitrite. **Formic acid addition** before the precipitation steps permits the consolidation of tetravalent uranium and the generation of a sol more concentrated in uranium. (This is the so called **formate method**).

Analogous to the uranium - thorium sol case, **ORNL** decided to develop a simpler process for the generation of the uranium sol by **Solvent Extraction** [MCB67, WYM68]. In a first phase the uranyl nitrate solution is **reduced** by hydrogen (cf. **appendix 9**). In a second phase, nitrates are **extracted** using **AMBERLITE LA2**™ (according to the same process for mixed uranium and thorium sols (cf. § 4.3.1.2). This process, known as **CUSP process** (for **C**oncentred **U**rania **S**ol **P**reparation [LLO70, WYM73], was developed to a semi – pilot plant stage and was patented by ORNL [MOR68]. Sols with a stability of more than 30 days were obtained for uranium concentrations of 1 M and a NO_3/U ratio of 0.5.

CNEN also used solvent extraction process to obtain uranium sols [COG67, ZIF68]. In contrast to ORNL, the reduction of uranium to the IV valence state is made after nitrates extraction (cf. **appendix 10**). It yields sols more concentrated in uranium (2 to 3,5 M) and less impoverished in nitrates (NO_3/U = 1). Nevertheless, little information is given on the stability of these sols and the capacity of the installation developed.

4.3.1.4 Plutonium (PuO_2) sols

For the development of plutonium sols **ORNL** first used the hydroxide **peptisation** method (cf. § 4.3.1.1). As for thorium, plutonium hydroxide in the IV valence state is obtained by precipitation from a solution of plutonium nitrate. The precipitate formed is washed with water and peptised in concentrated nitric acid at 90 °C. After concentration and denitration, stable plutonium sols with a concentration of 1 - 2 M were obtained for a NO_3/Pu ratio of 0.1 to 0.2 [HAA67, WYM68]. The capacity of their installation permitted the production of 100 g quantities of PuO_2 particles (cf. § 4.3.2).

In order to simplify and automate the process by remote control, with the perspective of a later industrial development, **ORNL** studied a **solvent extraction** process similar to that developed for $ThUO_2$ and UO_2. In this case, AMBERLITE LA2™ was not used rather a **long chain alcohol** of the n-hexanol type. This process named **APEX process** (Alcohol - Plutonium nitrate Extraction) was developed to the same extent and gave similar results as the hitherto used process. [LLO70, WYM73].

CNEN also studied plutonium sol formation by an **extraction process** with **PRIMENE JMT**™ [COG67, ZIF68]. If one separates the plutonium handling aspects, the principle of the process is relatively simple because the sol generation, contrary to the thorium case, can be performed in only one extraction stage (cf. **appendix 10**). This process was studied at the laboratory scale and an extrapolation to larger scales was considered (but not developed) within the Italian development program for the manufacture of plutonium based fuels [SCH68]. Nevertheless, development to larger scale was achieved only for the GSP-SNAM process (cf. § 4.4), when CNEN and AGIP-Nucleare laboratories harmonised their efforts [GAL70].

Belgonucléaire (CEN - Mol) worked also, in the frame of an agreement with the DRAGON project, on the development of plutonium based kernels using a sol gel type process [BAI68]. The **peptisation** of a plutonium hydroxide precipitate following a process analogous to that of ORNL was used. The process was developed at the laboratory scale to demonstrate its feasibility. Thereafter, Belgonucléaire worked on the characterisation of kernels produced by AGIP-Nucleare by the GSP process [BAI73].

4.3.2 Gelation by dehydration (ORNL)

The gelation process developed by ORNL [HAA67, WYM68] consists of the extraction of water molecules from the actinide sol by alcohol dehydration using 2-ethyl-1-hexanol (2EH). The flow-sheet of the ORNL installation is shown in **appendix 11**. The different stages of the process are:

(1) Dispersion of the sol in the form of drops (sol feeder),

(2) Suspension of the drops in 2EH (forming column),

(3) Separation of gelled microspheres from 2EH (microspheres settler),

(4) Regeneration of the 2EH by decantation and distillation,

(5) Drying and calcination of particles.

The technology of each operation of the process was studied (forming column, separation and recycling of the solvent, drying of particles...). In particular, several devices, whose principles are represented schematically in **appendix 12**, for sol injection were evaluated.

This installation was operated on a pilot scale for the manufacture of particles of UO_2 and $ThUO_2$ with production capacities of 3 kg/day and 10 kg/day respectively [WYM73]. An installation operating on the same principle was put in operation for the manufacture of PuO_2, $ThPuO_2$ and $UPuO_2$ microspheres. The capacity of this installation, placed in gloveboxes, was suitable for 100 g batches [WYM68]. Some of these batches were used for HTR kernel production for the Peach Bottom reactor [SAN73]

4.3.3 Gelation by extraction of nitrates (CNEN)

The process developed by CNEN consists of the extraction of nitrates while dispersing the sol into droplets. The dispersing solvent is a long chain alcohol (ALPHANOL-79™ from Shell), containing the PRIMENE JMT™ (at concentrations of 1 to 2%). This alcohol is saturated in water (3 to 4%) in order to avoid the extraction of water before the nitrates, which could result in sphere damage. The alcohol also contains 0,1 to 0,5% of SPAN-85™, a surface tension agent that facilitates the formation of spheres [COG67, ZIF68]. This process was practised at the laboratory scale and was not developed further due to advantages presented by the GSP and HMTA processes (cf. § 4.4 and 4.5).

4.3.4 Gelation by modification of the pH (KEMA)

This gelation process was studied initially by KEMA [HER64, KAN67], and has numerous variations. It is a predecessor of both GSP and HMTA processes described in the following chapters (c.f. § 4.4, 4.5 and 4.6). The principle of the process lies in the provocation of sol gelation by increasing the pH (chemical gelation). The basic donor used for the modification of the pH is ammonia (or ammonia solution), because the ammonium ion can be eliminated easily during drying and calcination steps. The base can act in two modes, either it intervenes from outside of the sol drops, i.e. external gelation, or it is already present in the sol, i.e. internal gelation.

4.3.4.1 External gelation

The process studied by KEMA [HER64, KAN67] required the dispersion of the sol as droplets in an organic solvent containing the dissolved ammonia. The solvent used by KEMA was carbon tetrachloride diluted in toluene, while the sol was developed according to the previously described methods. Studies made by KEMA on this process were not pursued, because the internal gelation method was preferred in their laboratories.

Variations of this process were proposed by KFA-Jülich (cf. § 4.6), but the sol preparation was different and, in certain cases, the process is more like GSP that to external gelation.

4.3.4.2 Internal gelation

In the case of the internal gelation process [KAN67, HER68], the ammonia source can be urea [HER64], HexaMethylTetrAmine (HMTA) or a mixture of the two [KAN67]. These compounds are stable at ambient temperature, but liberate ammonia on heating beyond 90 °C for urea and about 50 °C for HMTA. For implementation of the process KEMA preferred to use a combination of urea and HMTA, in order to benefit from the respective advantages of both products: a better stability of the urea at low temperature and a higher ammonia production at lower temperatures for HMTA.

In this process, the sol is mixed with urea and HMTA at a temperature lower than 10°C to avoid the premature decomposition of HMTA. The resulting solution is dispersed into droplets in an organic solvent maintained to a temperature superior to 50 °C. The temperature depends on the proportions of urea and HMTA. The higher the HMTA content, the higher the gelation temperature (50-70 °C), but lower sol preparation and maintenance temperatures are required (0 °C).

The organic solvent used by KEMA was tetra-chloro-ethylene (TCE), which is poorly miscible and has a density greater than water, which permits its separation from water at the gelation head. Other solvents can be used, e.g. 2-Ethyl-1-hexanol (2EH) [PRI68].

4.4 The GSP process (External Precipitation)

The Gel Supported Precipitation process (GSP) requires the preparation of a solution of the actinide nitrate. This is mixed with a soluble organic polymer solution, which provides a structural support during

precipitation (gelation) of the actinide. The precipitation of the actinide is achieved using ammonia coming from the fluid in which the droplets are dispersed i.e. external precipitation. Additionally other additives are present in the initial solution (or broth) i.e. a tensile to facilitate droplet formation, a modifier to limit the polymer deterioration, which can be an important aspect if highly active actinide isotopes are used. The polymer also permits the adjustment of the viscosity of the solution so that it is sometimes known as a thickener.

The process was developed initially in Italy in 1964 by the SNAN organisation, and was patented at that time [BRA64, DIN66]. It was further developed at the beginning of the 1970's by AGIP-Nuclear (AGN) who took over SNAMs activities within the ENI group [GAL70, BRA70a, BRA70b, FAC73]. As it is shown in the picture in **appendix 13**, it was developed extensively not only in Italy but in other countries also.

4.4.1 SNAM process

In the SNAM process, the polymer employed was METHOCEL 90HG™ (METhyl-HydrOxy-propyl Cellulose), a relatively low-priced soluble organic polymer (Cellulose Ether type) supplied by Dow Chemicals Corporation. The modifier agent was the Tetra-hydro-furfuryl alcohol (THFA), also known as 4-HF). No tensile was used. Concentrations in the broth were 0.5 to 0.7 M for the actinide, i.e. 120 to 170 g/l for uranium, and between 5 and 10 g/l for METHOCEL™, which should give a typical viscosity of about 60 mPa.s [BRA70a, BRA70b]. THFA was added at volume content of about 5 to 30% (cf. **appendix 13**).

The formation of drops was achieved by dispersing the broth in a cylinder containing ammonia gas above a concentrated ammonia solution. The dispersion device was a simple needle or capillary protected by a sheath air flow to ensure that gelation does not occur on the disperser itself due to ammonia penetration therein The size of the drops formed can be modified by changing the internal diameter of the capillary, the viscosity of the feed solution, and sheath-air flow (cf. **appendix 14**).

In relation to the initial SNAM process, the Italian group made other modifications such as the rotary cup atomiser [GER82] for the production of smaller (<200 μm) polydisperse particles, or the addition in low quantities (0.2%) of tensides (e.g. Newt X-100 and TRITON X-100™) that facilitate the formation of drops, notably when one uses a rotary atomiser. In a further adaptation of the process, microspheres containing controlled quantities of carbon were produced, presumably for carbo thermal reduction to give the corresponding carbide [BEZ77, BEZ80].

The layout of the pilot installation operated by AGIP - Nuclear in Italy is shown in **appendix 15**. Operations following the formation of micro-spheres are described to the chapter 4.7.

4.4.2 AERE - Harwell process

The process developed at Harwell is similar to the SNAM process [DRE67, HAR68, HAR70].

Particularities patented by the Harwell Centre are notably the use of a different organic polymer to METHOCEL™ [DRE67], or the utilisation of a uranyl fluoride solution derived from the hydrolysis of uranium hexafluoride [UKA70]. The tested polymers were polyvinyl alcohol (PVA) and polysaccharides (dextran, carob gum....). They indicated that these products are more soluble in the aqueous solutions of acidic metallic salts than METHOCEL™ and don't require the addition of tensile or modifier. Nevertheless, the choice of the polymer and its combination with tensile and modifier should also be assessed on a cost basis both for their purchase and disposal as waste.

The Harwell team also studied different disperser configurations, e.g. the multiflux injector (cf. **appendix 16**), and brought some improvements to the process, as for example reverse flow injection of ammonia solution to reduce the speed of particle fall (and therefore shock between particles) and the continuous regeneration of the ammonia solution [UKA70]. They also investigated the use of a foam above the ammonia bath to cushion the fall of the droplets from the ejector. [SIM71, BEA79].

The process was developed at Harwell to a semi - pilot scale (cf. **appendix 17**), notably, for the production of UO_2 particles [HAR70]. The pilot installation of BNFL at Springfields was based on this installation and technical information on the SNAM process provided in an agreement with AGIP–Nuclear. The main BNFL objective was to use this technology to construct an installation for vibropacked plutonium fuel at their Windscale (now Sellafield) site [TAY73]. This was not pursued following the demise in interest in vibropacked fuel at the end of the 1970's.

4.4.3 General Atomics and NUKEM processes

The industrial processes developed by General Atomics (GA) and NUKEM were presumably inspired by the Italian and English investigations [HUS73, HOB74, BEA79, HUS77, HUS77a, HEI85].

The flow sheet of their process is equivalent to SNAM. Both, however, used polyvinyl alcohol (PVA). GA used the PVA named Mowiol™. The uranium concentration in the feed solution was of the order of 160 g/l and a THFA content of about 30-40%. The NUKEM process had a metal (thorium or uranium) content between 100 and 250 g/l; the type of PVA or modifier is not given in their publications and patents. Though the data available is not always consistent, their SGMP studies indicated that the metal concentration was as high as 300 g/l with PVA concentrations of 30 g/l [PIN88]. There are indications that the control of the Th feed solution was exacting covering not only the metal concentration, but also the free nitrate concentrate, pH, conductivity and density. Denitration by ammonia addition is implied. In a further publication NUKEM indicated that the pH of the Th/U feed solution should be between 3.5 and 4.0 [KAD76].

Both organisations used a vibrating nozzle to disperse the feed solution, which could select the droplet size based on the aperture and operational frequency. In its industrial installation NUKEM had a set of 3 reactors each equipped with 6 injectors. The typical flow rate in each injector was 0.24 kg(Th+U)/h, which corresponds to a production rate of 4 kg/h, 100 kg/day and 25 t/year [HUS73].

Aspects of the processes had been patented. For instance, GA patented a special design for the vibrating nozzle, which is not based on electromechanically vibration of the nozzle but on pressure vibrations of the broth before the nozzle [WEI73, WEI 76]. In another patent they describe an apparatus for gelation without giving specific details of the chemistry [EGL79]. In the same way, HOBEG and NUKEM proposed special designs for the nozzle (multi-electromechanical vibrating nozzle) [HOB74] and for the repartition of the gas in the gelation device [HUS75].

At the beginning of the 1990's, a last design had been proposed by NUKEM [THE92], which seems not had been used for industrial manufacturing of THTR fuel, but for last HTR German module developments. This latest design utilises a vibrating plate with several holes instead of needles, for the injection of the broth, and with special design for NH_3 injection and the forming of a foam on NH_4OH surface.

4.4.4 Studies made by the CEA

Investigations made by the CEA for the manufacture of HTR kernels by the GSP process are few. They involved the acquisition of a General Atomics unit and verified the GA specifications for HTR kernels could be reproduced.

Thereafter, studies moved toward the manufacture of mixed oxide powders ($UPuO_2$) for transformation in pellets. Thus deformed spheres 50 and 250 μm in diameter and suited for pellet production were required rather than HTR kernels. At the same time (1980 – 1986) a similar programme was launched in an agreement between the CEA, AGIP-Nuclear, ENEA and ITU at Karlsruhe [GER91]. Studies were made at the CEA/Grenoble, in Italy and in Karlsruhe. At this time, activities in Italy were reduced, but continued in Karlsruhe where a laboratory scale plutonium unit was installed [COG79, GER91].

Part of the objectives of this collaboration was the construction of a pilot installation with a capacity of 5 kg/d in U - Pu at the CEA/Cadarache. A laboratory installation was acquired by the CEA from ENEA/AGIP. The GSP process was modified in order to get particles capable to give pellets. In particular, the concentration in THFA was reduced to about 5% and the rotary cup atomiser [GER82] for polydispersed particles was used.

At the end of the 1980's, CEA activities in this frame were stopped, due partly to difficulties in nuclearisation of facilities for plutonium and also because in industry (COGEMA/Belgonucleaire) Pu solutions at the final stages of reprocessing are converted to oxide before being shipped to the installations for powder metallurgy, which became the norm for the production of fuel pellets.

In the beginning of the 1990's, small capacity equipment was transferred then to the UO_2 Laboratory of the CEA/Cadarache (cf. **appendix 18**) to make studies on composite pellets containing to macromasses dispersed in a matrix. Tests on the development of gadolinium cerium and uranium oxide macromasses [BAL95] were performed. The initial tests did not succeed in the production of particles of the required size (Gd_2O_3 = 300 μm), due to the use of the rotary cup atomiser, which had been developed for small particle manufacture. Thereafter, the equipment was modified. A vibrating nozzle was installed and the geometry of the reactor was changed to put the nozzle horizontally, as in KFA/ICT studies (§ 4.6). With this new device (cf. **appendix 19**) a few tests on CeO_2 and UO_2 were performed. These tests were not pursued, as mechanical granulation was chosen in the frame of the program.

