

## Conversion of actinide solutions for the production of MA bearing fuels for Gen IV fast reactor systems

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**Abstract** – *The conversion of the solution to solid for fuels containing minor actinides for accelerator driven systems or Gen IV fast reactors cannot be made by conventional ammonia or oxalate precipitation as is the case in today's reprocessing plant. The small particle size and concomitant dust that is produced in subsequent processing steps will not permit use of these processes on industrial scale. Innovation is needed to avoid dust generating powders, and indeed to simplify the processes themselves. Two such processing routes have been developed at the JRC-ITU. The sol gel route has been used to produce fuel containing Am and Np for the SUPERFACT, TRABANT and other irradiation experiments. The infiltration process has also been established and fuels have been produced for the FUTURIX and HELIOS experiments.*

### INTRODUCTION

The fuel composition and specifications for the Generation IV Gas, Lead and Sodium Fast Reactor (GFR, LFR, and SFR) place severe requirements on the fabrication processes. The high level goals of Gen IV provide for group recycling of the actinides to ensure proliferation resistance in the fuel cycle. In this way, Pu would never be freely accessible for a potential misuse. In the US present Advanced Fuel Cycle Initiative (AFCI), this aspect is addressed and Pu separation from Np is not considered. In Gen IV, this restriction would be further enhanced with a group conversion (U, Pu, Np, Am and Cm) of the actinides separated during reprocessing. The difficulties might not ensue from the conversion itself, rather from the steps required thereafter, wherein the fuel would be brought to the required transuranic content by the introduction of U (depleted or natural), transformed in the desired chemical composition, and formed into the required shape for the irradiation facility being considered.

At this stage, it is not clear that this Gen IV high level goal can be met at all. Fig. 1-3 compare Gen IV fuel reprocessing and refabrication scenarios, with two other philosophies, which would certainly simplify the fabrication processes. The reactors will have a breeding gain just sufficient to produce enough Pu to remain sustainable. Thus after reprocessing, only the addition of  $U_{dep}$  to the fuel is required for the further generation of Pu. The scenario in Fig. 1 results in a homogeneously fuelled reactor core,

with a fuel that contains all minor actinides (MA). A step to separate the MA (possibly with the exception of Np) from the U,Pu stream is foreseen in the second scenario (see Fig. 2), to ease the fabrication and reduce costs, particularly in terms of contaminated effluent streams. The third scenario, (see Fig. 3) adopts a more extreme philosophy of separating the minor actinides (again, possibly with the exception of Np), but keeps them separated for refuelling the reactors. This philosophy is totally in line with heterogeneous fuelling of the fast reactor core. It also has the advantage that minor actinide streams are separated not just in the fuel, but possibly also at the fuel assembly level. Such a philosophy takes the advantage of today's ripe technology for U,Pu fuel fabrication, and limits the volumes of fuel containing the more troublesome minor actinides.

