

1N13950253

B.A.R.C.-1421

B.A.R.C.-1421



ADVANCED METHODS FOR FABRICATION OF
PHWR AND LMFBR FUELS

by

C. Ganguly
Radiometallurgy Division

1988

B.A.R.C. - 1421

B.A.R.C. - 1421

GOVERNMENT OF INDIA
ATOMIC ENERGY COMMISSION

ADVANCED METHODS FOR FABRICATION OF
PHWR AND LMFBR FUELS

by

C. Ganguly
Radiometallurgy Division

BHABHA ATOMIC RESEARCH CENTRE
BOMBAY, INDIA

1988

INIS Subject Category : E34.00; E35.00

Descriptors

PHWR TYPE REACTORS
LMFBR TYPE REACTORS
MIXED CARBIDE FUELS
MIXED OXIDE FUELS
FABRICATION
SOL-GEL PROCESS
MICROSPHERES
FUEL PELLETS
FUEL PINS
PLUTONIUM DIOXIDE
URANIUM DIOXIDE
THORIUM OXIDES
URANIUM NITRIDES
URANIUM CARBIDES
PLUTONIUM CARBIDES
PLUTONIUM NITRIDES
GADOLINIUM OXIDES
URANIUM 233
ADU
AUC
FUEL DENSIFICATION
IMPREGNATION
POROUS MATERIALS
GELATION
DENSITY
FLOWSHEETS
MICROSTRUCTURE

ADVANCED METHODS FOR FABRICATION OF
PHWR AND LMFBR FUELS

C. Ganguly

Radiometallurgy Division
Bhabha Atomic Research Centre
Bombay 400 085

ABSTRACT

For self-reliance in nuclear power, the Department of Atomic Energy (DAE), India is pursuing two specific reactor systems, namely the pressurised heavy water reactors (PHWR) and the liquid metal cooled fast breeder reactors (LMFBR). The reference fuel for PHWR is zircaloy-4 clad high density ($\gg 96\%$ T.D.) natural UO_2 "pellet-pins". The advanced PHWR fuels are UO_2 - PuO_2 ($\leq 2\%$), ThO_2 - PuO_2 ($\leq 4\%$) and ThO_2 - $U^{233}O_2$ ($\leq 2\%$). Similarly, low density ($\leq 85\%$ T.D.) $(UPu)O_2$ pellets clad in SS 316 or D9 is the reference fuel for the first generation of prototype and commercial LMFBRs all over the world. However, $(UPu)C$ and $(UPu)N$ are considered as advanced fuels for LMFBRs mainly because of their shorter doubling time.

The conventional method of fabrication of both high and low density oxide, carbide and nitride fuel pellets starting from UO_2 , PuO_2 and ThO_2 powders is "powder metallurgy (P/M)". The P/M route has, however, the disadvantage of generation and handling of fine powder particles of the fuel and the associated problem of "radiotoxic dust hazard". Hence, the P/M route, though acceptable for UO_2 and ThO_2 pellets, is not so attractive for routine fabrication of plutonium and U^{233} -bearing highly neutron and gamma active fuel materials in large batches.

The present paper summarises the state-of-the-art of advanced methods of fabrication of oxide, carbide and nitride fuels and highlights the author's experience on sol-gel-microsphere-pelletisation (SGMP) route for preparation of these materials. The SGMP process uses sol gel derived, dust-free and free-flowing microspheres of oxide, carbide or nitride for direct pelletisation and sintering. Fuel pellets of both low and high density, excellent microhomogeneity and controlled "open" or "closed" porosity could be fabricated via the SGMP route.

ADVANCED METHODS FOR FABRICATION OF
PHWR AND LMFBR FUELS

C. Ganguly

Radiometallurgy Division
Bhabha Atomic Research Centre
Bombay 400 085

1. INTRODUCTION

1.1 Nuclear Power Programme in India

India is pursuing a 3-stage nuclear power programme (Fig. 1) linking the fuel cycles of pressurised heavy water reactors (PHWR) and liquid metal cooled fast breeder reactors (LMFBR) for reasons of self-sufficiency and judicious utilisation of limited uranium ($\sim 70,000$ tons) but vast thorium ($\sim 480,000$ tons) resources. In stage I, the operating and forthcoming natural UO_2 (Nat. U = 99.3% U^{238} + 0.7% U^{235}) fuelled PHWR would deliver plutonium and depleted uranium ($< 0.7\%$ U^{235}) by-products for LMFBRs in stage II, which would breed U^{233} in thorium blanket. The $Th^{232}-U^{233}$ cycle would then feed self-sustaining PHWRs in stage III. In the event of delay in the LMFBR programme, as in the present case, it would be worthwhile to recycle a part of plutonium generated in stage I in the PHWR in combination with thorium to breed U^{233} . The U^{233} could gradually replace plutonium in subsequent cycles till the PHWRs are operated completely in the self-sustaining $Th^{232}-U^{233}$ mode. Thus, the 3-stage nuclear power programme utilises the inherent advantages of Pu^{239} and U^{233} fissions in fast and thermal neutron spectrums respectively.

1.2 Ceramic Nuclear Fuel Cycle

Fig. 2 illustrates the important steps in nuclear fuel cycle for power reactors. The cycle is initiated with U^{235} since the other two fissile species, namely Pu^{239} and U^{233} , are not available in nature. In India, uranium occurs mainly in the uraninite ore of Bihar and thorium is found in significant quantities in monazite deposits of Kerala and Tamilnadu. Monazite also contains uranium. In the Uranium Corporation of India (UCIL), Jaduguda, Bihar, the uranium ore is subjected to leaching, solvent extraction and ion exchange treatments, concentrated as magnesium

diuranate (MDU) and transported to the Nuclear Fuel Complex (NFC) in Hyderabad. In NFC, the MDU is converted to nuclear grade sinterable UO_2 powder via the uranyl nitrate, ammonium di-uranate (ADU) and UO_3 process intermediates and then consolidated and sintered to high density UO_2 pellets as shown in Fig. 3. Similarly, the Indian Rare Earth (IRE) processes monazite and produces nuclear grade, sinterable ThO_2 powder via thorium nitrate and thorium oxalate. Often, around 1% calcium nitrate or magnesium sulphate is added to thorium nitrate solution in order to have around 0.2% CaO or MgO 'sintering aid' doped into the oxalate-calcined ThO_2 powder. The ThO_2 powder is likewise cold-pelletised and sintered to high density pellets.