The installation in the CEA UO_2 Laboratory was stopped in 1995, but is being renovated in 2001 for use in the European program HTR-F in order to test the GSP process for UO_2 kernel production. The capacity of this installation is limited mainly by washing, drying and calcination steps and is of the order of 10s of grams.

4.4.5 Studies made at ITU

At the ITU the sol gel external gelation process was invoked with a view to pelletisation of the beads for the production of nuclear fuel pellets [COG79]. For these purposes a rotating cup type atomiser developed by AGIP was used [GER82] and laboratory scale installations were developed for Pu and minor actinide applications (cf. **appendix 20**). During the 1980's the ITU embarked on a major programme on the transmutation of actinides in collaboration with the CEA. In the frame of this programme $UPuAmO_2$ and $UNpAmO_2$ fuels and targets were fabricated and irradiated in Phenix [BAB99].

Actinide transmutation is now a major ITU programme and the GSP route has been used to manufacture a variety of non - U or Th based materials – the so called inert matrices, which are potential candidates for transmutation purposes as their neutronic inertness improves the transmutation rate. Candidate materials manufactured using the sol gel method at the ITU include ceria, magnesia aluminate spinel ($MgAl_2O_4$), yttrium aluminium garnet (YAG), and yttria stabilised zirconia $(ZrY)O_2$. At the time of this review, a new facility is under construction at the ITU for the production of minor actinide pellet type fuels and includes a sol gel device based on the rotating cup principle.

During the 1990's the same fabrication route has been used for various programmes dealing with Pu incineration (TRABANT) [ITU95], and LWR fuel performance during transients (MICROMOX). In addition a rodlet containing $ThPuO_2$ fuel prepared using this method is under irradiation in a German PWR. Compared to powder metallurgy routes, sol gel pelletisation has the unique advantage that an atomic solid solution of all the mixed oxides constituents is obtained. Thus materials produced in this way provide excellent benchmarking standards for fuel performance testing.

Smaller scale simple needle dispersion devices are still used in the ITU, when small quantities of materials (< 10 g) are prepared by the gel supported precipitation route. The main requirement is usually the atomic homogeneity of the mixed oxides. Within the ITU programmes, however, monodisperse particles with high degrees of sphericity are not required, and were not sought. It is on the basis of ITU

experience with these simple devices and in other areas that ITU is building its capabilities to produce kernels within the HTR-F programme.

4.5 The HMTA process (Internal Gelation)

The internal gelation process using HMTA has numerous versions and is often referred to as the KEMA process [BIS73, BEA79, HAA80], the H-process (by KFA) [FÖR70a, HUS73], U(VI)-process (also by KEMA) [VAN70, KAN73], or simply the internal gelation process [MAK73].

The process developed initially by KEMA [VAN70] (cf. § 4.3.4.2) is similar to GSP in that a solution, or broth, of the actinide salt is used rather than a sol. This process was applied for the first time by KEMA to the manufacture of uranium dioxide particles [VAN70].

The principle of the process for uranium consists of the preparation of a concentrated (3 M, i.e. 700 g/l) solution of uranyl nitrate deficient in nitrates ($NO_3/U = 1.6$), and of a solution containing a mixture of HMTA and urea, cooled to 0 °C (cf. **appendix 21**). The two solutions are mixed together and are maintained at 0°C to avoid the premature decomposition of HMTA. At this temperature, the mother solution is stable for about 24 hours [BEA79]. In another variation of the process (cf. **appendix 22**), the solution of uranium nitrate can be mixed with urea, which stabilises uranium, before being mixed with the HMTA [BEA79]. As for the process previously described in the chapter 4.3.4.2 the mother solution is dispersed and collected for gelation in an organic solvent maintained at a temperature higher than 50 °C, but typically between 70 and 110°C depending on the required gelation speed. Tetra-chloro-ethylene (TCE) has a boiling point of 121°C and a density of 1.6 g/cm^{-3} and can be used alone or mixed with an oil of paraffin [KAN73, BEA79, MCE01], or with silicone oils [URB77, BIS73, DAU95]. In certain cases, tetrachloroethylene was used [SPE81], but the temperature is limited to 80 °C due to its lower boiling point (85 °C).

This process used on a laboratory scale for uranium by KEMA [VAN70, HER73, KAN73] was developed to a pilot scale with a capacity of 20 kg/d by INTERFUEL at Petten for the development of vibropacked fuel [SEN75]. A smaller pilot was constructed to develop particles of $UPuO_2$. This installation was used to manufacture some pins, which were radiated then in the High Flux Reactor (HFR) at Petten [SEN75], but it was decommissioned presumably at the end of the 1970's.

The HMTA process was used for spherical particle development by other laboratories, as for example at ORNL [BEA79, SPE81], the Czech institute of Research REZ [BAR73a, BAR73b, URB77] or at EIR-Würenlingen [BIS73, DAU95]. Other variations of the process were developed in Russia [MAR73, MCE01], KFA/IRW-Jülich [FÖR70a, FÖR70a, FÖR77, HUS73] and ITU Karlsruhe [LOU70, LOU71, LOU74]. In addition the process has also been tested and improved in Japanese laboratories [YAM88].

ORNL made a very detailed comparative survey of sol gel processes for the manufacture of particles intended for vibropacked fuel of the sphere-pac type [BEA79, HAA80]. In this case the objective is to get three sizes of particles: fine (< 100 µm), medium (200-350 µm) and large (800-1200 µm). ORNL showed that their sol gel process by dehydration (cf. § 4.3.2) can be used to manufacture the fine fraction, that the HMTA process is better for the preparation of the fine and the large, but that the GSP processes and HMTA are equally good for the medium sized particles. Other criteria also need to be considered in the process choice.

In Czechoslovakia studies on basic mechanisms in internal gelation were concentrated on uranium at a laboratory scale [BAR73a, BAR73b, URB77].

In Russia a pilot installation for the manufacture of uranium dioxide microspheres was presented in the beginning of the 1970's. A schematic design is shown in **appendix 23** [MAK73]. Operating conditions were close to those of KEMA and the Russians mention the development of particles whose size is adjustable between 10 and 1200 µm. Unfortunately, little information is available on product features or the capacity of the installation. This experience is probably being used now in their choice of the HMTA process for the development of kernels of plutonium dioxide in the frame of the GT-MHR

project [MCE01]. Rather than Silicon oil, they plan to use tetrachloroethylene to provide the necessary heat to release the ammonia from the HMTA [MCE01].

In Germany, at the end of the 1960's, despite the adoption of the GSP process by NUKEM and HOBEG for the manufacture of the ThO_2 and $ThUO_2$ kernels of the AVR and THTR reactors [HUS73], researchers of KFA/IRW-Jülich studied an alternative process called the H-process (for Hydolysis-process), which bears many similarities to the KEMA process [FÖR70a, FÖR70b, FÖR77]. One difference in relation to the KEMA process lies merely in the fashion of introduction of urea and HMTA in the initial solution before gelation. The urea then the HMTA is introduced directly in the concentrated (500 g/l) uranyl nitrate solution.

The process of KFA/IRW-Jülich was put operation at a pilot scale for the manufacture of uranium dioxide and dicarbide kernels. The capacity of the installation was of about 5 kg/d of UO_2 and the particle size was 200 µm. Some kernels of this type were irradiated to 50% FIMA in the AVR reactor [HUS73]. Researchers of KFA/IRW-Jülich worked with EIR-Würenlingen on the development of mixed oxide $UPuO_2$ microspheres [FÖR77]. After 1977 it seems that researchers of KFA/IRW-Jülich didn't pursue their activity in this domain.

At EIR-Würenlingen investigations started at the end of the 1960's to study the development by sol gel of microspheres of mixed uranium and plutonium carbides for vibropacked fuel [BIS70, BIS73]. Originally interested in the true sol gel processes developed by ORNL (cf. 4.3.2) and KEMA (cf. 4.3.4) [BIS70], they moved to the HMTA process. [BIS73]. Plutonium is introduced in the broth before gelation by mixing a concentrated plutonium nitrate solution without free acid with a uranium solution containing urea and HMTA. Carbon powder was mixed with the solution while being maintained at low temperature. As mentioned above, they worked with KFA/IRW-Jülich in this development stage. During 1980-1990 EIR became part of PSI and they developed other fuel forms (nitrides, carbides, pellets...) and more recently plutonium incineration targets, which are based on Yttria stabilised zirconia rather than UO_2 as a matrix. Facilities, for uranium and plutonium, are in operation at the laboratory scale [LED86, LED90, LED92, DAU95]. In the 1980's PSI patented a variation of the internal gelation process which dispensed with the use of the hot oil to decompose the HMTA [JUN84, LED84]. In this innovation, the droplets from the vibrating oriface based through a microwave cavity, which supplied the thermal energy to generate ammonia from the feed solution constituents. This development was tested at the time, but was not pursued.

The researchers of ITU started their investigations at the end of the 1960's in the true sol gel processes of ORNL (cf. § 4.3.2) and CNEN (cf. § 4.3.3) type for the development of mixed $UPuO_2$ oxide particles [LOU68]. Their choice then moved toward a process similar to KEMA's, but differed in the preparation of a the PuO_2 sol mixed with the urea and the HMTA before the uranium solution [LOU70, LOU71, LOU74]. The PuO_2 sol was prepared according to the peptisation method presented previously (cf. § 4.3.1.4). This method was patented in the beginning of the 1970's by ITU [LOU71], but it doesn't present any advantages over the current Swiss process due to the preparation of the plutonium sol.

4.6 The EG process (External Gelation)

Researchers of KFA-Jülich at the institute of Chemical Technology (ICT), studied alternatives to the GSP and HMTA processes. The first method [HUS73, ZIM75], called KFA - Precipitation – Process was applied to the development of ThO_2 and $ThUO_2$ kernels and tried, according to authors, to combine the advantages and to suppress inconveniences of sol gel and pseudo sol gel processes. In a first step, a sol or pseudo sol of thorium is prepared in a solution of thorium nitrate neutralised by ammonia and dispersing the precipitate in the form of a sol by agitation and heating at a temperature of about 100 °C. This operation is similar to peptisation (cf. § 4.3.1.1) but does not require nitric acid. The concentration of the sol thus formed can reach until 2 to 3 M [RIN77]. Thereafter it is dispersed in an organic solvent the Methyl-Iso-Butyl-Ketone (MIBK) containing dissolved ammonia. The formation of spheres takes place in an organic solvent as for the HMTA process, but the gelation mechanism uses external diffusion of ammonia, as in the GSP process. After gelation of the sphere surface in the organic solvent the complete gelation is made in a concentrated ammonia solution as shown in the diagram in **appendix 24**. The aim of the organic solvent is to reduce the mechanical stress on the spheres as they pass through the interface

with the ammonia solution. In addition, in the organic phase their immiscibility is an advantage in improving their sphericity.

In a later study [RIN77, NAE78, RIN79], a simplification of the previous process was made by dispersing the sol in a gas containing ammonia, as for the GSP process. In this process the injector is not vertical but horizontal to the solution so that the trajectory of particles in gas is increased for a reduced reactor height – a development that makes it more favourable for use in a glove box. Besides, this design reduces the particle fall velocity (cf. **appendix 25**). This process was applied to thorium based compounds and was called EGT (External Gelation of Thorium process) by KFA. In the case of uranium it was called EGU (External Gelation of Uranium). In this last case, considering the impossibility of obtaining a stable sol of U(VI) (cf. § 4.3.1.3), researchers of KFA use urea to complex and consolidate uranium, and also ammonium nitrate to peptise uranium.

EGT and EGU processes were operated by KFA at a small pilot plant scale (cf. **appendix 26**), whose capacity was of about 5 kg/d for $ThUO_2$ [RIN79].

Toward the beginning of the 1980's their studies were reoriented toward the development of pellets with the help of powders from EGT and EGU processes [ZIM85, GAN87, ZIM88]. This process became known as SGMP (Sol Gel Microsphere Pelletisation) and was applied to other compounds such as $UCeO_2$, whereby Cerium was used to simulate Plutonium (for MOX). These studies were stopped at KFA toward the end of the 1980's and continued at BARC (Bhabha Atomic Research Centre) in India, with whom KFA collaborated [GAN87, GAN91], where the SGMP process was used to the manufacture pellets of UO_2 and mixed oxide $UPuO_2$ with 4% Plutonium. Afterwards, however, it appears they preferred to use a HMTA process to develop powders. The BARC process is similar to PSI and has a capacity of a few hundred grams [GAN91].

4.7 Washing, drying, calcination, reduction and sintering of kernels

Operations of washing, drying, calcination, reduction and sintering of kernels do not depend significantly on the process employed, though three are some differences between HMTA and GSP processes.

Even though HOBEG do not mention them in the process used by NUKEM [HUS73, HOB74], an ageing operation of gelled spheres is preferable in the case of the GSP process. Thus they are kept for some time in ammonia solution to finish the gelation process. The length of this operation depends on the concentration of ammonia and the temperature. At AGIP-Nuclear an ageing of 1.5 - 2 hours in concentrated ammonia solution at 30 °C was recommended [BRA70b, FAC70]. For their process KFA/ICT-Jülich indicate that a length of 30 minutes in the ammonia (7N) at 60 °C is sufficient [NAE79].

In the GSP process, washing is achieved generally by the de-mineralised water [BRA70b, FAC70, HAR70] possibly containing a little ammonia [RIN79]. This washing eliminates ammonium nitrate in gel, which is necessary to avoid gas build up in the spheres during the calcination step, and also risk of explosion of ammonium nitrate when dry. Sometimes this first aqueous washing is followed by a second washing in isopropanol that completes the elimination of the ammonium nitrate and begins the dehydration of the product. This path was followed by NUKEM [HUS73]. For the operation of drying NUKEM recommends drying under air in a slight under pressure (650 mbar) at 100 °C for 4 hours [HUS73, KAD76]. AGIP-Nuclear preferred azeotropic distillation in the CCl_4 [BRA70b, FAC70] and KFA/ICT-Jülich recommended drying under humid air at 180 °C for ten minutes [NAE79].

For the HMTA process the operation of ageing is not necessary. In the initial KEMA investigations, washing was achieved using demineralised water containing a little ammonia (pH = 8.5 ; 40 °C; for 1 - 2 hours) [KAN67, BEA79, MCE01]. An alternative proposed by KEMA [VAN70] and used also by others [FÖR70b, MAK73, BIS73, LOU74, DAU95] is a pre-washing in a volatile organic solvent such as CCl_4 or distilled oil. This pre-washing permits elimination of the gelation solvent, which has a high viscosity and boiling point (TCE, 2EH, silicone oil, etc.), before the aqueous washing [HAA80]. The drying operation is generally achieved under air at a temperature of 70 to 120 °C [VAN70, FÖR70b, LOU74, DAU95], under humidified air, or under saturated steam at 200 °C [HAA80, MCE01].

The drying of the beads can be performed using isopropanol as mentioned above. At CNEN, an azeotropic drying process was used [FAC73a, FAC73b]. This method is gentle and the beads are heated more uniformly than in direct thermal drying. Both methods were evaluated at CNEN in the early 1970's. At the ITU this azeotropic drying procedure is still used in its laboratory scale GSP production of fuels and other materials.

The calcination, reduction and sintering operations are not specific to the type of process. The calcination is achieved between 300 and 800 °C to eliminate organic residues, to strengthen the spheres and possibly to adjust the porosity. The reduction and sintering are achieved in a classic way under H_2 or Ar/H_2 while the thermal cycle is adapted to reach the required final density (typically between 1300 and 1700 °C). It has been indicated that in particular the calcination should be performed in a rotary type kiln [PIN88]

4.8 Conclusion

The choice of sol gel type process for the development of HTR kernels must lie between the GSP, EG or HMTA processes. Contrary to true sol gel these processes do not require sol preparation, which can be long, complex and even unreliable.

The EG process can be considered as a variation of the GSP process. Its main difference from the GSP process is the absence of an organic polymer in the initial solution, which may facilitate washing operations and eventual risk of cracking during thermal treatments or by radiolysis, especially if plutonium is used. Nevertheless, it is more difficult to obtain good shaped spheres without polymer.

Advantages and drawbacks of the GSP and HMTA processes, identified in the literature are summarised in **appendix 27**.