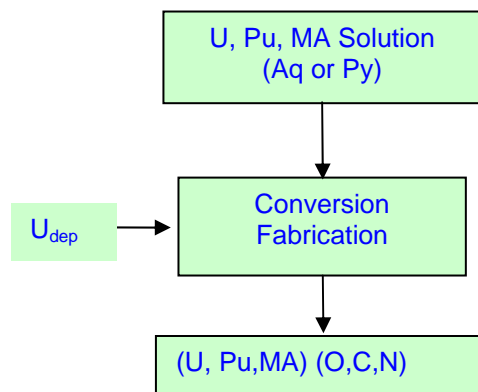


Fig 1. Gen IV Group conversion

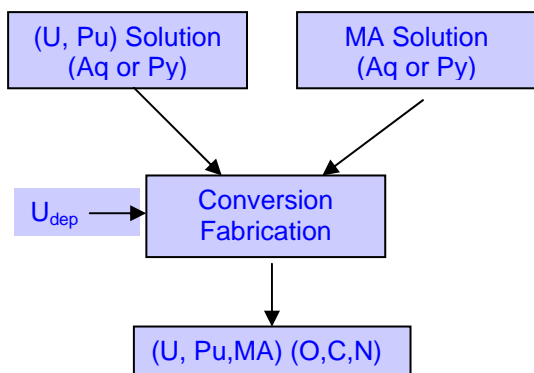


Fig. 2. Homogeneous fuel from separated feed lines

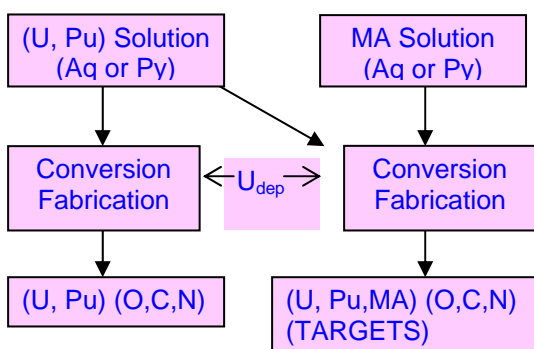


Fig. 3. Targets

### Fabrication facilities

When dealing with transuranic elements, the use of gloveboxes is required to prevent risk of incorporation of highly toxic radioactive materials into tissue or the body. In addition, MA will require further biological shielding. Lead provides shielding from  $\gamma$  emitters and a combination of water, lead and cadmium (or boron) provides shielding from neutrons, emanating directly through radioactive decay (e.g.  $^{244}\text{Cm}$ ) or by  $(\alpha, n)$  reactions typically with light elements (O, N or C) either in the fuel or in the aqueous and organic solvents of the reprocessing solutions.

The incorporation of the minor actinides in the fuel necessitates not only shielding but also automation of the entire process from conversion to the solid all the way through to assembly loading in the reactor. In addition, the reprocessing and fuel fabrication for Gen IV should all be integrated in a single installation at the reactor site. While today's MOX plants for

pellet production are highly developed with extensive (actually complete) automation, they are so designed that operator intervention can be made via gloveboxes. Minor actinide presence in the fuel can necessitate use of hot cells or hybrid laboratories, combining glovebox standards with remote operation by telemanipulators [1]. Transposing MOX fuel fabrication philosophy will probably not be satisfactory for another reason, namely dust, or if this path is pursued, solutions to eliminate it must be found. Both MOX fabrication facilities (Melox in France and SMP in the UK) operating today base their fabrication routes on powder metallurgy methods. Dust is only an issue in that it must be cleaned up. Introduction of minor actinides leaves dust not just as an undesirable nuisance, rather an unacceptable interference. **For minor actinide fuels, processes devoid of dust production are not just desirable, they are essential.**

### CONVERSION TO OXIDE

Conversion to oxide is at the moment the only logical route for aqueous liquid to solid conversion. Oxide fuel for fast reactors was a well developed technology. Former fast reactor fuel relied on the separation (by the PUREX process) of U and Pu in the reprocessing step, so that the pellet production plant had a feed of  $\text{UO}_2$  and  $\text{PuO}_2$  as raw materials, from which blends could be made, and following a milling procedure, the pellets compacted and sintered. This dual feed system (see Fig. 4) had the advantage that the blend for individual fuel pins or assemblies could easily be manufactured. This is tried and tested technology for U and Pu oxide recuperation, and is used commercially today.

PUREX reprocessing processes follows the same principle today. After aqueous separation of the fission products, the actinides remain in an acidic solution in the form of nitrate salts, which are converted to oxide, via a precipitation step. In the PUREX reprocessing plants, U and Pu are separated and are converted in independent installations into solids. For uranium, ammonia hydroxide precipitation can be considered, especially as the biological protection requirements can be relaxed once the Pu is separated.

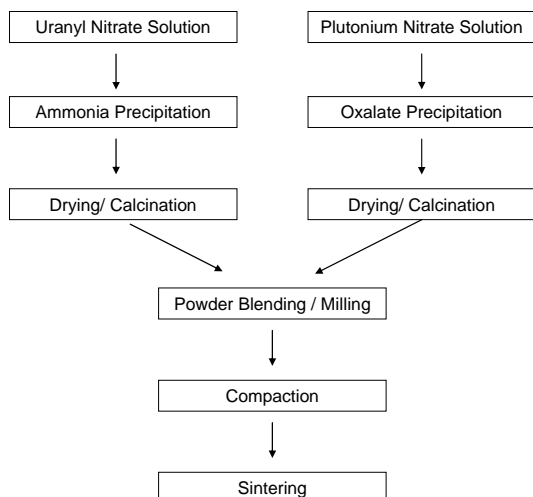


Fig.4. Former fast reactor MOX fuel production

Due to the risk posed by ammonium nitrate, Pu is generally precipitated by the addition of oxalic acid in solution or solid form. The Pu oxalate is thermally treated to give the oxide. Both of these methods are tried and proven procedures in industry today. Recent progress in France, however, indicates that a co-precipitation of U,Pu oxalate salts may be possible under certain conditions [2]. Data on the actinide recovery rate from solution have yet to be published.