For PHWR fuel, the sintered UO_2 pellets are stacked in zircaloy2/4 cladding tubes and encapsulated by resistance welding. The natural UO_2 fuel specification and requirement for operating PHWR 235 MW(e) and the forthcoming PHWR 500 MW(e) are summarised in Table 1. For LMFBR blankets high density ThO_2 or depleted UO_2 pellets are loaded in stainless steel (type 316) cladding tubes and encapsulated by TIG welding. Zircaloy clad depleted UO_2 pins are also used in PHWR during initial start up for flux flattening. ThO_2 could also be used for this purpose.

The sub-assemblies of spent UO_2 fuel are highly radioactive and contain besides the bred fissile Pu^{239} and its isotopes, depleted uranium and significant quantities of highly β - γ active fission products. Similarly, the irradiated ThO_2 blanket would contain besides the fissile U^{233} (and U^{232}), thorium and β - γ active fission products (in-situ fission of U^{233}). After allowing the short-lived fission and daughter products to decay in storage pool for sufficient time (> 6 months), the sub-assemblies are taken in heavily shielded reprocessing plant, where after mechanical decladding the uranium and thorium based materials are subjected to PUREX and THOREX process respectively. Both processes involve acid dissolution, solvent extraction and ion exchange for purification and extraction of uranium, plutonium and thorium as their nitrate solutions. The plutonium and thorium nitrate solutions are converted to PuO_2 and ThO_2 powders via the oxalate route and the UO_2 powder is mostly

obtained by the ADU route. The recycled fuels are fabricated in the same way as fresh fuel, thus completing the ceramic nuclear fuel cycle.

It is possible to produce gel microspheres of UO_2 , PuO_2 , ThO_2 or their mixed oxides starting from the heavy metal nitrate solutions. If needed, carbon black particles could be uniformly admixed to the sol or solution prior to gelation in order to produce gel microspheres containing a mixture of oxide and carbon.

U^{235} , U^{238} and Th^{232} bearing fuel/blanket materials are radioactive (α emitters) but have relatively low specific activity. Hence, these materials are allowed to be handled in controlled area with proper ventilation without any special containment like glove boxes or hot cells. Pu^{239} and U^{233} have high specific activity and radiotoxicity (α emitters) and contain other isotopes which have high gamma and neutron activity necessitating the use of leak-tight glove boxes or shielded hot cells. Further, a high degree of remotisation and automation is needed for fabrication of Pu^{239} and U^{233} bearing fuels in order to keep personnel exposure to radiation to a minimum.

1.3 Conventional and Advanced Fuels

The conventional and advanced fuels for thermal and fast reactors are listed in Table 2. The conventional fuels for thermal and fast reactors are UO_2 and $(UPu)O_2$ respectively. The fabrication, in-reactor performance, reprocessing and refabrication aspects of these fuels have been established in several countries, including India, on an industrial scale. An advanced fuel is one which introduces significant advantages in an established or new reactor or its fuel cycle, but which fuel is not yet commercially established. An advanced fuel should meet the following requirements, partially or fully:

- (i) utilise 'U' & 'Th' resources judiciously
- (ii) ensure high burn-up without failure
- (iii) ensure high linear and specific power ratings without failure
- (iv) ensure high conversion or breeding ratio (short doubling time)
- (v) ensure ease of fabrication, dissolution during reprocessing and minimisation of problem in radioactive waste generation and disposal.

1.4 Fabrication of PHWR & LMFBR Fuels

The different methods for fabrication of PHWR and LMFBR fuels are as follows:

Conventional Method

- Powder-pellet (POP) route for oxide, carbide and nitride; starting materials: ammonium di-uranate (ADU) derived UO_2 powder and oxalate derived PuO_2 and ThO_2 powders.

Advanced Methods

- Advanced POP route for UO_2 and $(U,Pu)O_2$ involving:
 - ammonium uranyl carbonate (AUC) / ammonium uranyl plutonyl carbonate (AUPuC) processes for preparation of UO_2 & $(UPu)O_2$ powders respectively
 - low temperature oxidative sintering (LTS)
 - dopants (eg. TiO_2) for large grain oxide pellets
- Hot Impact Densification (HID)
- Pellet Impregnation for $ThO_2-U^{233}O_2$ ($\leq 2\% U^{233}$)
- Vibro-sol for oxide, carbide & nitride fuels
- Sol-gel-microsphere-pelletisation (SGMP) of oxide, carbide & nitride fuels

The conventional "Powder-pellet" (POP) route is currently followed in most countries for fabrication of both low ($\leq 85\%$ T.D.) and high ($\geq 94\%$ T.D.) density oxide, carbide and nitride fuels. The major drawback of this process is generation and handling of fine powder or dust particles of the fuel which is responsible for "radiotoxic dust hazard". In enriched or natural UO_2 and ThO_2 plants the radiotoxic aerosols may cause health hazard and in Pu and U^{233} fuel fabrication plants, the fine dust particles of the fuel deposit on the inner surface of the hot cells/glove boxes and equipment causing increase in background radiation levels, necessitating frequent decontamination operation. Further, fine powders have poor flowability and are not suitable for remote processing and automation. For preparation of carbide and nitride fuels, additional disadvantages of POP route are more number of process steps and the susceptibility of these materials to oxidation and hydrolysis. Carbide powder is pyrophoric.