The advantages of the GSP process are essentially:

- The simplified preparation of the initial solution (broth);
- The absence of a high temperature organic solvent for gelation;

Its disadvantages are principally:

- The mastering of the sphere forming, ageing and washing steps, and in particular the sphere volume changes that occur on drying

In the case of the GSP process (for uranium), the initial solution can be prepared directly from a relatively low concentration solution of uranyl nitrate or by the dissolution of UO_2 by nitric acid (which may need free acid removal). The HMTA process requires a concentrated solution of uranyl nitrate (700 g U/l) deficient in nitrates (NO_3/U =1.6). To prepare this latter solution it is necessary to use a uranium VI oxide (UO_3 type), to minimise the quantity of necessary nitric acid for the dissolution, or to extract nitrates by solvent extraction.

In the case of the HMTA process, the initial solution (« broth ») must be maintained at low temperature (0°C), used quickly (within 24 hours) and dispersed in an organic solvent maintained between 70 and 100°C. Nevertheless, the formation of spheres and washing operation seem less difficult.

In conclusion, the best sol-gel process to produce HTR kernels seems to be the GSP method. It yields good kernels in the range between 200 and 800 µm, with a high production rate, and with a process which can be developed on a large scale. It is the only one, which has been developed to an industrial level for the fuels of Fort-Saint-Vrain and THTR reactors.

5 –POWDER AGGLOMERATION

The Powder Agglomeration route was developed initially in England [SHE63, SHE67, FOR72, ALL77] and Belgium [GOR63] for the production of particles of uranium carbide (cf. § 3.1). It then became the reference process for the manufacture of uranium dioxide kernels for the reactor DRAGON [BAS71]. It was also used for the manufacture of UO_2 kernels by SFEC and the CEA in France for the DRAGON project [AUD72] and of ThO_2 in the frame of a agreement between CEA and General Atomics in the 1970's.

5.1 Principle

The principle of the process is concerned with the agglomeration of very fine powders of actinide oxides (U_3O_8, UO_2, ThO_2...), possibly with the addition of carbon for carbide fabrication. In this way larger particles are made by progressive agglomeration of the fine powders.

The size of the agglomerates "seeds" are usually between 150 and 250 µm. The specific surface area of the initial powder are, in the case of UO_2 and carbon, are the order of 2 to 4 m^2/g and 15 to 30 m^2/g, respectively [SHE63, FOR77, BAS71].

The preparation of the agglomerates requires several stages. In the first the initial powder is mixed with a binder (e.g. 3% stearic acid for the SFEC/CEA process) and possibly with recycled powder, which act as the "seeds". The quantity of recycled powder is of the order of 20%, depending on specific processing conditions. This recycled powder and the initial powder can be activated by a milling step, which can increase its specific surface. The second stage of the process involves sieving the agglomerates to select particles with the required size (150 - 250 µm).

The "seed" particles are placed in an agglomerator of cylindrical shape, which is subjected to an off center axial rotation. In the case of the process used for DRAGON at Winfrith the device was made of aluminium with an internal silicon rubber protection layer on the polished surface. This device was a GALLENKAMP PLANETAR MILL™ (which gives the term GALLENKAMP agglomerator). In the CEA process the agglomerates were placed on simple plastic bowls from a TEMA ROTARY SIEVER™, which gives the name TEMA agglomerator.

The progressive addition of the fine powder to the growing agglomerates is achieved by hand, while controlling visually, the progress of the operation. The flow of fine particles must be adjusted according to the size of the agglomerates. It is increased as the agglomerates increase in size. For automation and remote use, the flow of the powder is adjusted by a screw and is controlled by the mass in the agglomerator.

When the particles have the desired size, the agglomerator is stopped and the powder removed from the agglomeration bowl. The agglomeration time is determined for given powders and then standardised for the production line. The size of particles is controlled visually in the bowl and by inspection following withdrawal of samples during the agglomeration process.

After sampling, the powder is sieved in the desired granulometry class, and a part of the non conforming size particles is recycled for the manufacture of further agglomerates. For automation of the process, a sampling device can be incorporated by raising of a central cone in the agglomeration bowl.

Kernels generated in this way are calcined in air, as in other processes, to eliminate organics, before being sintered under hydrogen to reach the desired density.

5.2 Application

The Powder Agglomeration process was operated at a pilot scale, at Winfrith and Springfields for the manufacture of UC_2 and UO_2 particles, at SFEC for the manufacture of UO_2 kernels and at the CEA for the manufacture of ThO_2 kernels. This process was used for the production of several tens of kilos of kernels for HTR fuel for the DRAGON reactor. Kernels with sizes between 200 and 1000 μm, and porosity adjustable between 5 and 20%, had been achieved using this process [ALL77].

5.3 Conclusion

The Powder Agglomeration process has the advantage that the fissile matter is not in solution form, which permits handling of larger material quantities without risk of criticality. It is relatively simple and requires conventional powder metallurgy equipment. Compared to the sol gel type processes it is more difficult to extrapolate to an industrial scale. Indeed, appropriate operational conditions have to be set on line and demand a high level of operator ability. Process parameters (concentration, flow, temperature...) are difficult to define to guarantee a consistency in the final product. The properties of the kernels depend on the characteristics of the initial powder and the link is not easy to identify. The initial size of the "seeds" could vary between 150 and 200 μm, 180 and 250 μm or simply lower than 400 μm. The duration of agglomeration can vary from minutes to several hours, which depends on the adhesion qualities of the powder. Operator intervention is usually required to avoid formation of a combination of large particles and small agglomerates.

In relation to sol gel type processes, the product is of inferior quality particularly in terms of the sphericity of the kernels (Φ_{max}/Φ_{min} = 1.1 to 1.2) and in the particle size distribution ($2\sigma \approx 10\%$) [PRI68, RIN79].

6 - PROCESSES FOR CARBIDES AND OXYCARBIDES

In this chapter, the processes of fusion under vacuum (Fusion-process) and impregnation of a resin (Resin-process), used in the past for the development of HTR kernels are presented. They only permit the manufacture of carbides and oxy-carbides.

6.1 Fusion process

The Fusion process is described sparsely in the literature [RAG63, RAG65]. It is mentioned under the VSM (for Vanek, Smith and Miertschin) process, in a monograph dealing with the historical development of HTR fuel [MOR83].

In a first step a mixture of carbon and UO_2 and/or ThO_2 powders are agglomerated in roughly spherical particles [RAG63]. After sieving and selection of the require size range the agglomerates are dispersed in a graphite fine powder and placed in a high temperature furnace. The particles suspended in graphite are heated progressively in vacuum between 2100 and 2300 °C to convert the oxide to carbide and then heated further until a temperature slightly superior to the point of fusion of the carbide (UC_2 = 2400 °C, $UThC_2$ = 2450 °C, ThC_2 = 2650 °C), to induce fusion of the particles. Particle fusion gives high density and a good spherical shape. Their dispersion in the graphite powder suppresses coalescence between them. After conversion the graphite powder is separated from the particles by crushing and sieving. The output of the conversion is about 80%, and gives final particles with diameters between 175 and 250 µm, from agglomerates with an initial size of 300 to 420 µm [RAG63].

This process yields very dense particles (density close to the theoretical density) due to the fusion. It was used in the early manufacturing campaigns to produce $UThC_2$ kernels for the Peach Bottom reactor in the 1960's [RAG63]. Nevertheless, it was abandoned thereafter [RAG65], on account of the technical difficulties of the high temperature process. Besides, it is not applicable to the synthesis of oxides or mixed oxides (or at least not without further difficulty), due not only to the graphite but also the higher fusion temperature of the oxides (UO_2 = 2850 °C, ThO_2 = 3200 °C, PuO_2 = 2450 °C).

6.2 Resin process

The Weak Acid ion - exchange Resin process or more simply the Resin process was developed initially by ORNL [HAA72, HAA74, NOT76, WEB77a, WEB77b and HAA78], and used by General Atomics and the CEA/DMG [MOR77] for the manufacture of kernels of UC_xO_y type for the Fort Saint-Vrain project.

The principle of this process lies in the impregnation of uranium in an ion exchange resin formed from spherical particles with a calibrated size. These particles were then treated thermally to transform them in oxy-carbides or carbides, depending on the calcination conditions.

The different stages of the process were:

- Geometric calibration and selection of the resin particles in aqueous medium,
- Partial drying,
- Sorting by shape,
- Impregnation of uranium,
- Washing and drying (100 °C),
- Carbonation (600-1200 °C),
- Conversion to UC_xO_y (1500-1800 °C).

Ion exchange resins are commercial products with low cost. The first stage of calibration is necessary to reduce the divergence in the final product. Tests were made on a large number of commercial resins as, e.g. Duolite C464™ (Diamond Shamrock - USA, Diaprosim - France) or Lewatit OC1001™ (Bayer - Germany).

The operation of uranium impregnation is achieved by circulation of uranyl nitrate through a resin particle bed. Two variations of the process were proposed: either the resin is used without particular conditioning and the operation of impregnation takes place by exchange of the H^+ ions of the resin and the UO_2^{2+} ions of the solution (acidic cycle), or the resin is pre-conditioned by ammonium ions, so that production involves the exchange of NH_4^+ and UO_2^{2+} (ammonium cycle). The acidic cycle was used by both ORNL and CEA/Grenoble. The ammonium cycle was used by General Atomics. The advantage of the acidic cycle is the obvious reduction in the number of steps, the disadvantage is the need for a de-nitrated uranyl nitrate solution.

Operations of washing (with water) and of drying (in air) can be achieved directly in the impregnation reactor without further manipulation of the particles.

Thermal treatment and conversion are achieved in a fluidised bed furnace, which can also be used for particle coating. The firing steps eliminate water and transform the resin in carbon. The thermal cycle of the subsequent treatment can be used to adjust the properties of the final material (density, C/U ratio). After 1000-1200 °C, the product is composed of finely divided uranium dioxide in a matrix of porous carbon. The conversion (between 1500 and 1800 °C) gives the carbo-thermal-reduction of the uranium oxide by the carbon of the matrix, to give oxycarbide, monocarbide or dicarbide. The O/C ratio and U/C are adjusted by the temperature and partial pressure of CO in the furnace.

The process was brought to pilot scale (about 1 kg/h) at ORNL for the manufacture of UC_xO_y particles ($x \approx y \approx 1$) [HAA78]. It was at an interesting stage for industrial development and yields kernels with satisfactory morphological features for the HTR application ($\Phi_{max}/\Phi_{min} \approx 1.1$ and $2\sigma \approx 5\%$) [WEB77, HAA78].

7 - OTHER PROCESSES

7.1 Mechanical granulation

The process of mechanical granulation of a powder is used classically for the physical forming of ceramics [RIN86], notably for the manufacture of UO_2 pellets for the LWR fuel [CHO91]. The principle of this process is the precompaction of powders, which are crushed into mechanically strong agglomerates (granules), which are then sieved to select the required granulometry.

This process is simple enough to put operation. It is dry and thereby increases criticality margins. It can be industrialised using, for example, rotary presses with high throughput. From a low-density powder, it gives strong, dense and cohesive agglomerates suitable for pressing UO_2 pellets [CHO91]. The shape of these granules is irregular so that a spheroidisation step is necessary. Spheres are thus obtained by their reciprocal abrasion.

Mechanical granulation followed of spheroidisation is used in the UO_2 Laboratory of the CEA/Cadarache, for the manufacture of macromasses, to study heterogeneous LWR fuels (cf. § 4.4.5). Following this process, the sphericity factor (Φ_{max}/Φ_{min}) is about 1.5 to 1.7, which is too high for HTR applications. Appendices 31 and 32 compare particles produced by the mechanical granulation and sol gel methods.

Given the poor sphericity, mechanical granulation does not conform to HTR requirements.

7.2 Spray - drying

In the spray drying process [RIN86, LUK89], a fine powder of the desired compound (for example UO_2) is dispersed in a solvent. This solution or suspension is dispersed into droplets in a hot gas flow to evaporate the solvent. In the majority of cases the solvent is water and gas is air. The atomisation operation associated with fast drying yields powder agglomerates that kept the memory of the spherical shape of the precursor droplets.

The preparation of the initial solution is a delicate stage of the process, because the powder must be distributed homogeneously throughout. To achieve high drying rates, the powder concentration must be as high as possible, but still with a sufficiently low viscosity to atomise the solution. For UO_2, the dry matter is about 60 to 65% for a viscosity of the order of 150 mPa.s. To obtain higher powder ratios energy must be supplied in the form of ultrasound or turbine disperser or by addition of a dispersing organic, such as DARVAN C™ (ammonium polymethacrylate). A binding organic is also added to the initial solution, in order to strengthen the powder agglomerates during drying of the droplets. Polymers of the polyvinyl alcohol (PVA) type are used frequently for this operation [RAN86, LUK89].

The atomisation conditions define the final particle size. The more the droplet size is reduced, the more the surface / volume is raised, and therefore the speed of evaporation is faster. The use of an injector in the very dilute conditions will yield particles of small size (some microns to a few tens of microns).

In the case of UO_2, it is possible to get particles in the 10-100 μm range within a chamber with a few tens of centimetres in diameter.

Increasing the size of the particles requires the modification of the atomisation method and the diameter of the chamber. The maximal sizes of particles obtained by atomisation are in the order of 400 to 500 μm, for 5 m chambers [RIN86, GRA91].

For the manufacture of HTR kernels a densification stage is necessary. For UO_2, the density of the agglomerates after atomisation is the order of 3 $g.cm^{-3}$. Densification would lead to a volume reduction by a factor between 3 and 4, and ultimately to a kernel diameter reduction of about 1.5.

If one considers a maximal size of 450 µm for particles obtained by atomisation, the maximum diameter of the kernels after sintering is about 300 µm. However, this value corresponds to a surrounding wall of 5 m. If one considers a reasonable volume for an installation using fissile material a maximum diameter of 1 m should be considered and thus the maximal particle size is about 200 µm [RAN86], i.e. a kernel size of 100-150 µm. This size is too small for HTR applications (cf. § 2).

Therefore the spray drying process is considered unsuitable for HTR fuel kernel fabrication.

8 - CONCLUSION

Many investigations have been made since the beginning of the 1960's, on the development of dense spherical particles for the development of HTR fuels or vibropacked fuels for PWR's and FBR's. These investigations considered several processes that were developed to pilot or industrial scale, especially in the 1970's. Thereafter the majority of these activities were stopped.

Of these processes, the pseudo sol gel process by precipitation on a supporting gel (GSP) became the industrial reference. Other processes such as the Resin-process, the Powder Agglomeration process or the HMTA-process were developed to pilot scales, but were not pursued further due to the reduction in HTR activities at the end of the 1970's. The Resin-process should not be considered further as it only gives carbides and oxycarbides.

The main interest of the Powder Agglomeration process is the absence of liquids to increase criticality margins. Besides, it seems simple enough to operate and requires the relatively classic equipment already in use in the domain of the powder metallurgy.

The HMTA process presents an interesting alternative to the GSP process. Indeed, this process has technical advantages that can be taken into account as: easiest spheres forming and washing steps.

Alternative processes, never used for HTR fuel, such as Spray Drying and Mechanical agglomeration have been evaluated and found unsuitable.

Finally, based on a bibliographic review, the choice of a process for the development of HTR kernels leads to the GSP process. Mainly it yields good kernels in the range between 200 and 800 μm, with a high production rate, and with a process which can be developed at a large scale. It is the only one, which has been developed for industrial application for the fuels of Fort-Saint-Vrain and THTR reactors.

Nevertheless, HMTA process presents an interesting alternative because can yield the same quality of kernel on a wider size range (between about 80 and 1200 μm, which is not necessarily needed for HTR fuel). The sphere formation is easier and even guaranteed. The washing step may also be easier. The broth preparation and hot oil steps and waste handling are more problematic.

For both processes, a particular point of the assessment concerns the management of chemicals, wastes and scraps, which will also influence the process choice. For instance, in the case of GSP process, the quantity of liquid waste seems to be a little higher and mainly composed of aqueous ammonia based solutions. For the HMTA process the liquid waste seem to be mainly composed of organic liquid waste (oil and organic washing solvent). Then the choice of the process depends also on the policy chosen to manage such a products. Local issues and legal stipulations of the country, or area, where the plant is foreseen may even decide the choice.