For Gen IV processes still need to be developed to convert the U,Pu,Np,Am,Cm stream to a single phase oxide. Ammonia precipitation is possible, but not appreciated due to the risk of explosion of the product  $\text{NH}_4\text{NO}_3$  when dry. Assuming these problems are overcome, the U:Pu:MA ratios are given by that of the fuel exiting the reactor after irradiation and subsequent cooling. Following reprocessing, addition of depleted U is necessary to compensate for the U consumed in the production of Pu during the previous irradiation of the fuel. Unfortunately, this needs a further powder blending step, and would be facilitated if the adjustment were made before conversion, i.e. just before the conversion of the metal nitrate solution to solid.

In comparison to the past, where the fuel was minor actinide free, a major problem arises when one considers that group reprocessing and homogeneous recycling strategies immediately imply that the entire fuel production plant be contaminated with minor actinides, bringing with them the need to install extensive shielding, remote operation and automation.

Consideration must be given to the quality of the powder, in terms of its particle size, when it is generated in the conversion step. Conventional precipitation methods result in very fine powders (typically 2-5  $\mu\text{m}$ ), which easily become airborne and contaminate the internal surfaces in the glovebox. Despite the experience of the past, new solutions to the production must be invoked. One of these was tested at the JRC-ITU in the 1980's for the production of the fuels for the SUPERFACT irradiation experiment [3]. MOX fuels with Am, and Np were produced using the sol gel route (see Fig. 5), which at its heart relies on an ammonia precipitation, but maintains the intermediate product not in the form of powder, rather beads with diameters between 20 and 600  $\mu\text{m}$ , depending on the characteristics of the droplet dispersion device. Extension of this process to Cm is possible in principle, but very rigorous cost evaluation and processes to deal with ensuing **highly active neutron and alpha emitting waste** need development.

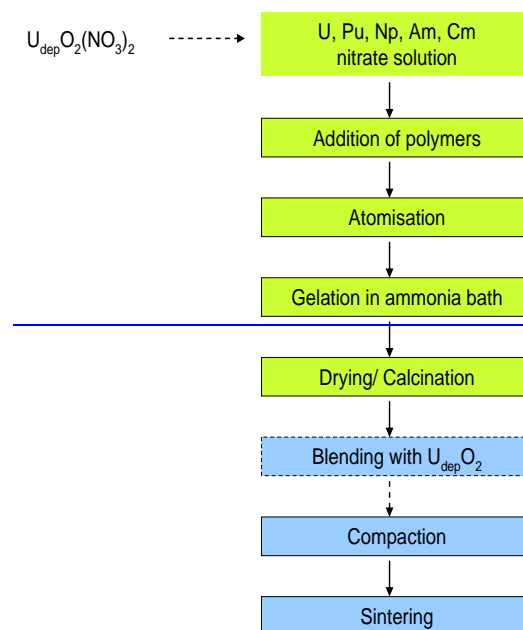


Fig. 5. Sol Gel route for group conversion of Gen IV fuels

Examples of fuels produced using this sol gel route are given below. The homogeneous feed solution is dispersed into droplets, which are collected in an ammonia bath, where gelation provides a droplet to particle conversion. The solid beads obtained are washed, dried using an azeotropic distillation procedure and calcined.

The size of the beads is largely determined by the viscosity of the feed solution and the characteristics of the device used to disperse the liquid into droplets. Using a rotating cup disperser, the calcined beads have diameters between 30 and 150  $\mu\text{m}$ ; an example of a  $(\text{Pu}_{0.40}\text{Np}_{0.05}\text{U}_{0.55})\text{O}_2$  fuel is shown in Fig. 6. This polydisperse size distribution of the beads facilitates their compaction (typically at pressures between 300 and 600 MPa) to give pellets, which, when sintered in a suitable atmosphere, reach densities greater than 90% of the theoretical value (TD).