Advanced fabrication methods focus mainly on reduction in operator dose by remote and automated processing. The other aims are minimisation

of process steps and fabrication cost and improvement in microstructure of fuel for improved burn-up. Table 3 summarises the objectives of advanced fuel fabrication methods from the point of view of safety, economics and performance.

The present paper summarises the author's experience on fabrication of both conventional and advanced PHWR and LMFBR fuels via some of the advanced methods, highlighting, in particular, the sol-gel-microsphere-pelletisation (SGMP) process.

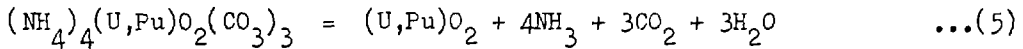
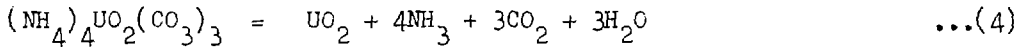
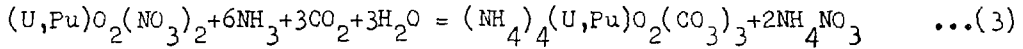
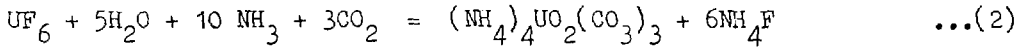
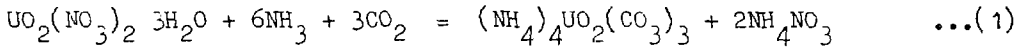
2. ADVANCED POP ROUTE

2.1 AUC & AUPuC Processes

For preparation of sinterable grade UO_2 powder from UF_6 or uranyl nitrate hexa hydrate (UNH), precipitation of ammonium di-uranate (ADU) followed by thermal decomposition (800-1150 K), H_2 -reduction and stabilisation is the oldest and still the most widely used process. The ADU route is also followed in NFC for preparation of both natural UO_2 (from UNH) and enriched UO_2 (from imported UF_6) powders.^(1,2) The UO_2 powder thus produced is extremely fine (< 1 micron) and not free-flowing, thereby requiring additional process steps, namely, hammer milling, precompaction and granulation for pelletisation in high speed automatic hydraulic or mechanical presses. Investigations in NFC have revealed that: (i) the ADU derived UO_2 powder should have specific surface area in the range of 2.4 - 2.8 m^2/g for obtaining acceptable sintered pellets, (ii) in ADU route minor deviations in production parameters often caused variation in density and microstructural defects in sintered pellets. Generation and handling of fine powder is the major problem in the ADU route.

The alternative ammonium uranyl carbonate (AUC) process (Fig. 4) developed and followed extensively in FRG,⁽³⁾ also accepts UF_6 and UNH feed materials and produces free-flowing UO_2 powder, suitable for direct pelletisation. Ammonium uranyl plutonyl carbonate (AUPuC) process⁽⁴⁾ is an extension of the AUC route and is also followed in FRG for co-precipitation of $(U,Pu)O_2$ powder containing upto 30% Pu. The chemical reactions involved

in AUC/AUPuC process are as follows:



Unlike ADU, AUC/AUPuC is crystalline, free-flowing and has relatively coarse grain (~ 40 micron). Calcination of AUC/AUPuC at around 650°C produces oxide powder which is relatively coarse (10-20 micron), free-flowing and having specific surface area of around $5\text{ m}^2/\text{g}$. Process steps like hammer milling, precompaction and granulation are avoided and the powder is directly pelletised.

Addition of binder, lubricant or pore former is not needed. Further, AUC derived powder is not that sensitive to minor variations in production parameters and is also used for fabrication of $\text{UO}_2\text{-Gd}_2\text{O}_3$ fuel pellets for light water reactors. ⁽²⁾ The coprecipitated uranium gadolinium mixed oxide, thus prepared avoids free Gd_2O_3 in sintered pellets ensuring excellent microhomogeneity of the burnable poison 'Gd' in fuel pellets.

2.2 Low Temperature Sintering

In conventional process, UO_2 and $(\text{U,Pu})\text{O}_2$ pellets are sintered at high temperatures ($> 1700^\circ\text{C}$) with long soaking period (4-8 hours) in high purity reducing gas ($\text{Ar}+\text{H}_2$, N_2+H_2 or cracked ammonia) in order to produce sintered pellets of high density ($> 94\%$ T.D.) and controlled oxygen to metal (O/M) ration. The sintering cycle takes approximately 24 hours. The high energy requirement and high cost of high purity reducing gas make the sintering step expensive.

The solution to this problem has been achieved in the "low temperature, short time oxidative sintering" (LTS) technique developed in FRG where the process is popularly known as NIKUSI. ⁽⁵⁾ In LTS or NIKUSI

the high cation diffusion coefficient, ' D^U ' of uranium in hyperstoichiometric UO_{2+x} [$D^U(x) \propto x^2$] is utilised for enhancing the sintering kinetics. For this, 'x' in starting UO_{2+x} and oxygen partial pressure ' P_{O_2} ' of sintering furnace are closely controlled. The NIKUSI process uses a two zone continuous sintering furnace (Fig. 5) (with nitrogen/vacuum lock) for densification and reduction. First, the pellets are densified by sintering in CO_2 at around $1100^\circ C$ for 0.5 hour. Next, the stoichiometry is adjusted by hydrogen treatment for half an hour at the same temperature. The NIKUSI process is now being followed on an industrial scale in FRG for preparation of both UO_2 and $(UPu)O_2$ containing upto 30% plutonium. As a result of reduction in sintering temperature ($1700^\circ C$ to $1100^\circ C$) and shorter sintering cycle (≤ 8 hours) the energy saving in LTS is upto 25%. Further, cheaper heating element (Kanthal) could be used in place of tungsten and molybdenum. The H_2 consumption is also lowered leading to 10% savings in gas cost.