GLOSSARY:

AERE - Harwell: Atomic Energy Research Establishment Harwell at UKAEA, Berkshire, United Kingdom,

AVR: Experimental HTR reactor at Jülich Germany; 46 MW_{th} / 15 MW_e; begin 1966, coupling to the network 1967, stop 1988,

AGR: Advanced Gas - Cooled Reactor, graphite/gas reactor intermediate between the UNGGS and HTR concepts, coolant = CO_2 (TCO_2 (500 °C), experimental reactor that functioned in the 1960's at Springfields in England

AWRE(-Aldermaston): Atomic Weapons Research Establishment at Aldermaston, United Kingdom,

BNFL: British Nuclear Fuel Limited

CEA/DMG : Commissariat à l'Energie Atomique / Department de Metallurgy de Grenoble

CEN-Mol : Centre d'Etude de l'Energie Nucléaire de Mol-Donk, Belgique

CNEN : Comitato Nazionale per l'Energia Nucleare , Italian research organisation later ENEA.,

DRAGON: European HTR Project (OECD) (1959-1976), UKAEA controlling interest, to which was also associated USA

DRAGON Reactor Experiment (DRE): Experimental European HTR Reactor at Winfrith in England; 20 MW_{th} (without production of electricity); start 1964, stop 1975,

EIR: Swiss Institute of Research on Reactors at Würenlingen, that became thereafter a component of the Paul Scherrer Institut (PSI)

ENEA : Ente per le Nuove technologie l'Energia e l'Ambiente (anciennement CNEN) , Italian research organisation

FBR (LMFBR): Fast Breeder Reactor

%FIMA = at% = rate of fission = number of atoms heavy fissioned as a % of the number of initial heavy atoms (U+Pu+Th...)

Fort Saint - Vrain: Industrial American HTR prototype Reactor in Colorado; 837-842 MW_{th} / 330 MW_e; start 1974, coupling to the network 1976, stop 1989, didn't function at full power (factor of load 16%), numerous shut downs

GA: General Atomics, San Diego, USA; notably main of US operator of the HTR path

W.R GRACE. & Co. : American company in the domain of the specialty chemistry

GT-MHR: Gas Turbine Modularized Helium - Cooled Nuclear Reactor, international HTR reactor project, 600 MW_{th} / 300 MW_e, of which one of objectives is to burn Russian weapon plutonium (participants Russia (MINATOM), USA (GA), Japan (Fuji) and France (Framatome))

HCOOH: formic acid

HEU: highly enriched uranium

HOBEG: HOCHTEMPERATUR-REACTOR-BRENNELEMENT G.M.B.H.; Hanover, Germany; HTR fuel fabricator

HMTA: HEXA-METHYLENE-TETRAMINE (CH2)6N4

HTR: High Temperature Reactor, reactor of particles moderated by graphite and cooled by helium, (T_{helium} 750-950 °C)

HTTR: High Temperature engineering Test Reactor, Japanese experimental reactor 30 MW_{th} without production of electricity, start 1998,

ITU: European Institute for Transuranium Elements, Karlsruhe, Germany

JAERI: Japan Atomic Energy Research Institute

KFA: KernForschungsAnlage, Research center at Jülich in Germany, today FZJ: Forschungszentrum Jülich

KEMA: Keuring sieve Electrotechnische Materialen Arnhem; Dutch research center at Arnhem

LEU: lightly enriched uranium

MOX: Mixed OXides, fuel in the form of sintered pellets frittées of mixed oxide of uranium and plutonium for LWR

NFI: Nuclear Fuel Industries

NUKEM: Nuklear Chemie und Metallurgy G.m.b.H. ; German operator of the cycle of the fuel

ORNL: Oak Ridge National Laboratory, USA,

Peach-Bottom Reactor (PBR): American experimental HTR reactor in Pennsylvania; 115 MW_{th} / 40 MW_e; start 1966, coupling to the network 1966, stop 1974,

Peptisation: formation of type peptide link

PNC: Power reactor and Nuclear fuel development Corporation

PSI: Paul Scherrer Institute, Swiss research institute composed of several sites near Villingen,

PWR: Pressurised Water Reactor

RFL: Reactor Fuel element Laboratories, UKAEA, Springfields, UK,

SNAM: subsidiary of the holding Italian ENI, as well as AGIP-Nucleare

TCE: TetraChloroEthylene (or perchloroethylene) C2Cl4 (CCl2=CCl2)

THTR(300): Thorium High Temperature Reactor; German industrial prototype HTR reactor at Schmehausen; 750-756 MW_{th} / 300 MW_e; start 1983, coupling to the network 1985; stop 1989; factor of load inferior to 30%

UKAEA: United Kingdom Atomic Energy Authority

Urea (or carbanine): NH_2-CO - NH_2

UNGG: reactor with Uranium Natural Graphite and Gas, coolant = CO_2 (TCO_2 (400 °C)

USAEC: United States Atomic Energy Commission

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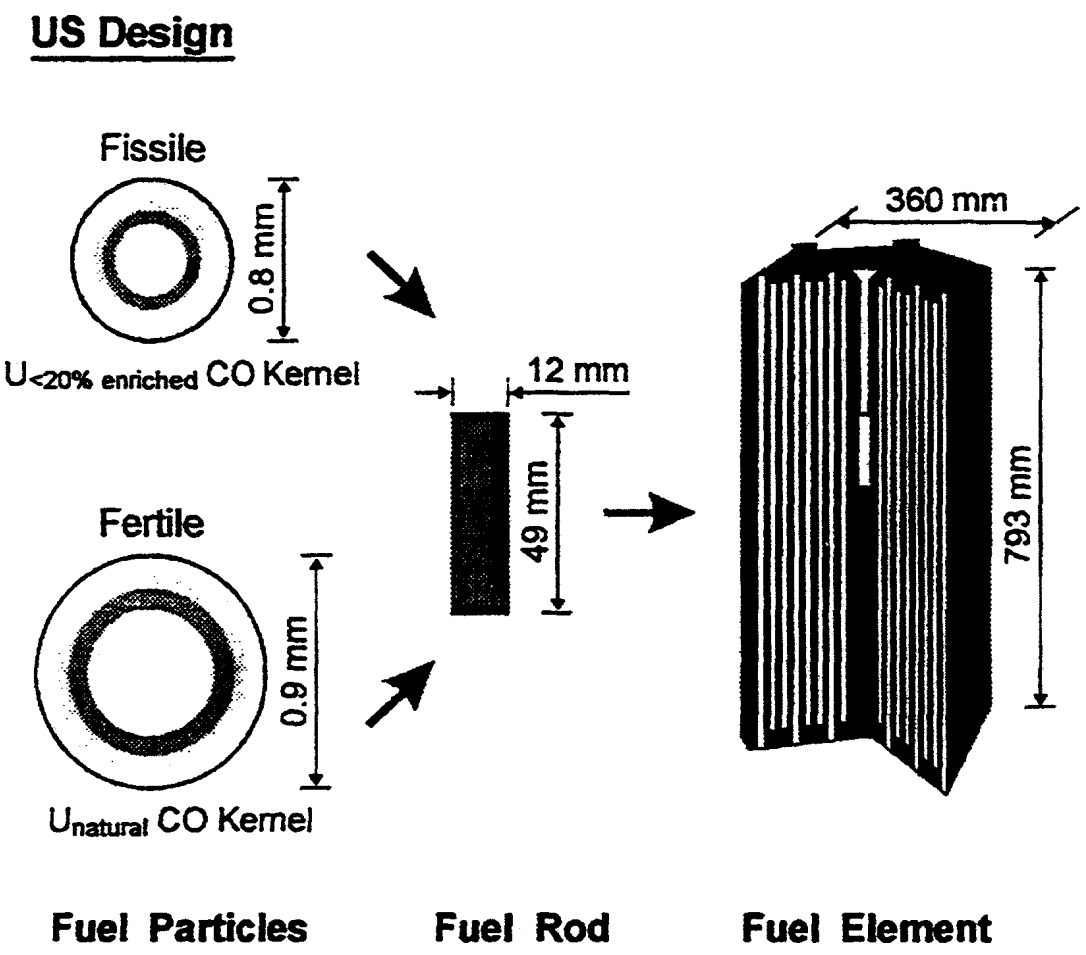
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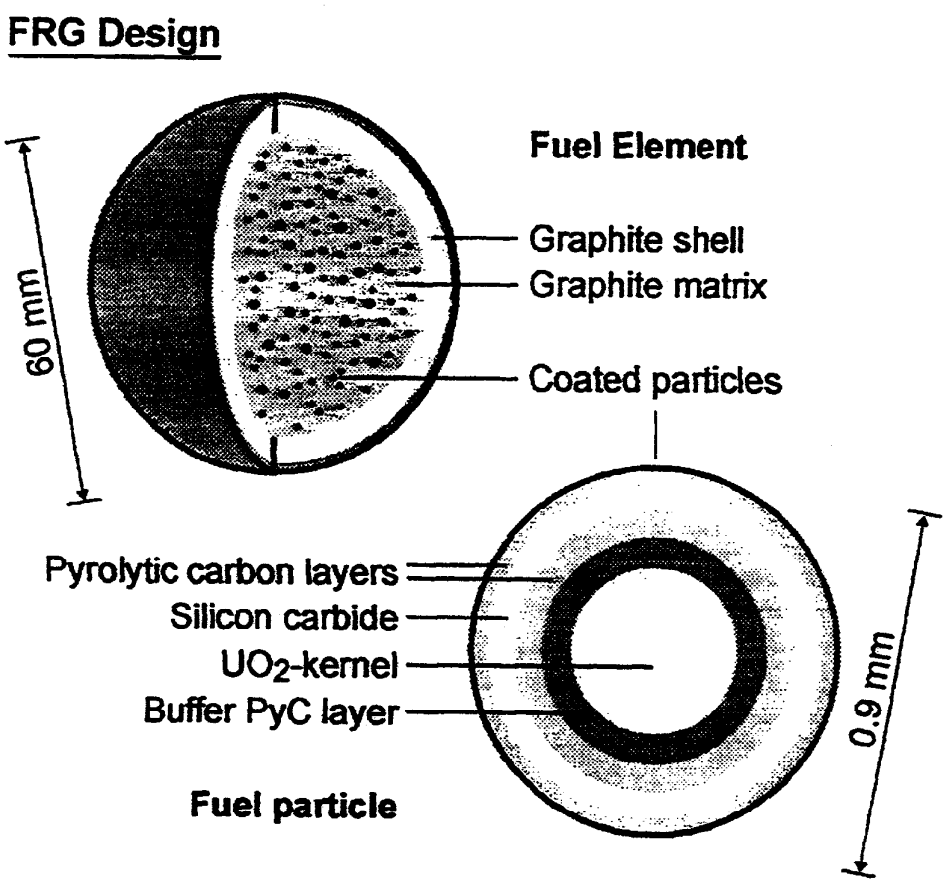
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APPENDICES

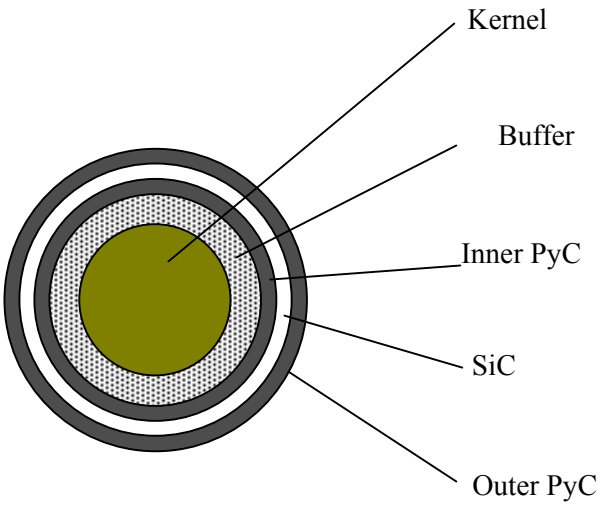
Appendix 1: Schematic principle of GA fuel element concept [IAEA97]



Appendix 2: Schematic principle of German fuel element concept [IAEA97]



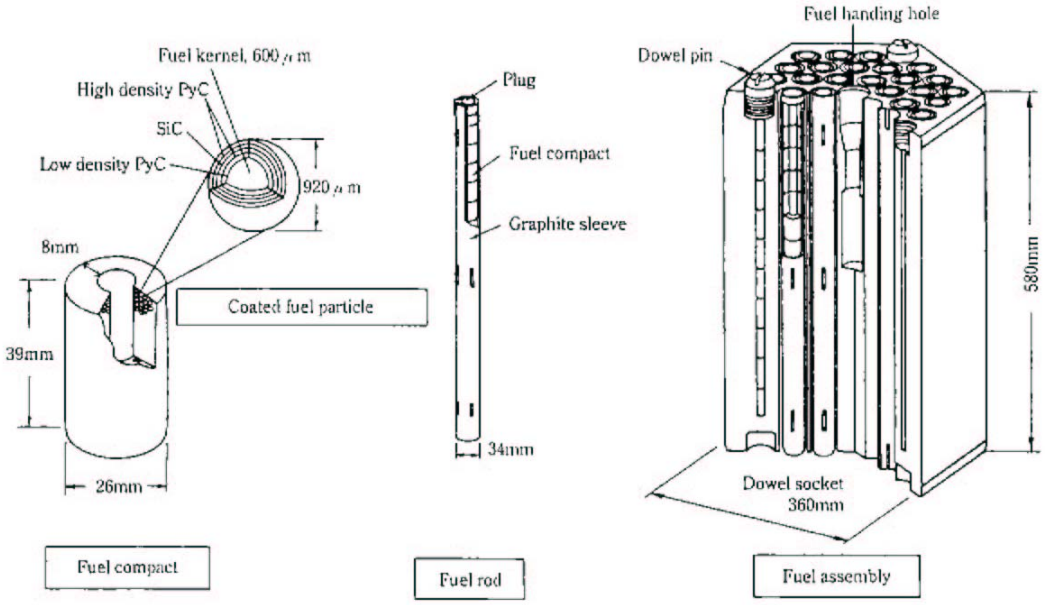
Appendix 3: Schematic principle of the SiC-TRISO particles



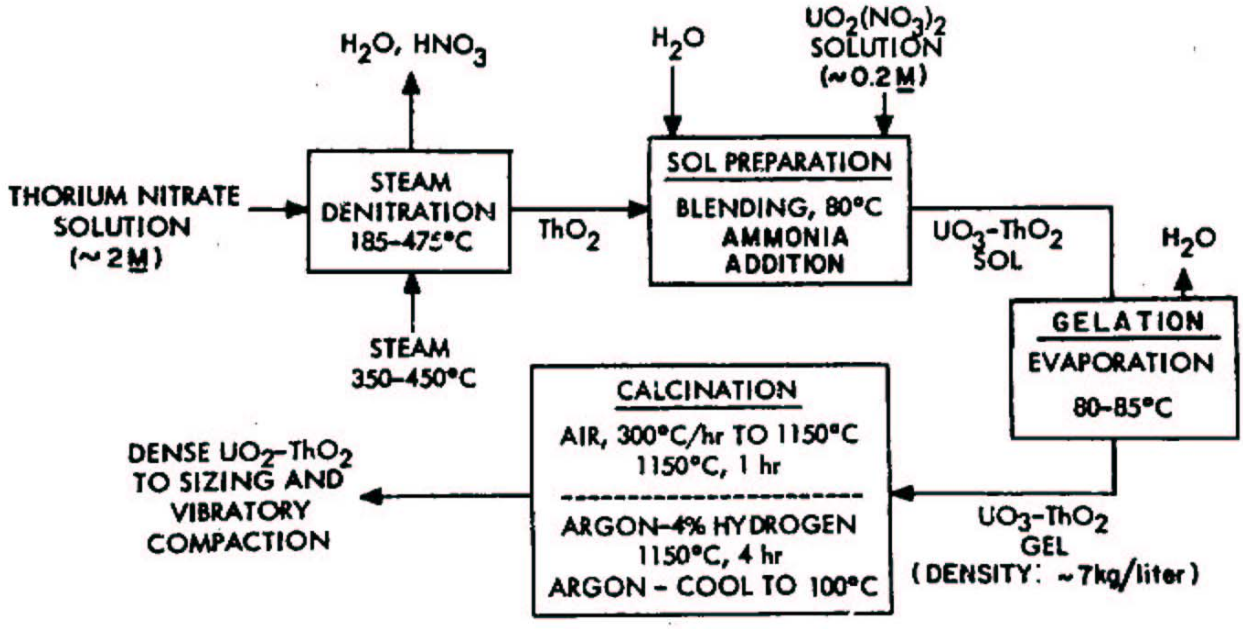
Appendix 4: List of pilot or industrial installations using the pseudo sol-gel GSP process in the 1970's [BEA79]