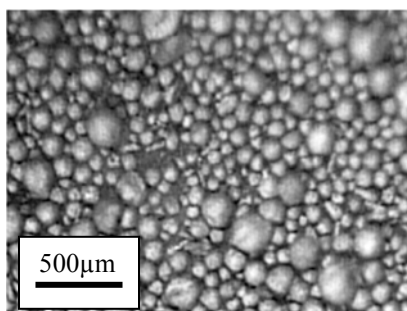


Fig. 6.  $(\text{Pu}_{0.40}\text{Np}_{0.05}\text{U}_{0.55})\text{O}_2$  beads produced using the sol-gel method

The sol-gel method has been used to fabricate actinide incineration fuels  $(\text{Pu}_{0.40}\text{Np}_{0.05}\text{U}_{0.55})\text{O}_2$  and  $(\text{Pu}_{0.43}\text{Ce}_{0.57})\text{O}_2$  for irradiation in HFR Petten. An  $\alpha$ -autoradiograph of a sectioned  $(\text{Pu}_{0.40}\text{Np}_{0.05}\text{U}_{0.55})\text{O}_2$  annular pellet is shown in Fig. 7; a uniform distribution is indicated. In this case an ideal solid solution is formed and has been confirmed by X-ray diffraction measurements.

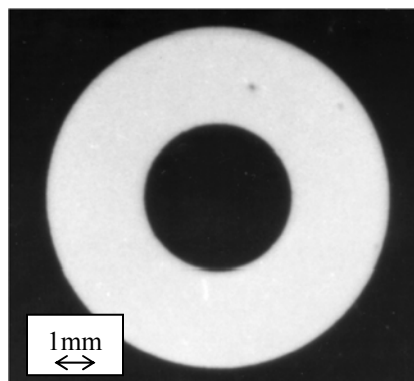


Fig. 7.  $\alpha$ -autoradiograph of a polished radial section of a  $(\text{Pu}_{0.40}\text{Np}_{0.05}\text{U}_{0.55})\text{O}_2$  pellet

A fuel  $(\text{U}_{0.96}\text{Pu}_{0.02}\text{Am}_{0.02})\text{O}_2$  for the incineration of americium was also manufactured by this method. Again an ideal solid solution of all components and a uniform distribution of the Pu and Am is obtained (see the  $\alpha$ -autoradiograph of an axial section of a pellet in Fig. 8a). The optical micrograph in Figure 8b shows that no fractures occurred during fabrication and indicates that the pellet pores are all less than 200  $\mu\text{m}$ . The density of the pellet was 93%TD.

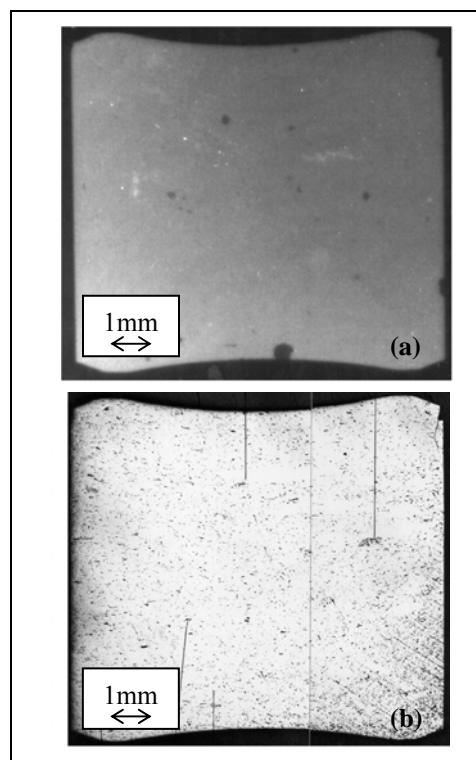


Fig. 8.  $\alpha$ -autoradiograph (a) and optical micrograph (b) of a polished axial section of a  $(\text{U}_{0.96}\text{Pu}_{0.02}\text{Am}_{0.02})\text{O}_2$  pellet

The JRC-ITU has developed a process that shows promise for the production of dust free oxides (see Fig. 9). A relaxation in the high level Gen IV goal of group processing is required, however, two streams would be required at the reprocessing plant. From the first (majority flow), porous beads are manufactured by a sol gel method to give the (U,Pu) oxide in the form of microspheres (20-120  $\mu\text{m}$  in diameter). These microspheres are sufficiently porous to act as a host for the second stream containing minor actinides, which are introduced by infiltration of their nitrate solution. Following calcination, the oxide is formed. At this stage the material consists of two distinct oxide phases corresponding to the streams from the

reprocessing plant. Due to the excellent sintering properties of the sol gel microspheres, however, a solid solution is obtained on heating. There are no liquid wastes containing minor actinides, and the conversion results in the difficult to handle minor actinides being securely located in particles that do not generate dust.