By combination of AUC/AUPuC process and LTS (NIKUSI) it would, therefore, be possible to fabricate high density UO_2 and $(UPu)O_2$ fuel pellets economically. The steps involving generation and handling of fine powder, namely hammer milling, precompaction and granulation could also be avoided, thus minimising the radiotoxic dust hazard.

3. HOT IMPACT DENSIFICATION (HID)

Hot impact densification (HID) is a recent technique in which high speed compaction and densification of green pellets are achieved in the plastic temperature region. The NUKEM laboratories in FRG has demonstrated the feasibility of HID on a laboratory scale with UO_2 and UC powders.⁽⁶⁾ A prototype equipment is being developed in NUKEM. In HID process, a green pellet is heated in a tube furnace open at both ends to high temperature (~ 2470 K) and subsequently densified and shaped in a cold die at ~ 650 MN/m² in a very short duration (≤ 1 ms). A fast driven punch transports the hot (plastic) pellet in a coaxially located floating cold die having a bottom punch. After pelletisation, the bottom punch is pushed downward for ejection of the pellet. Since the fast-driven top punch has to move only in one direction for heating, densification and ejection of the pellet (Fig. 6), a high pellet compaction speed is possible. An additional advantage of HID process is close dimensional

tolerance of pellets which require no subsequent centreless grinding. It is possible to fabricate nearly 1 pellet per second via the HID technique. The HID process is, however, yet to be established on a commercial scale.

4. PELLETT IMPREGNATION TECHNIQUE

The "pellet impregnation" concept has been demonstrated successfully on a laboratory scale in BARC for fabrication of high density $\text{ThO}_2\text{-UO}_2$ ($\leq 2\%$) pellets⁽⁷⁾. This technique would be suitable for fabrication of highly γ active $\text{ThO}_2\text{-U}^{233}\text{O}_2$ fuel for PHWR. In pellet impregnation process (Fig. 7), partially sintered, low density ($\leq 80\%$ T.D.) ThO_2 pellets are first fabricated in a conventional and unshielded area. Next, these pellets are transferred in a shielded facility and impregnated in uranyl nitrate (U^{233}) solution followed by rinsing, drying and high temperature (~ 1973 K) sintering. Densification ($\geq 96\%$ T.D.) and complete solid solution formation take place during the sintering step. Thus, U^{233} bearing fine powders are avoided and handling of U^{233} is restricted only in certain shielded portions of the fuel fabrication plant. Process steps involving conversion of uranyl nitrate to UO_2 powder, mixing-grinding of ThO_2 and UO_2 powders are not needed. The limitation of the impregnation technique is that the amount of open porosity in partially sintered ThO_2 pellets and the solubility limits of uranyl nitrate in HNO_3 limits the capability of introducing U^{233} in ThO_2 to upto 2% . This does not, however, restrict the impregnation technique for fabrication of PHWR fuel since the U^{233} enrichment envisaged in $\text{ThO}_2\text{-U}^{233}\text{O}_2$ is around 1.5% . The method is yet to be demonstrated on a large scale.

5. VIBRO-SOL PROCESS

The "Vibrosol" process, also known as "vi-pac" or "sphere-pac" route essentially consists of three steps, namely:

- preparation of gel microspheres (0.1 mm to 2 mm) of oxide or oxide-carbon mixture from uranium, plutonium or thorium nitrate feed solutions
- calcination or reaction-sintering of these gel microspheres for production of high density ($\geq 96\%$ T.D.) oxide or carbide/nitride microspheres (0.01 to 0.8 mm) respectively

- vibro-packing (vipac) of microspheres of one, two or three sizes in fuel tubes.

The vibrosol process avoids generation and handling of fine powder. The dust-free and free-flowing microspheres minimise radiotoxic dust hazard and process losses and are suitable for remote and automated fuel fabrication. Vibrosol route is particularly attractive for carbide and nitride fuels because the number of process steps are less (Fig. 8) compared to POP route and pyrophoric carbide powder are neither generated nor handled. Further, since the heavy metal nitrates are mixed in the liquid state, vibrosol fuels have a high degree of microhomogeneity. Apart from this, vibrosol route has the maximum flexibility of operation because fuel cladding tubes of any internal dimensions can be easily vibrofilled to a wide range of smear density (60-90% T.D.) by packing microspheres of one, two or three sizes.

The different sol-gel techniques developed and utilised for preparation of gel microspheres of the fuel have been well documented⁽⁸⁾ and are summarised in Table 4. Processes using "ammonia" to cause rapid gelation of droplets are most popular. The ammonia gelation is achieved either "externally" via NH_3 gas and NH_4OH or "internally" via an added ammonia generator (eg. hexa methylene tetra amine (HMTA)). The external gelation of thorium (EGT) and uranium (EGU) processes of KFA, FRG and that of NUKEM, FRG have been extensively used for fabrication of oxide and oxide-carbon gel microspheres. These were calcined and reaction-sintered to high density oxide and carbide microspheres respectively for use in high temperature gas cooled reactors (HTR). Unlike, other sol-gel processes, the EGT and EGU have the advantage of not using any polymeric thickner. The KEMA internal gelation process has been used to a great extent in EIR, Switzerland particularly for fabrication of $\text{UO}_2+\text{PuO}_2+\text{C}$ gel microspheres. These were "reaction-sintered" at around 1600°C in vacuum to high density carbide microspheres and vibrofilled in SS 316 cladding tubes. Lately, the EIR has demonstrated the use of microwaves to heat the droplets and has thus eliminated hot silicon oil (and hence additional waste stream) for triggering of the decomposition of HMTA to form ammonia.⁽⁹⁾ EIR is currently producing (UPu)N microspheres

via this route by reaction-sintering the oxide-carbon gel microspheres in flowing N_2+H_2 atmosphere. The operating plant in the Fuel Chemistry Division, BARC is also based on the internal gelation process and has been extensively utilised for fabrication of UO_2 microspheres. ⁽¹⁰⁾

The sol-gel plant generates large quantities of highly radioactive liquid wastes. It is, therefore, desirable to integrate sol-gel plant with spent fuel reprocessing plant because the latter is designed to handle large quantities of radioactive liquid wastes.