Process	**Plant Site**	**Kernel composition**	**Capacity (kg/day)**
SNAM	Milan, AGIP-Nuclear	UO_2 , ThO_2 , $ThUO_2$	10
SNAM	Casaccia, Rome, CNEN	PuO_2 , $UPuO_2$	3
SNAM	Springfields, BNFL	UO_2	20
KFA	KFA, Jülich	ThO_2 , $ThUO_2$	12
AERE	Harwell	UO_2 , PuO_2 , $UPuO_2$	17
HOBEG	Hanau	UO_2 , ThO_2 , $ThUO_2$	18
NUKEM	Hanau	ThO_2 , $ThUO_2$	60 - 100
GA	San Diego	ThO_2	240
GA	San Diego	UO_2	24

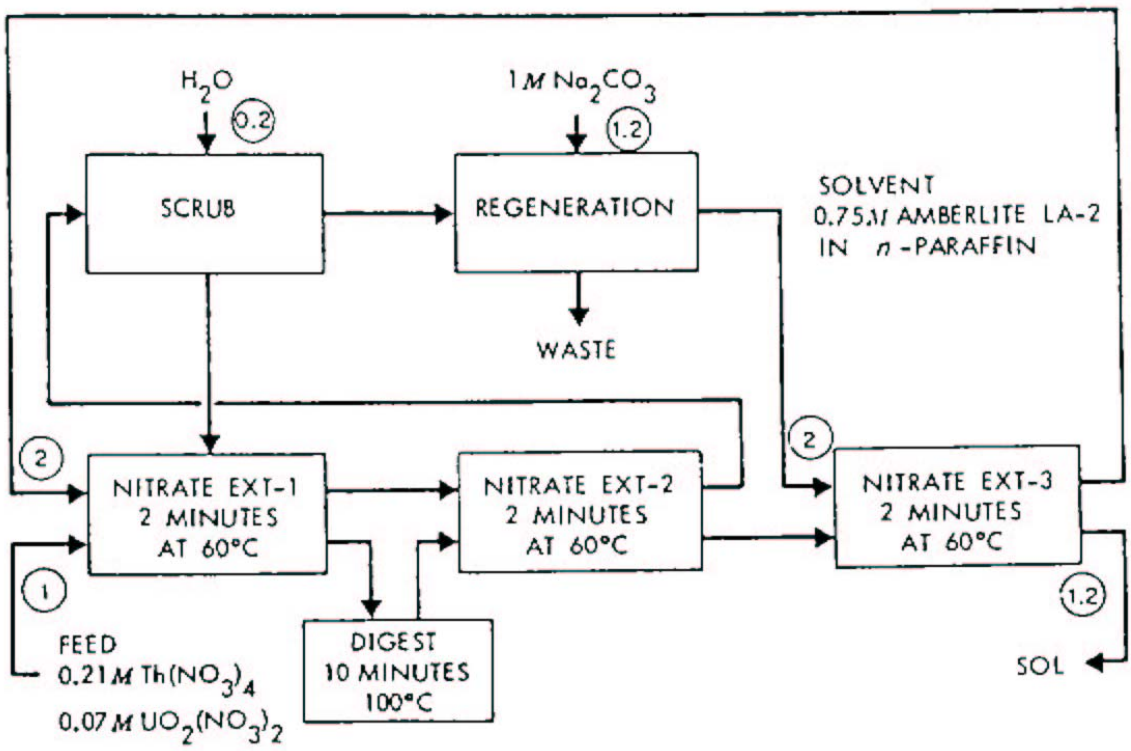
Appendix 5: Schematic principle of the fuel kernel and element for the Japanese test reactor HTTR-40 [JAE00, SAW99a, SAWW99b, KIT97, AIEA97]



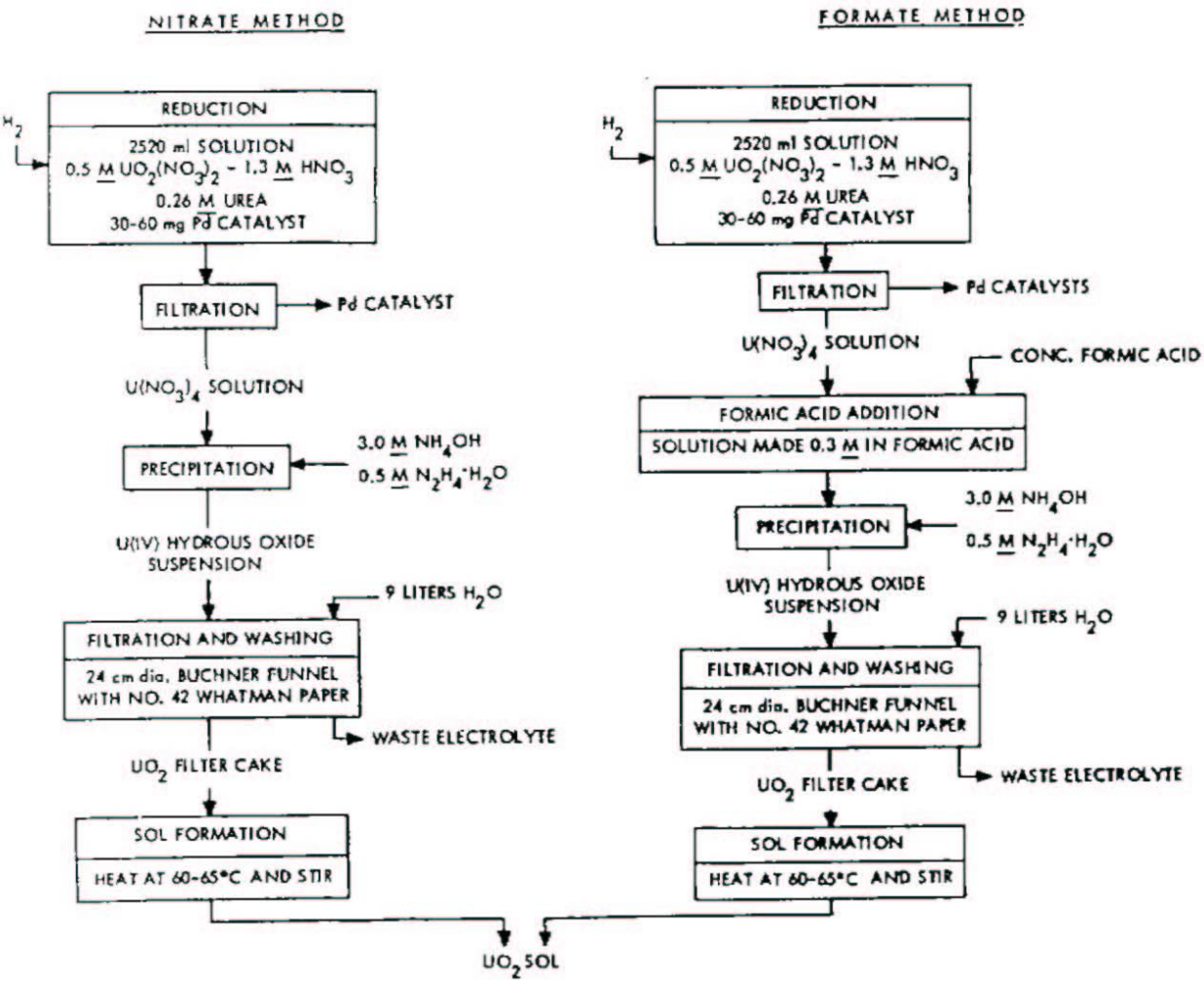
Appendix 6: Schematic principle of the ORNL hydrothermal denitration and gelation by dehydration processes [MCB67]



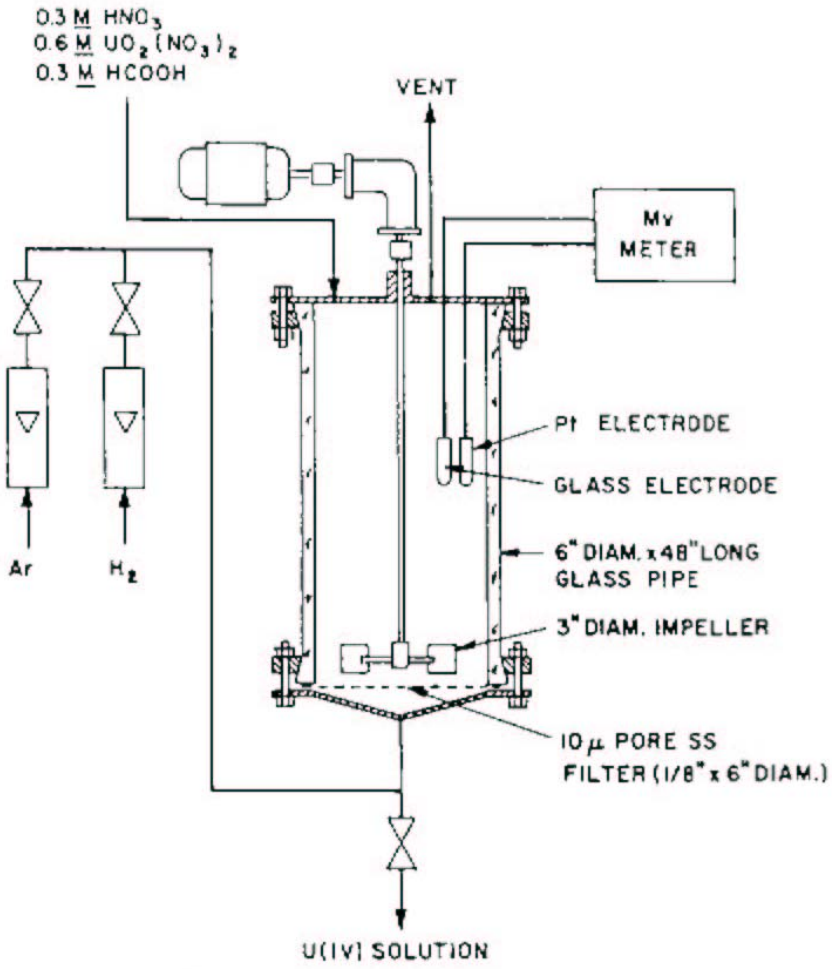
Appendix 7: Schematic principle of the ORNL denitration by solvent extraction process [WYM68]



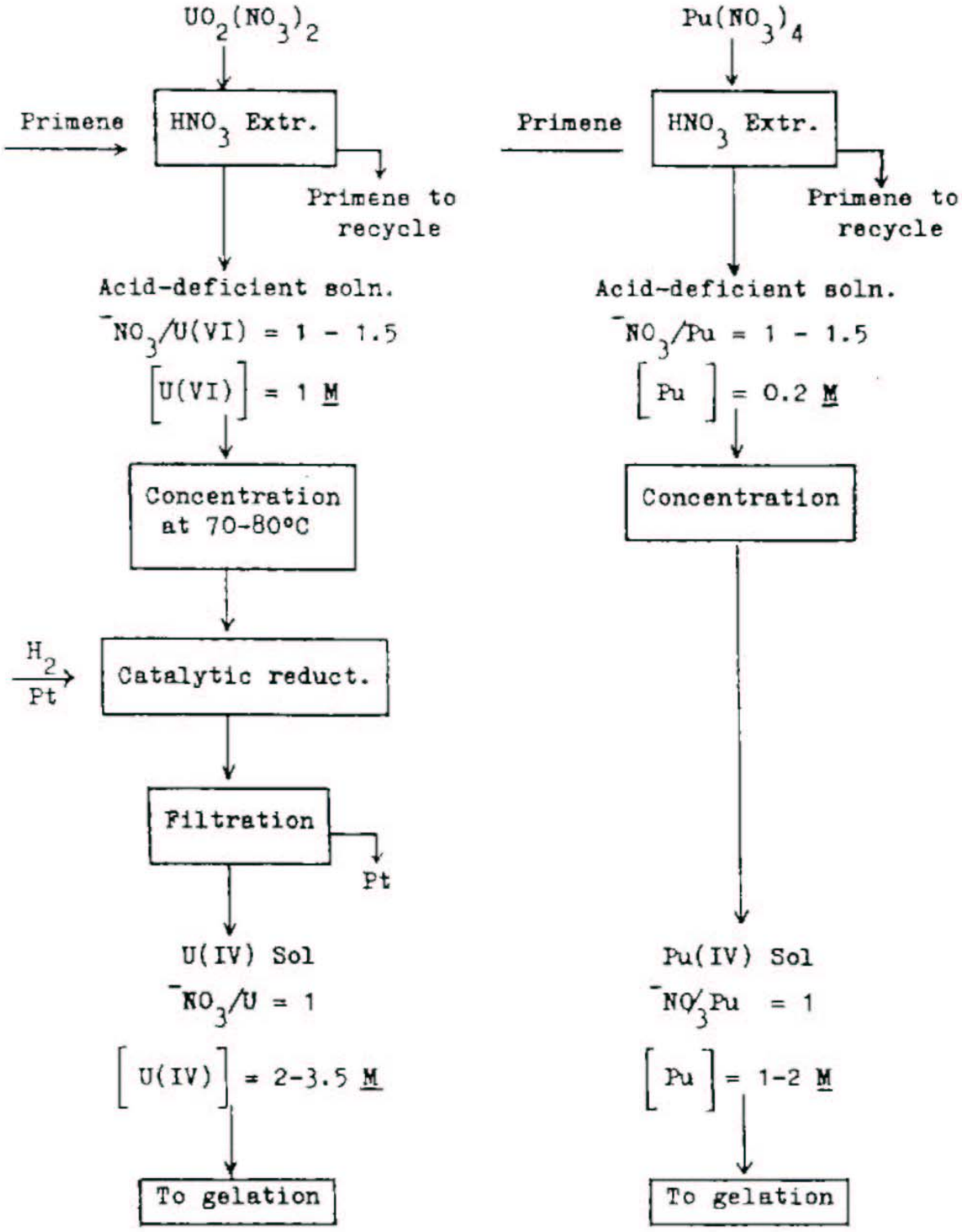
Appendix 8: Schematic principle of the ORNL UO_2 stable sol production process [MCB66]



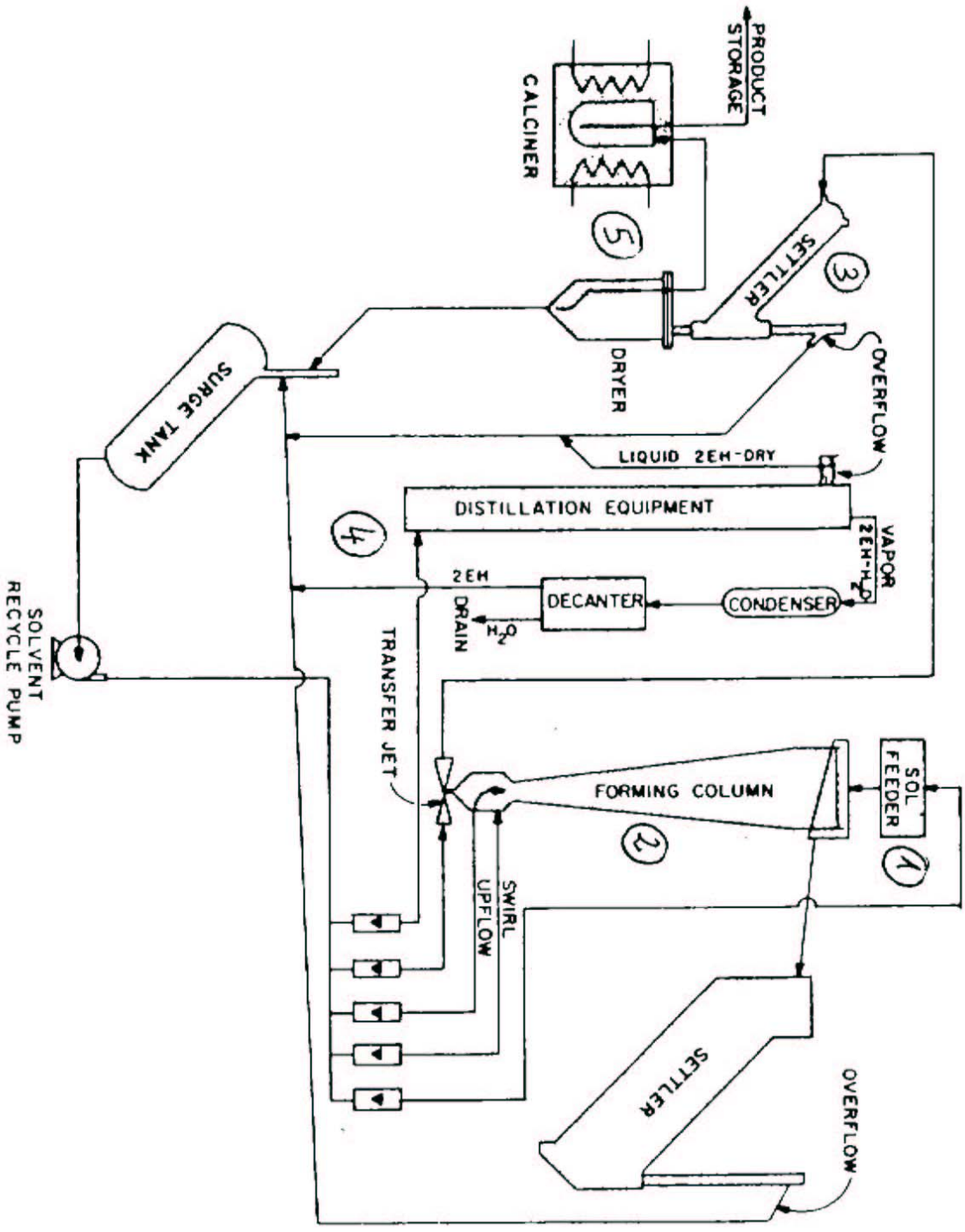
Appendix 9: Reduction of uranium to the IV valence in solution at ORNL [WYM68]