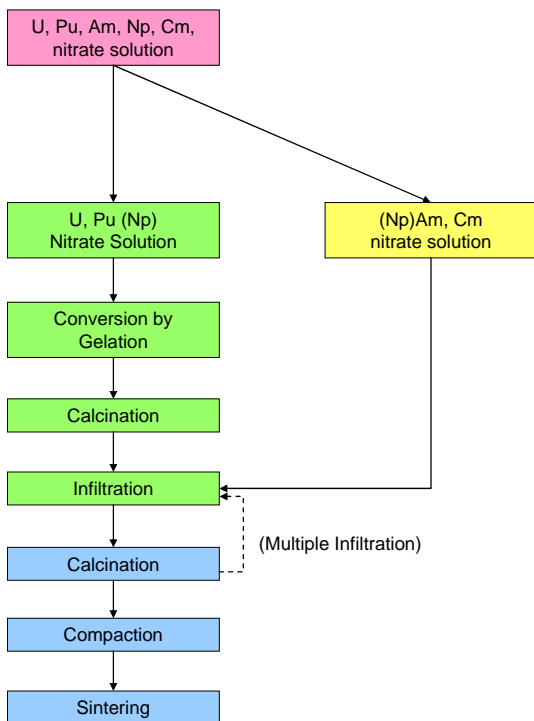


Fig. 9. Production of Gen IV oxide fuels by infiltration

Three options on the splitting of the reprocessing streams are presented in **Error! Reference source not found.** Based on present JRC-ITU experience, the separation denoted MA INF (Minor Actinide infiltration) is the most favourable. Stream 1 is used to fabricate porous (U,Pu) $O_2$  or possibly (U,Pu,Np) $O_2$  microspheres, which are then infiltrated with the minor actinide (Np),Am,Cm solution of stream 2. In this case the oxide spheres (due to their Pu content) are more resistant to dissolution by the nitric acid in stream 2, and furthermore, the free nitric acid content therein can be kept low due to the absence of Pu. The most technically difficult route is posed by the option denoted TRU INF as it requires separation of the entire transuranics (TRU). All U in stream 1 is used to generate  $UO_2$  porous beads, which are then infiltrated with the TRU Pu,Np,Am,Cm solution of stream 2. Technological difficulties to be overcome are the

reduction of the acidity of the solution in stream 2, and the resistance of the  $UO_2$  microspheres to dissolution. A test has been made at the JRC-ITU on the infiltration of Am nitrate into  $UO_2$  beads on a very small scale [4], demonstrating its feasibility. Infiltration of  $PuO_2$  solutions into  $UO_2$  beads remains to be tested and is a challenge as the nitric acid content cannot be reduced too much as otherwise a Pu precipitation occurs

The third option denoted DEL TRU INF (or Diluted Transuranic Infiltration) represents a very specific case. Again  $UO_2$  microspheres are formed from stream 1. In contrast to the TRU INF route, not all U is stripped from stream 2, and it is envisaged that the Pu and U contents in stream 2 are near identical. This stream has the advantage that its nitric acid content can be readily reduced, leaving the  $UO_2$  microspheres less susceptible to dissolution. If the U and Pu contents are equal, however, then twice the mass of actinide infiltrant must be incorporated in the  $UO_2$  beads to reach the required Pu enrichment.

Flexibility in the production of fuels with different Pu enrichments is another fabrication necessity. Of the options described in **Error! Reference source not found.**, this is possible immediately in the TRU INF and DIL TRU INF options, where the quantity of Pu infiltrated is controlled in the infiltration step. In the MA INF option, it is also possible, but requires adjustment in the Pu enrichment in stream 1. Concerning effluents, all options produce no MA bearing liquid wastes. In the MA INF option Pu bearing liquid wastes would ensue.

Option	Stream 1 (sol gel conversion)	Stream 2 (Infiltration conversion)	Product
MA INF	U,Pu (Np)	(Np), Am, Cm	(U,Pu, Np,Am, Cm) $O_2$
TRU INF	U	Pu,Np,Am, Cm	
DIL TRU INF	U	U,Pu,Np, Am,Cm	

The infiltration method has been used extensively at ITU for the production of inert matrix fuels. These were in the main concerned with yttria stabilised zirconia, which due to its



insolubility is a readily usable matrix for infiltration. Fig. 10 shows such Am containing beads, which were then mixed with Mo powder to produce CERMET fuels as shown in Fig. 11.