For vibratory compaction of fuel microspheres various types of pneumatic and electrodynamic vibrators have been developed in USA, UK and Switzerland to achieve high compaction efficiencies. For smear densities typical of LMFBR fuels (75-80% T.D.) two size fraction particles, typically 750 micron and 70 micron, are used in the ratio of 3:1 in vi-pack pins. The highest achievable smear density of 90% T.D. is obtained by mixing the coarse, medium and fine (~ 8 micron) fractions in the ratio of 7:2:1. The rates of infiltration and settling of the fine particles in the voids formed by the packing of the coarse particles depend on the frequency, the wave form and the acceleration of vibration as well as on the particle shape and size fraction and the internal geometry of the cladding tube.

Vi-pack UO_2 , $(UPu)O_2$, $ThO_2-U^{233}O_2$ test fuel pins have demonstrated satisfactory performance in both thermal and fast reactors to burn ups comparable to pellet pins. However, the irradiation experience of vi-pack MOX, MC & MN fuel pins are very limited compared to the "pellet-pins".

Vibrosol fuel pins have, in general, the following limitations:

- (i) The maximum achievable smear density of fuel pin is 90% T.D. Vibrosol process is, therefore, not suitable for fabrication of high density PHWR fuel pins.
- (ii) Fabrication of Na-bonded carbide and nitride fuel pins for LMFBR is not possible.
- (iii) The studies on defect behaviour of vipack pins have shown that in the event of an accidental breach of the cladding tube, early in

life, more fuel particles are expelled to the coolant circuit, compared to "pellet-pin" and cause contamination and an increase in the radiation level of the primary coolant. The behaviour of defected vipack (UPu)C pins are currently being studied in EIR.

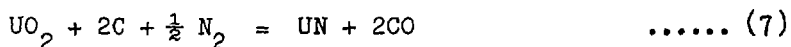
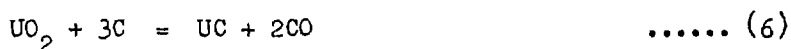
6. SOL GEL MICROSPHERE PELLETISATION (SGMP) PROCESS

The sol-gel-microsphere-pelletisation (SGMP) is a recent concept of fabrication of oxide, carbide and nitride fuel pellets of thorium, uranium and plutonium, starting from nitrate solutions of these heavy metals. The SGMP process utilises internal or external gelation process for preparation of dust-free and free-flowing gel microspheres of oxide or oxide-carbon mixture which after calcination (for oxide) or carbo-thermic synthesis (for carbide and nitride) are suitable for direct pelletisation and sintering. The SGMP process, in fact, combines the manufacturing advantages of "sol gel" process with the in-reactor performance advantage of the "pellet-pin". The advantages of the SGMP process are as follows:

- radiotoxic dust hazard is avoided since fine powder particles of fuel are absent
- dust-free and free-flowing microspheres (diameter 0.2 - 1.0 mm) facilitate remote processing
- excellent microhomogeneity is ensured in fuel pellets
- fabrication steps and pyrophoricity hazard are reduced for carbide and nitride (Fig. 8)
- fabrication of both low ($\leq 85\%$ T.D.) and high ($\geq 96\%$ T.D.) density fuel pellets of controlled "open" and "closed" porosity is possible
- unlike "vipack" pin, SGMP derived "pellet-pin" has lesser chance of fuel wash out particularly in the event of an early in-pile breach in cladding.

The SGMP concept, though attractive, did not prove to be successful in practice till 1984 and contradictory results have been published. During the last 4 years significant R & D has led to successful

production of ThO_2 , $\text{ThO}_2\text{-UO}_2$, $\text{ThO}_2\text{-CeO}_2$ (Ce for simulation of Pu), UO_2 , $\text{UO}_2\text{-CeO}_2$, $\text{UO}_2\text{-Gd}_2\text{O}_3$ (Gd as burnable poison in LWR), UC and UN pellets via SGMP route. Several modifications are needed in the conventional gelation processes in order to get gel microspheres suitable for pellet making. First, the molarity of the heavy metal nitrate feed solution should be low (≤ 1.0). Secondly, for preparing "porous" oxide microspheres around 30 g/litre carbon black "pore former" has to be added to the sol prior to gelation. The carbon black is subsequently removed by controlled air calcination at around 973 K for 24 hours in order to form pores in microspheres. "Non-porous" oxide microspheres are automatically produced in absence of carbon black in the sol. For fabrication of UC and UN microspheres, pre-determined amount of carbon black are added to the sol prior to gelation on the basis of the following chemical equations:



For UC, stoichiometric amount of carbon black is used but for UN 10% excess carbon is added.

The gel microspheres are washed and dried in humid air atmosphere. The dried "oxide microspheres" are subjected to controlled air calcination between 873 K and 1023 K (followed by Ar+H₂ treatment at 873 K for the UO₂ based microspheres) in order to get microspheres of desirable specific surface area, crushing strength and stoichiometry. For preparation of carbide and nitride microspheres the dried UO₂-C gel microspheres are subjected to carbothermic reduction in vacuum (1 Pa) and in flowing nitrogen respectively in the temperature range of 1573-1773 K for 2-8 hours. The UN microspheres are furnace cooled in Ar+8% H₂ atmosphere in order to minimise the U₂N₃ content. The oxide, carbide and nitride microspheres thus formed could be directly pelletised at around 350 MPa in most cases and sintered at 1773-1973 K for 4-8 hours in Ar+H₂ atmosphere. UO₂ based oxides were also subjected to low temperature oxidative sintering in CO₂.