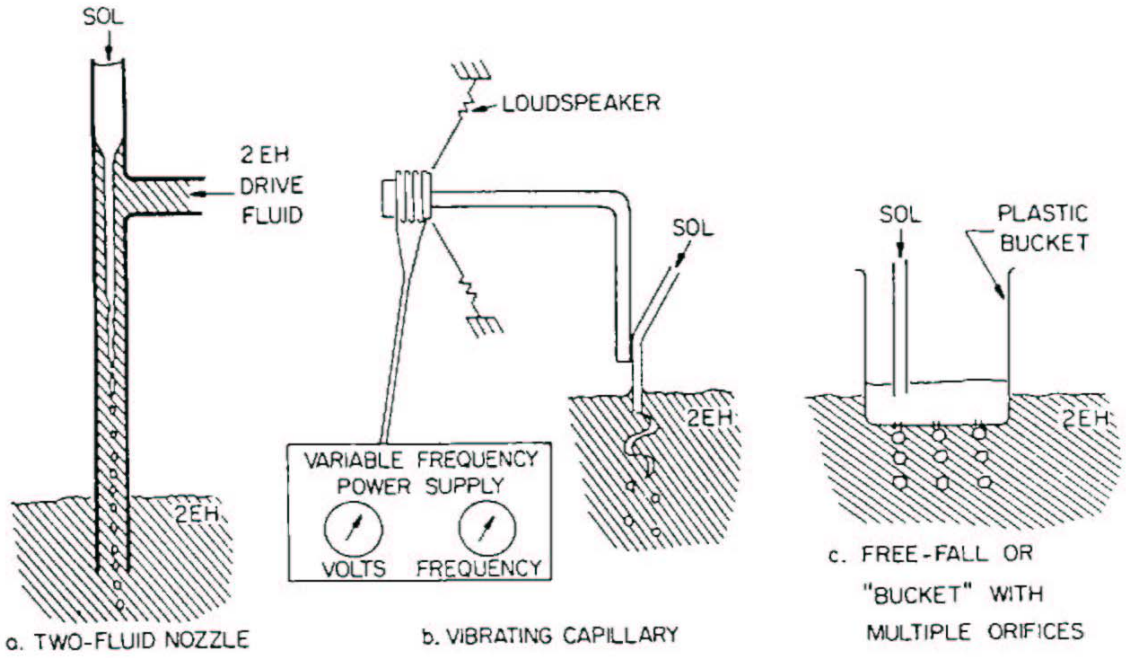
Appendix 10: Schematic principle of CNEN's processes for UO_2 and PuO_2 sol production [ZIF68]



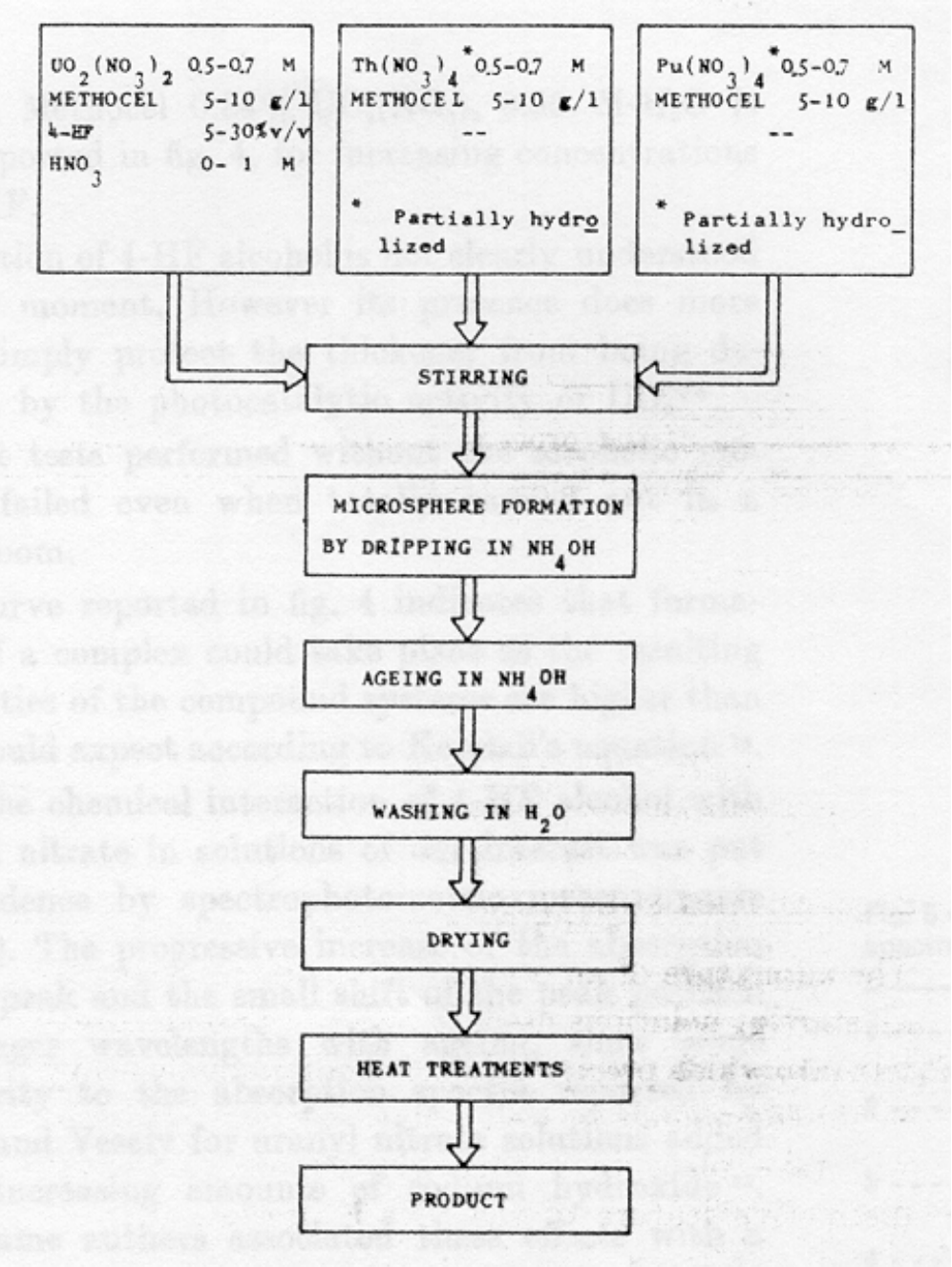
Appendix 11: Flow-sheet of the ORNL installation for microsphere production by dehydration [WYM68]



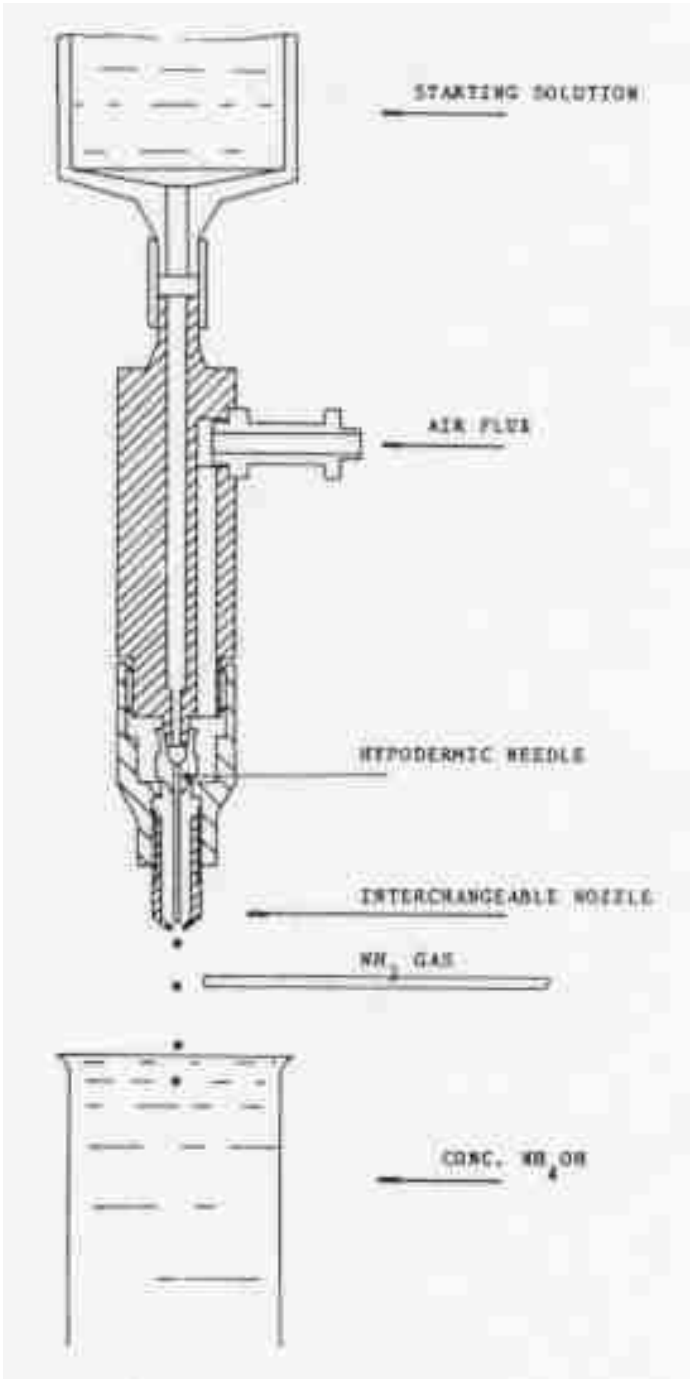
Appendix 12: Principle of the injectors studied at ORNL [WYM68]



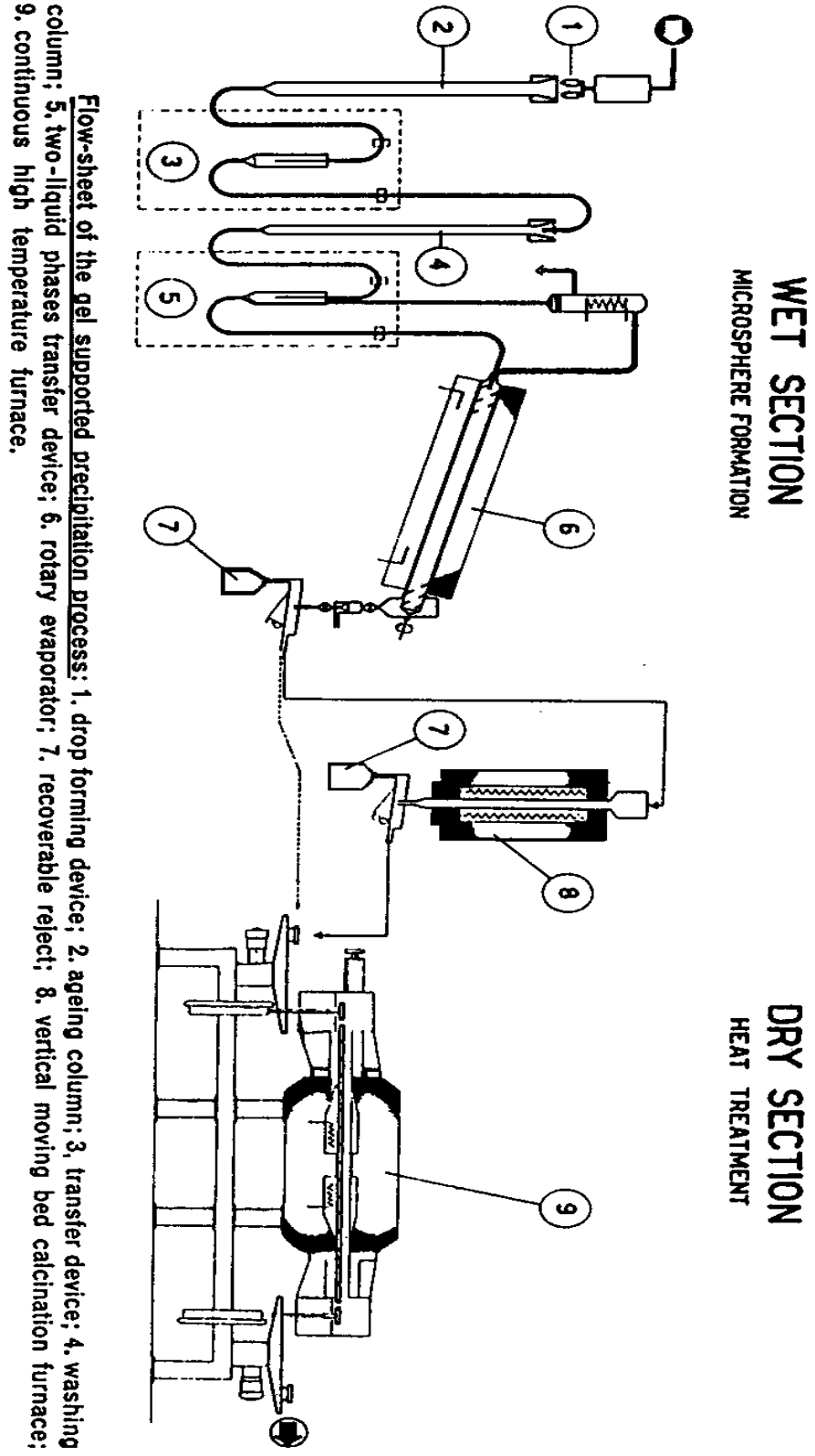
Appendix 13: Schematic principle of the GSP-SNAM process [BRA70a]



Appendix 14: Schematic principle of the double flux capillary injector used in the GSP-SNAM process [BRA70a]