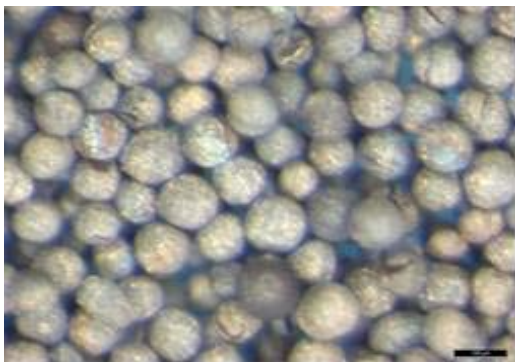


Fig. 10.  $(Zr,Y,Am)O_2$  beads prepared by a combination of sol gel and infiltration methods

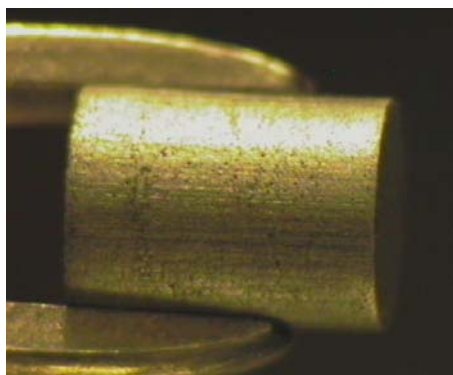


Fig. 11.  $(Zr,Y,Am)O_2$  - Mo CERMET pellet

The validation of this combined sol gel and infiltration method continues today for uranium based fast reactor fuel. It has been successfully tested for the production of  $(U,Pu,Am)N$  fuel, which has the additional complexity of incorporating carbon into the sol gel feed solution for a carbothermal reduction step, which converts the oxide to the nitride. In the first steps carbon is added to the mixed uranyl and Pu nitrate solution, and the sol gel conversion to the oxide performed. The product is  $(U,Pu)O_2 + C$ . In the next step the material is infiltrated with Am nitrate solution and calcined to give  $(U,Pu)O_2 + AmO_2 + C$  as an intermediate product, which is then heated in  $N_2$  to give the solid solution product  $(U,Pu,Am)N$  (see Fig. 12).

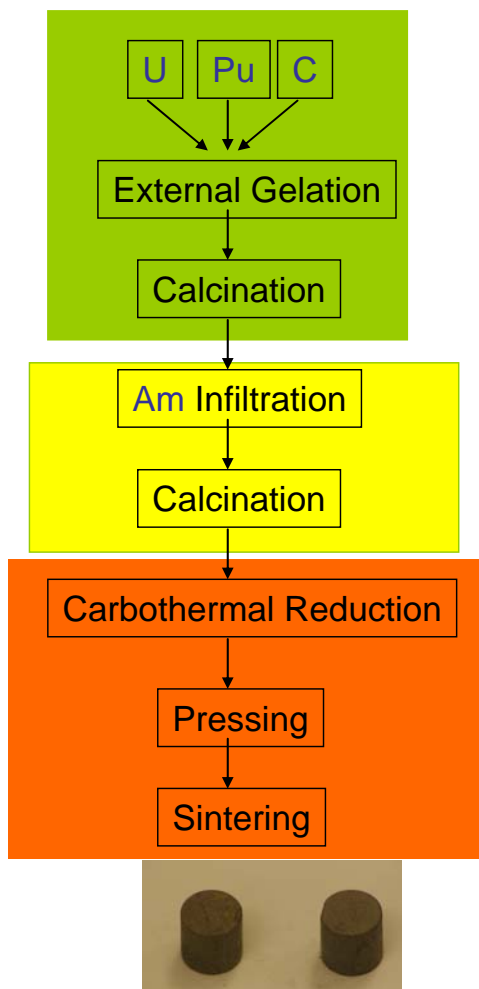


Figure 12: Sol Gel, infiltration, carbothermal reduction for the production of  $(U_{0.805}Pu_{0.175}Am_{0.02})N$  pellets

## CONCLUSIONS:

A thorough assessment of the appropriateness of Gen IV homogeneously fuelled reactor cores is urgently needed, as it will place enormous restrictions on the fuel and assembly handling plants. Adopting a heterogeneously fuelled core will permit the use of a conventional fuel plant for  $(U,Pu)$  fuel along side a dedicated facility for the minor actinide bearing targets. The latter plant will have a far reduced capacity.

**Of paramount importance for the production of MA bearing fuel is the development of advanced conversion processes, giving high quality products without dust production.**

Methods based on precipitation without control of particle size are unlikely to succeed, as the dust production will be untenable.

Methods such as sol gel and infiltration can provide a successful basis upon which the production of MA bearing fuel for both homogeneously and heterogeneously fuelled cores can be based.

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