The density of ThO_2 -2% UO_2 pellets prepared from "porous" and "non-porous" microspheres with or without CaO sintering aid is summarised in Fig. 9. Similar data were also obtained for ThO_2 and ThO_2 -4% CeO_2 pellets. The gel microspheres were prepared by the EGT process. The "non-porous" microspheres (Fig. 10a) had relatively high crushing strength (20 N/microsphere) and retained their individual identity even after pelletisation at high pressure (840 MPa) and sintering at high temperature (1973 K), resulting in low ($\leq 85\%$ T.D.) density pellets and "black-berry" structure (Fig. 10c) with microsphere boundaries and "open" pores. The "porous" microspheres (Fig. 10b) on the other hand had low crushing strength (2.5 N/microsphere) and disintegrated completely during pelletisation at 350 MPa and lead to sintering pellets of high density ($\approx 95\%$ T.D.) with "closed" pores and no microsphere boundary (Fig. 10d). The "closed" pores were spherical in shape, 2-5 micron in diameter and uniformly distributed (Fig. 11). CaO was found to act as a sintering aid for ThO_2 , ThO_2 -2% UO_2 and ThO_2 -4% CeO_2 . Ca^{+2} substituted for Th^{+4} resulted in the formation of oxygen ion vacancies leading to enhanced volume diffusion of thorium ion and improved densification during sintering.

UO_2 , $(\text{U,Ce})\text{O}_2$ and UO_2 - Gd_2O_3 gel microspheres prepared by EGU process could be calcined, pelletised and sintered to high density pellets reproducibly from both "porous" and "non-porous" microspheres calcined at 973 K. However, the "non-porous" microspheres led to sintered pellets with "black-berry" structure and "open" pores. Figs. 12(a) and (b) show the microstructure of UO_2 pellet prepared from EGU derived "non-porous" and "porous" calcined UO_2 microspheres. Similarly, EGU derived "porous" UO_2 - Gd_2O_3 microspheres led to high density pellet without any microsphere boundary (Fig. 12c) or "open" pore. Similarly, gel microspheres of UO_2 -C, prepared by the internal gelation process of BARC, could be air calcined and reduced to form "porous" and free-flowing microspheres which could be easily pelletised directly and sintered to high density UO_2 pellets (Fig. 12d) with uniformly distributed "closed" pores in the diameter range of 2-10 micron. ⁽¹⁵⁾ The uniform distribution of pore and their diameter (2-10 micron) in UO_2 pellet prepared by SGMP led to around 10% increase in the thermal conductivity of UO_2 pellets compared to the UO_2 pellet prepared by the conventional powder route (Fig. 13).

Low temperature (1673 K) oxidative sintering (LTS) of UO_2 based pellets in CO_2 for short duration (≤ 1 hour) also led to high density pellets. For effective LTS, oxygen to metal ratio in the starting UO_2 and UO_2-CeO_2 microspheres was kept in the range of 2.10 - 2.40.

For synthesis of UC and UN microspheres, high specific surface area ($\sim 100 \text{ m}^2/\text{g}$) and chemical reactivity of UO_2-C gel microspheres enhanced the kinetics of carbothermic reduction process. Nearly pure UC and UN microspheres could be produced in batches of around 250 g after carbothermic synthesis at relatively low temperature (~ 1673 K) for short duration (~ 4 hours). The microspheres could be consolidated by direct pelletisation (DP) and sintered to low density ($\leq 80\%$ T.D.) pellets. Milling, followed by cold pelletisation (MFP) led to increase in the sintered pellet density (Table 5) by approximately 5%. Since UC, PuC, UN and PuN are isostructural (NaCl type FCC) and have complete solid solubility and similar thermodynamic and thermophysical properties, the data generated for UC and UN are likely to be valid for (U,Pu)C and (U,Pu)N too.

7. CONCLUSION AND RECOMMENDATION

7.1 High density natural UO_2 fuel pellets for PHWR could be economically fabricated via: (i) AUC-LTS (NIKUSI) or (ii) SGMP-LTS (NIKUSI) avoiding simultaneously generation and handling of fine powder. The method could also be extended to $UO_2-Gd_2O_3$ and $(U,Pu)O_2$ pellets (upto 30% Pu). The AUC-LTS and SGMP-LTS routes should be considered for the future natural UO_2 fuel expansion project in NFC and also for $(U,Pu)O_2$ fuel for PHWR and BWR in PEP, Tarapur.

7.2 For $ThO_2-U^{233}O_2$ and ThO_2-PuO_2 advanced fuels for PHWR, the SGMP process is definitely more suitable than the conventional POP route particularly from the point of view of reduction in radiotoxic dust hazard, remote processing and automation. CaO dopant enhances sintering and high pellet density is obtained at a relatively low temperature (≤ 1773 K).

7.3 For preparation of $(U,Pu)O_2$, $(U,Pu)C$ and $(U,Pu)N$ fuels for LMFBR, the SGMP process (Fig.14) is superior to the conventional POP route. This is more

so for mixed carbide and nitride because the process steps are less. Further, fine carbide powder which is pyrophoric is avoided. The SGMP route should, therefore, be developed on a commercial scale for fabrication of the forthcoming prototype fast breeder reactor 500 (PFBR 500) fuels.