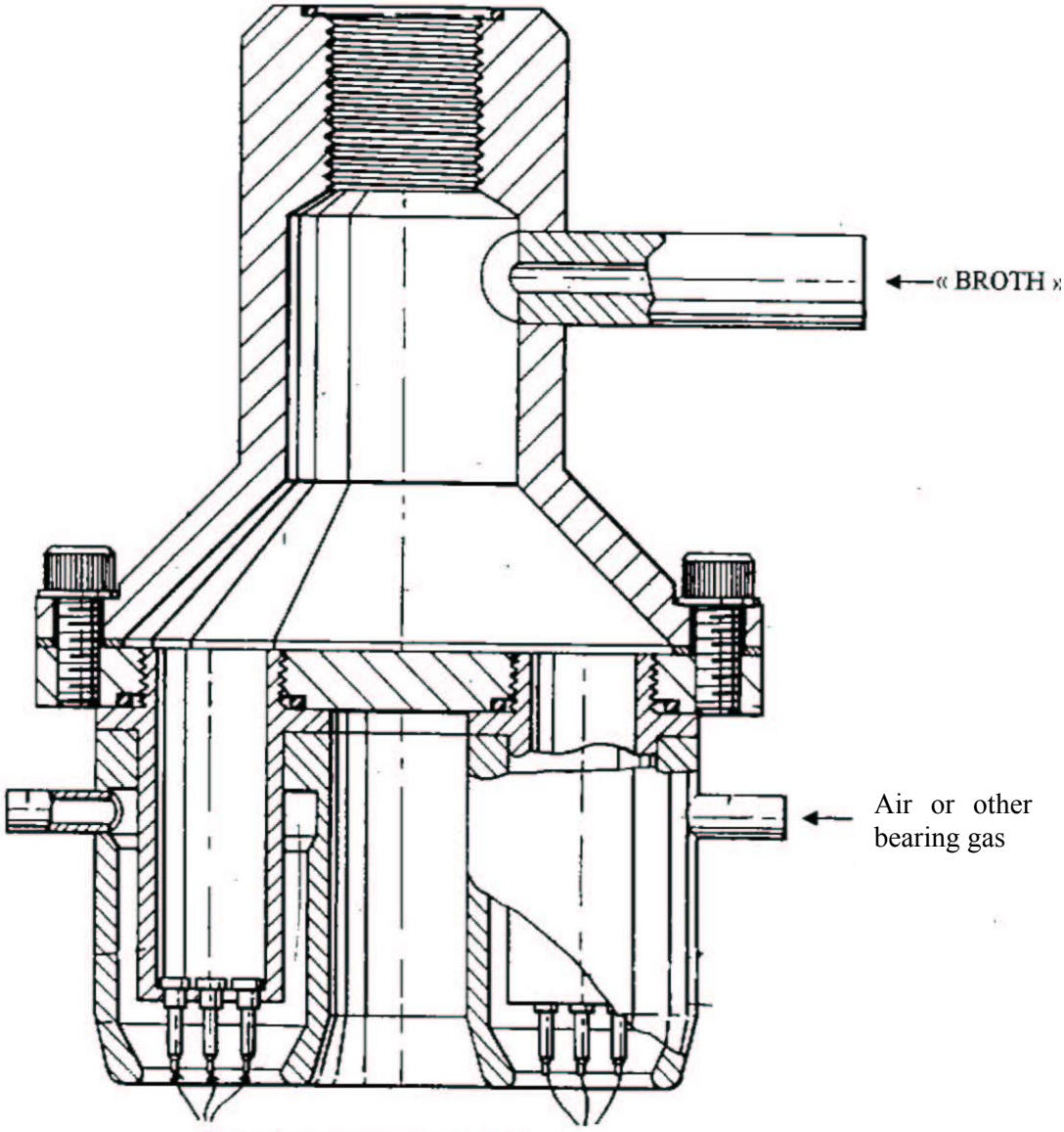


Appendix 15: Schematic diagram of GSP-SNAM pilot installation of AGIP - Nucleare in Italy [FAC70, BRA70b]

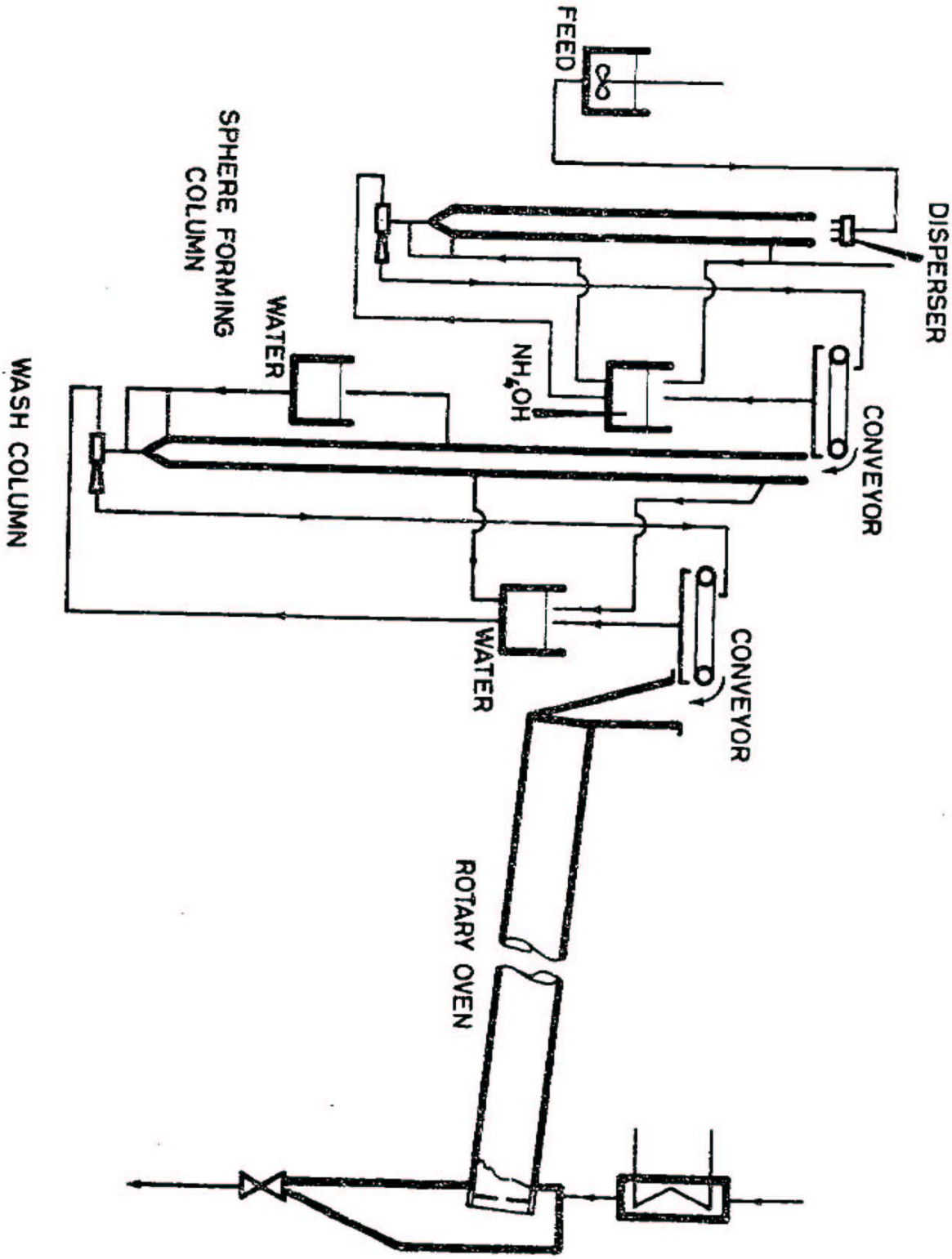


Flow-sheet of the gel supported precipitation process: 1. drop forming device; 2. ageing column; 3, transfer device; 4. washing column; 5. two-liquid phases transfer device; 6. rotary evaporator; 7. recoverable reject; 8. vertical moving bed calcination furnace; 9. continuous high temperature furnace.

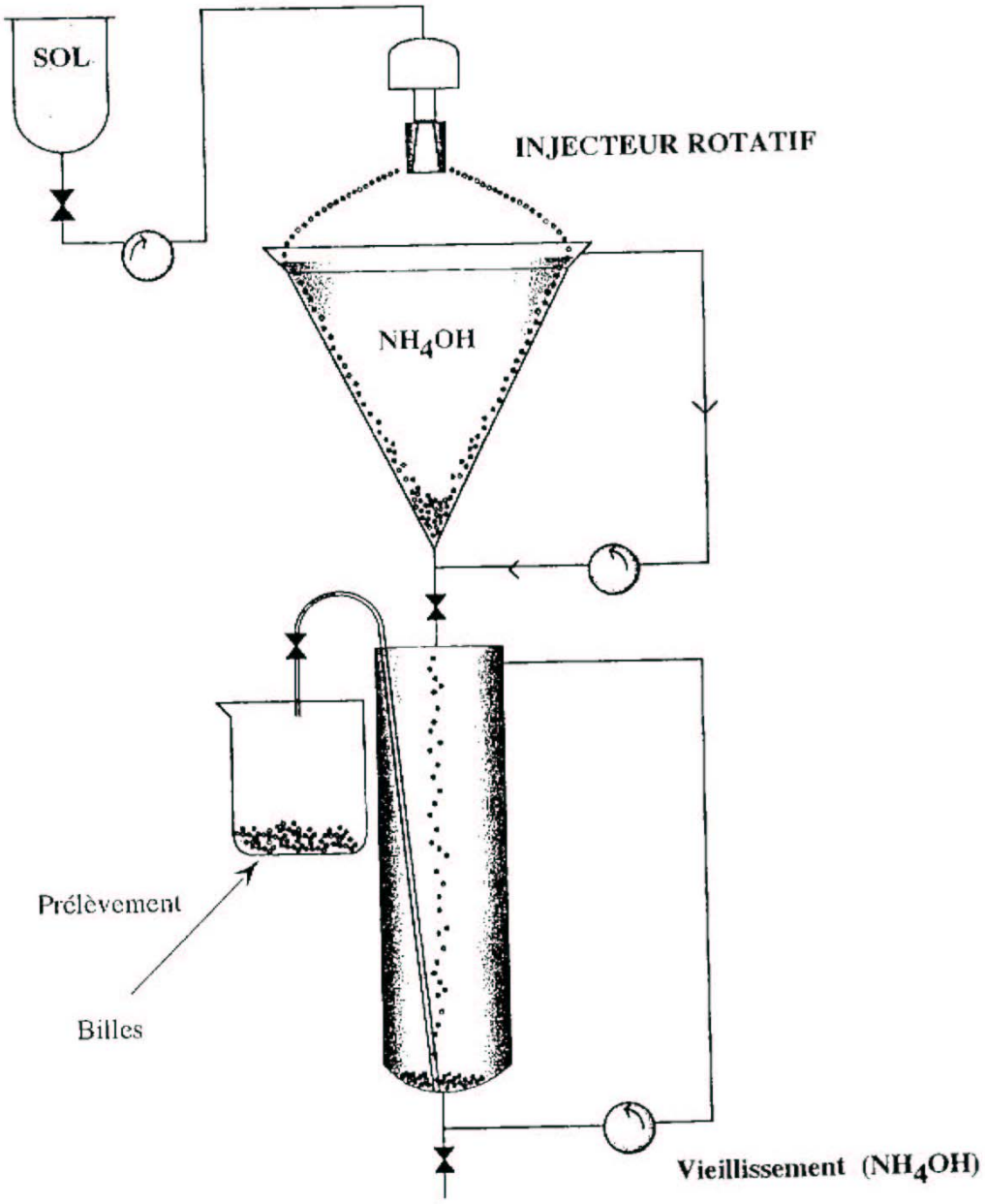
Appendix 16: Schematic diagram of a multiflux liquid disperser used at AERE -Harwell [UKA70]



Appendix 17: Schematic diagram of the GSP pilot installation at AERE - Harwell [HAR70]



Appendix 18: Schematic diagram of the GSP device with a rotary cup disperser, originally used for U-Pu fuel pellets studies at CEA/Cadarache



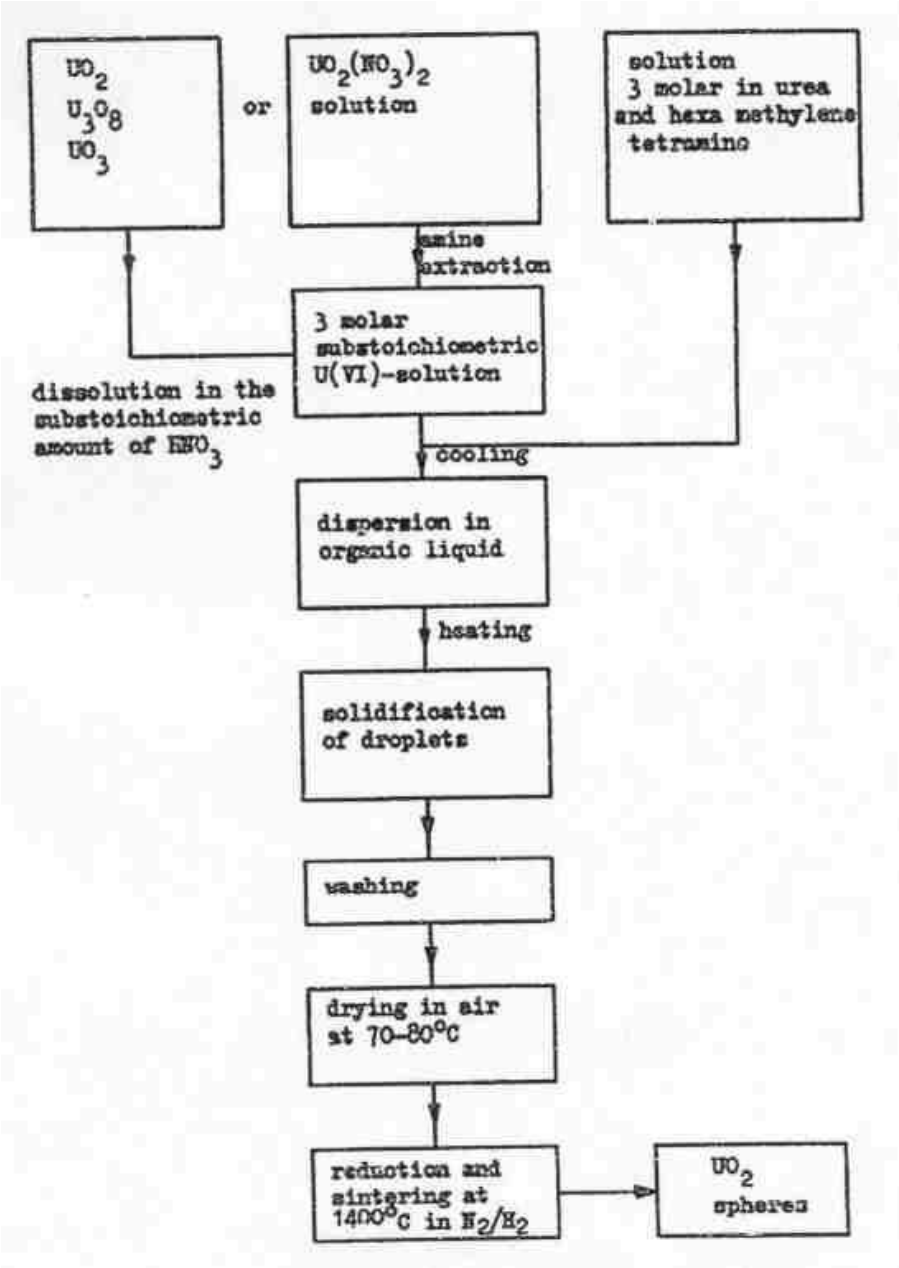
Appendix 19: Picture of the GSP device for kernel manufacturing tests at CEA/Cadarache



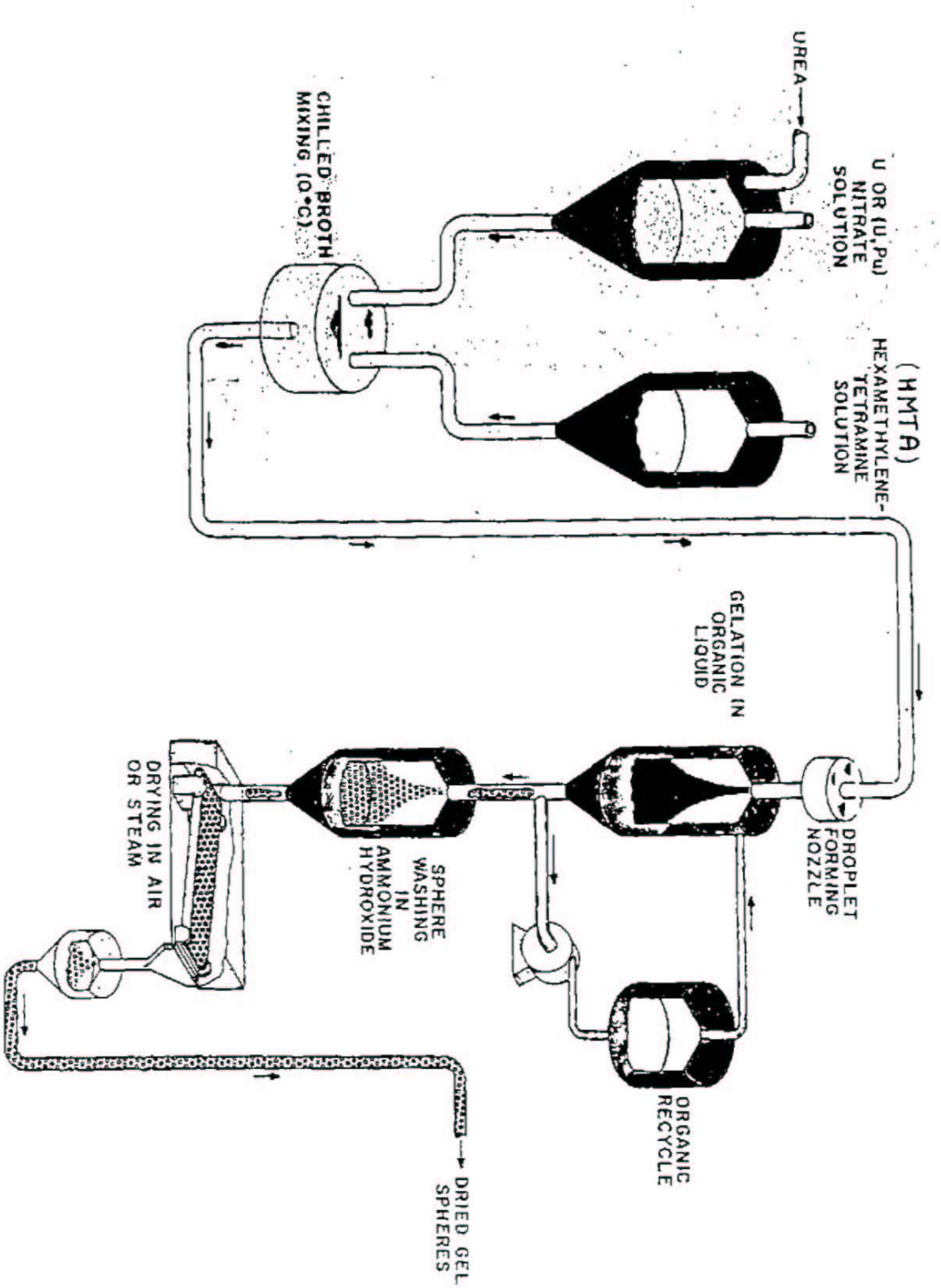
Appendix 20: Picture of the ITU rotary cup sol-gel equipment for production of polydispersed sized particles



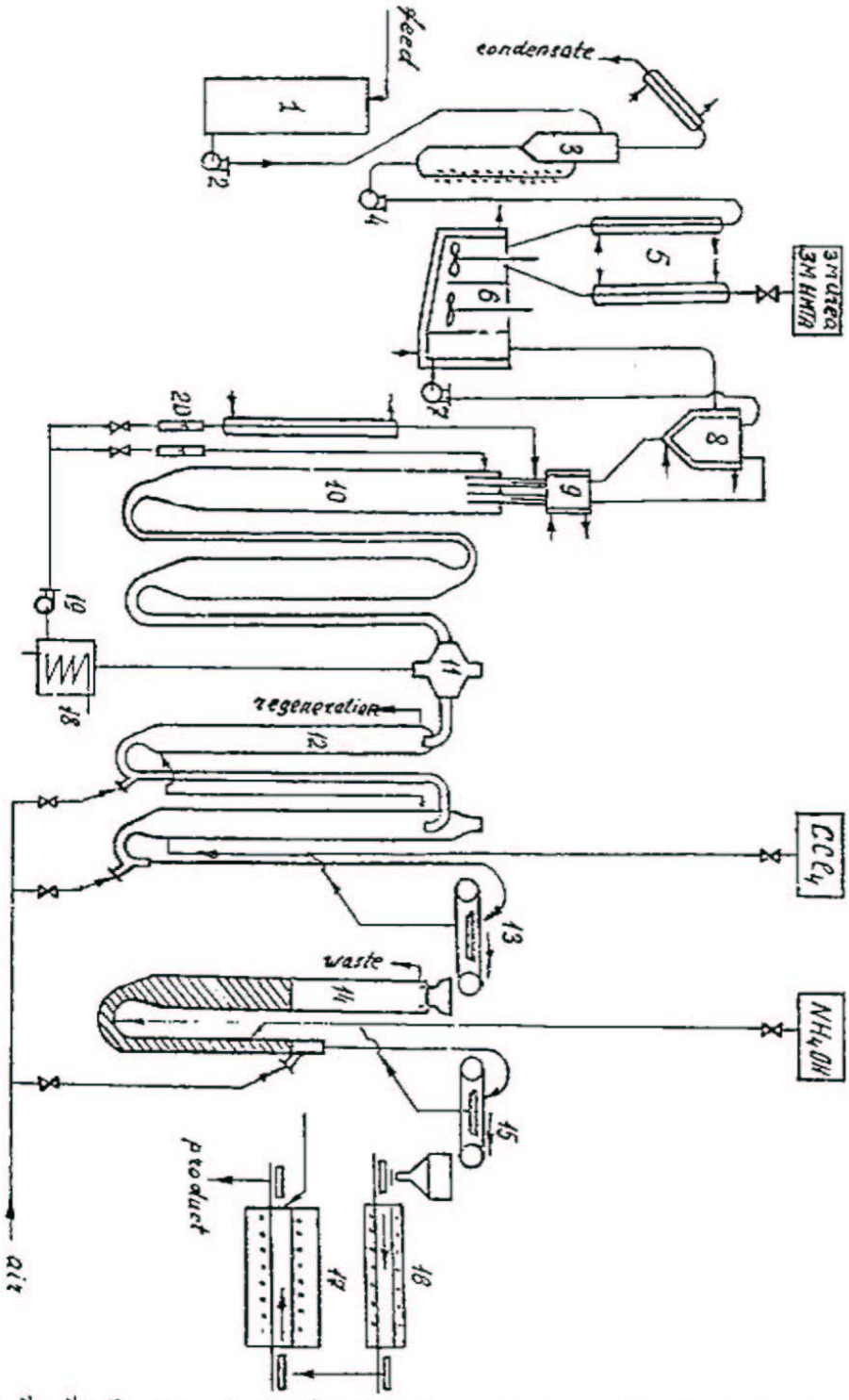
Appendix 21: Schematic diagram of the KEMA HMTA process [VAN70]



Appendix 22: Schematic diagram of the ORNL HMTA installation [BEA79]

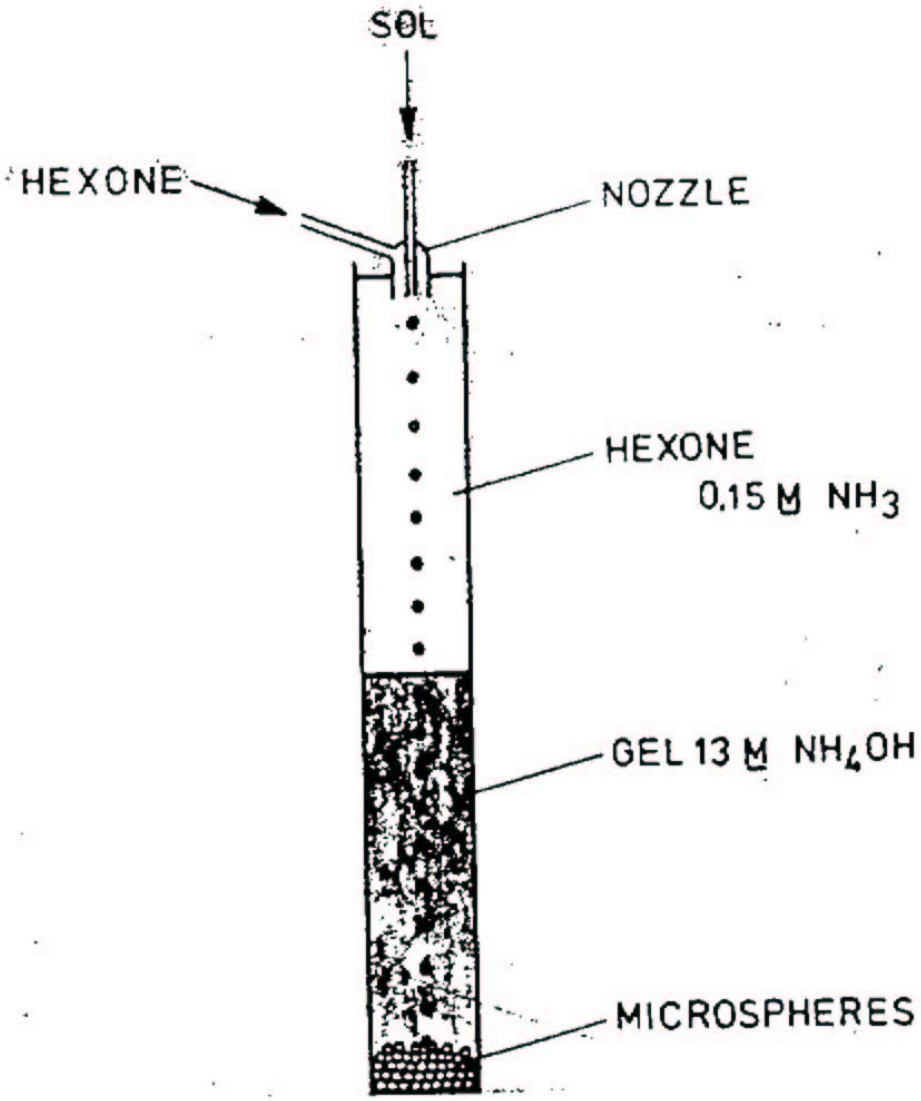


Appendix 23: Schematic diagram of the Russian HMTA pilot installation [MAR73]

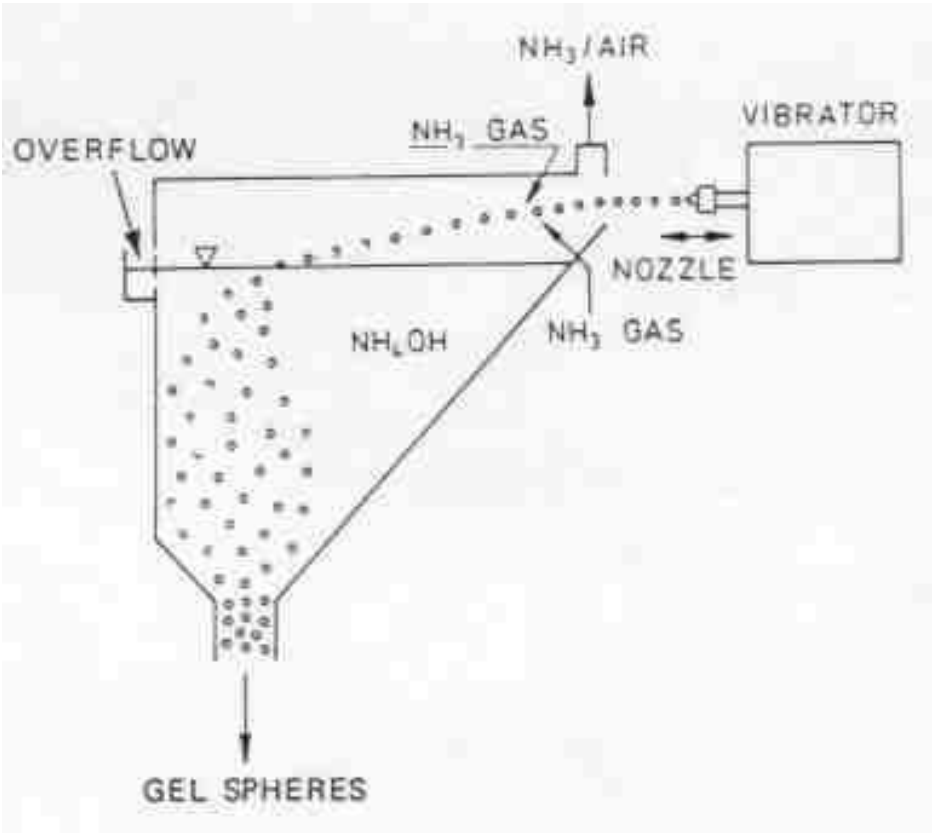


1-initial solution pot
2-proportioning pump;
3-evaporator;
4-proportioning pump
5- refrigerator;
6-mixer;
7-proportioning pump;
8-head tank;
9-dispersing device;
10-gelation columns
11-oil separation apparatus;
12-washing columns;
13-filtering trough;
14-ammonia column;
15-filtering and drying apparatus;
16-pre-drying furnace;
17-sintering furnace;
18-heat exchanger;
19-pump;
20-rotameters.

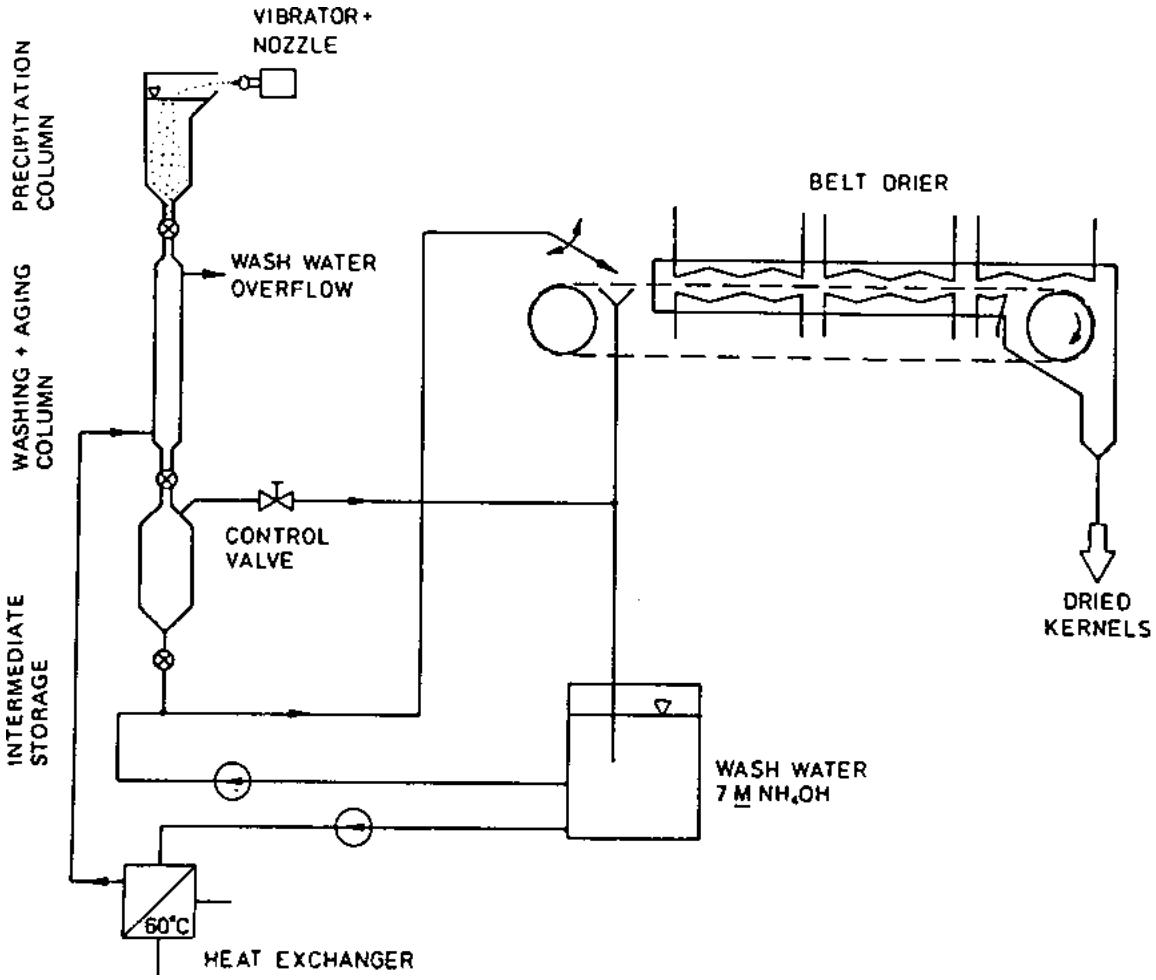
Appendix 24: Flow sheet for the KFA/ICT-Jülich MIBK (hexone) process [ZIM75]



Appendix 25: Schematic diagram of the EGU-KFA/ICT-Jülich gelation reactor [NAE79]



Appendix 26: Schematic diagram of the EGU-KFA/ICT-Jülich process [NAE79]



Appendix 27: Advantages and disadvantages of the GSP and HMTA processes

	Advantages	Disadvantages
GSP	- Initial solution simple to prepare - No organic solvent - Industrialization demonstrated in the 1970's and 1980's for UO_2, ThO_2 and $ThUO_2$ - Laboratory and pilot facilities for , $UPuO_2$, (PuO_2)	- Presence of an organic polymer and additives in spheres - Fragility of spheres (gelation starts at their surface), therefore ageing and delicate washing necessary
HMTA	- Homogeneous gelation of spheres (less fragile spheres) - Less delicate drying - Laboratory pilot facilities for ThO_2, $ThUO_2$, UO_2, $UPuO_2$, (PuO_2)	- Organic compound in spheres (urea, HMTA) - Initial solution concentrated, deficient in nitrates and maintained at 0°C - Heating to 70-100°C of the gelation reactor containing an organic solvent - No industrial experience (yet)