REFERENCES

1. N.K. Rao, H.C. Katiyar, R. Rajendran, B.P. Pande, V.B. Patro and V.A. Chandramouli; Chemical conversion routes - UO_2 fuels - characteristic factors influencing better performance. Proc. of Int. Sym. on Water reactor fuel element fabrication with special emphasis on its effect on fuel performance, 6-10 Nov., Prague (1978).
2. G.V.S.R.K. Somayajulu, V.A. Chandramouli, R. Rajendran, T.S. Krishnan, K. Balaramamorthy, A.P. Kulkarni, P. Balakrishna and P.S.A. Narayanan; PHWR/BWR fuel manufacturing experience in India. Proc. of Int. Sym.
3. H. Assmann and M. Becker; Technology of UO_2 fuel fabrication by the AUC powder process. Proc. of the European Nuclear Conference, May 6-11, Hamburg (1979).
4. H. Roepenack, V. Schneider, W.G. Druckenbrodt; Experience with the AUPuC - co-conversion process for mixed oxide fuel fabrication. Am. Cer. Soc. Bulletin 63, (1984).
5. W. Doerr, M. Peehs and H. Assmann; Advantages of the oxidative UO_2 sintering process "NIKUSI". Proc. of Fourth Int. ENS/ANS Conf., Geneva, June 1-6, Vol. 4 (1986).
6. M. Hrovat, H. Huschka, L. Rachor, G. Muehling and H. Zimmerman; Hot impact densification: a new method for producing high density ceramic pellets with close shape tolerances. Nucl. Tech., Vol. 58, July (1982).
7. C. Ganguly and G.C. Jain; Pellet impregnation technique for preparation of ThO_2-UO_2 fuel. Trans. PMAI-10 (1983).
8. IAEA-TECDOC-286, Utilization of particle fuels in different reactor concepts (1983).
9. G. Ledergerber; Internal gelation using microwaves. IAEA-TECDOC-352, pp. 165-174 (1985).
10. V.N. Vaidya, S.K. Mukherjee, J.K. Joshi, R.V. Kamat and D.D. Sood; A study of chemical parameters of the internal gelation based sol-gel process for uranium oxide. Jl. Nucl. Mat. 148, pp. 324 (1987).

11. C. Ganguly, H. Langen, E. Zimmer and E. Merz; Sol-gel microsphere pelletisation process for fabrication of high density ThO_2 -2% UO_2 fuel for advanced PHWRs. Nucl. Tech., March (1986).
12. E. Zimmer, C. Ganguly, J. Borchardt and H. Langen; SGMP - an advanced method for fabrication of UO_2 and MOX fuel pellets. Jl. Nucl. Mat. **152** (1988).
13. C. Ganguly, P.V. Hegde and A.K. Sengupta; Status of (UPu)C and (UPu)N fuel development in BARC. Proc. IAEA Tech. Meeting on advanced fuel for fast breeder reactors, Vienna, Nov. 3-5 (1987).
14. C. Ganguly; Sol gel microsphere pelletisation process for fabrication of high density ThO_2 blankets and ThO_2 -based PHWR fuels. Trans.
15. C. Ganguly; Sol gel microsphere pelletisation of ceramic nuclear fuels. Proc. of Austceram '88, Aug. 22-26, Sydney (1988).

Table 1 : Natural UO_2 fuel specification and requirement
for PHWR 235 MW(e) & PHWR 500 MW(e)

Basis of comparison	PHWR 235	PHWR 500
Fuel Pellet		
Diameter (mm)	14.24	12.18
Height (mm)	~ 20	~ 15
Density (g/cm^3)	10.60	10.60
% of theoretical density (T.D.)	96.5	96.5
Fuel Pin		
Outer diameter (mm)	15.27	13.08
Wall thickness (mm)	0.4	0.4
Length (mm)	493	493
Fuel Pins/Bundle	19	37
Bundles/Core	3672	5096
Weight of UO_2 /Bundle	15 kg.	22 kg.
Total UO_2 /Core	60 tons	111 tons
UO_2 Refuelling/Year	30 tons	80 tons

Table 2 : Ceramic fuels for PHWR & LMFBR

Reactor	Conventional Fuel	Advanced Fuels
PHWR	<p style="text-align: center;">Natural UO_2</p> <ul style="list-style-type: none"> - high density ($\geq 96\%$ T.D.) pellets - burn up : ~ 6500 MWD/t - conversion ratio : 0.6 - 0.8 - fabrication : in controlled area 	<ul style="list-style-type: none"> (i) UO_2-PuO_2 ($\leq 1\%$) (ii) ThO_2-PuO_2 ($\leq 4\%$) (iii) $ThO_2-U^{233}O_2$ ($\leq 2\%$) <ul style="list-style-type: none"> - high density pellets - burn up : 12000 - 18000 MWD/t - conversion ratio : 0.8 - 1.0 - fabrication : in controlled area inside -tight glove box with & neutron shieldings
LMFBR (commercial)	<p style="text-align: center;">UO_2-PuO_2 ($\leq 25\%$)</p> <ul style="list-style-type: none"> - low density ($\leq 85\%$ T.D.) pellets - burn up : ≥ 100000 MWD/t - breeding ratio : 1.1 	<p style="text-align: center;">(UPu)C & (UPu)N [$Pu \leq 20\%$]</p> <ul style="list-style-type: none"> - low density "pellet pins" or "vi-pack" pins - burn up : ≥ 100000 MWD/t - breeding ratio : 1.3 - 1.4

Table 3 : Ceramic nuclear fuel fabrication - objectives of advanced methods

Safety	Economics	Performance
<p>1) Avoid fine powder</p> <ul style="list-style-type: none"> - for minimising radiotoxic dust hazard - for minimising fire hazard (for carbide) <p>2) Automation & remotisation</p> <ul style="list-style-type: none"> - for minimising personnel exposure to radiation 	<p>1) Minimise process steps</p> <p>2) Reduce fuel synthesis & sintering temperatures</p> <p>3) Reduce gas cost</p> <ul style="list-style-type: none"> - recirculation & purification - use less expensive gas <p>4) Reduce process losses & rejects</p>	<p>1) Improved microstructure for higher burn up</p> <ul style="list-style-type: none"> - large (> 40) grain size (LWR & PHWR) - high density ($\geq 94\%$ T.D.) & 'closed' pore (LWR & PHWR) - low density ($\leq 85\%$ T.D.) & 'open' pore (LMFBR) - microhomogeneity

Table 4 : Summary of "dry" and "wet chemical" routes for preparation of fuel microspheres in the form of "oxide" and "oxide-carbon"

<u>Spherical Fuel Particles</u>	
Dry Route	Wet Chemical Route
<ul style="list-style-type: none"> - Powder agglomeration process with carbon black binder & water/organic solvents, UK - Binderless agglomeration of submicron powder, UK 	<ul style="list-style-type: none"> - ORNL sol-gel process (SOLEX, CUSP & APEX processes for $(ThU)O_2$ & PuO_2), USA - External gelation process of NUKEM, FRG (ThO_2, UO_2, $(UTh)O_2$, UC_2 & UC_xO_y) - SNAM external gelation process, Italy (UO_2 & $UO_2-20\%PuO_2$) - External gelation of thorium (EGT) process, KFA, FRG (for ThO_2, ThO_2-PuO_2, ThO_2-UO_2, $(ThU)C_2$) External gelation of uranium (EGU) process, KFA, FRG (for UO_2, UO_2-PuO_2, UC, UN) - KEMA internal gelation process, Netherlands adapted in EIR, Switzerland (UO_2, UO_2-PuO_2, $(UPu)C$ & UN) and BARC, India (UO_2, UO_2-PuO_2, UC & UN) - Internal gelation process of KFA, FRG (UO_2, FuO_2, ThO_2, UO_2-ThO_2, UO_2-PuO_2 ($UTh)C_2$)

Table 5: Results of initial trials on fabrication of UC/UN through sol-gel route

Sl. No.	Type	Carbothermic reduction parameters				Analysis after carbothermic reduction				Sintered pellet 1973 K, 4 h, A +H ₂				
		Carbon Stoic. in (UO ₂ +C)gel	Temp. K	Time h	Atmosphere	O w/o	C w/o	N w/o	U ₂ C ₃ / U ₂ N ₃ w/o	O w/o	C w/o	N w/o	U ₂ C ₃ / U ₂ N ₃ w/o	Density % T.D.
1.	Direct SCMP of UC	100% for UC formation	1673	4	Vacuum 1 Pa	0.1	4.85	0.05	10	0.12	4.80	0.05	~ 10	80
2.	Direct SCMP of UN	110% for UN formation	1773	8	N ₂ , 300 l/h cooled in A +H ₂	0.2	0.4	5.1	Traces	0.25	0.4	5.05	Nil	80
3.	Milling of UC microspheres followed by pressing & sintering	100%	1673	4	Vacuum 1 Pa	0.11	4.85	0.05	10	0.13	4.80	0.05	~ 10	85
4.	Milling of UN microspheres followed by pressing & sintering	110%	1773	8	N ₂ , 300 l/h cooled in A +H ₂	0.25	0.4	5.1	Traces	0.25	0.4	5.00	Nil	85

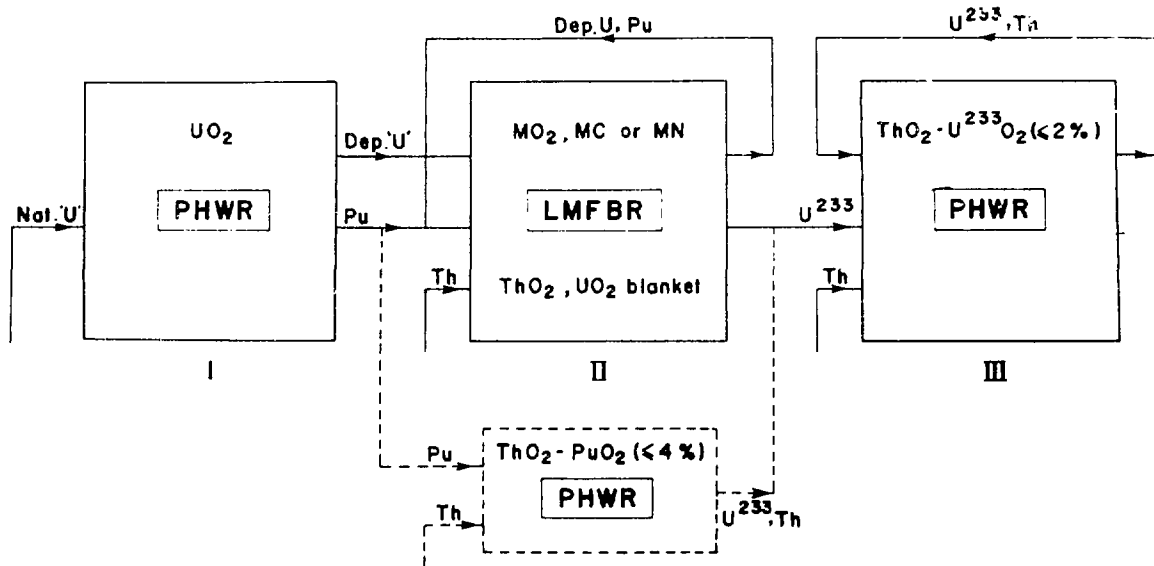


Fig. 1 : 3-stage nuclear power programme in India

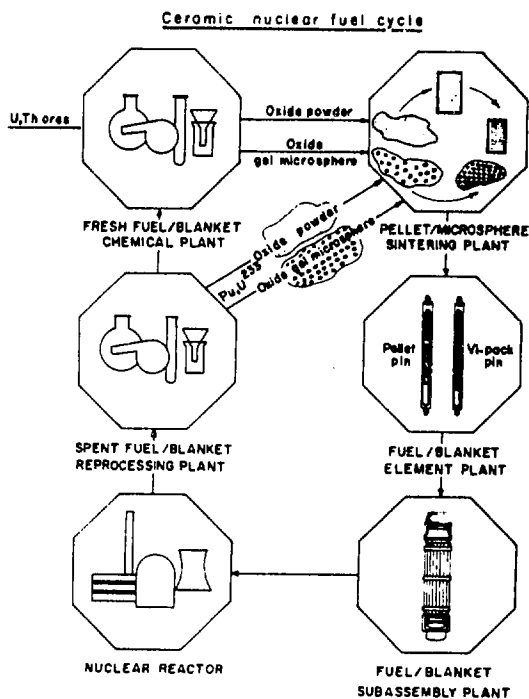


Fig. 2 : Important steps in ceramic nuclear fuel cycle for power reactors

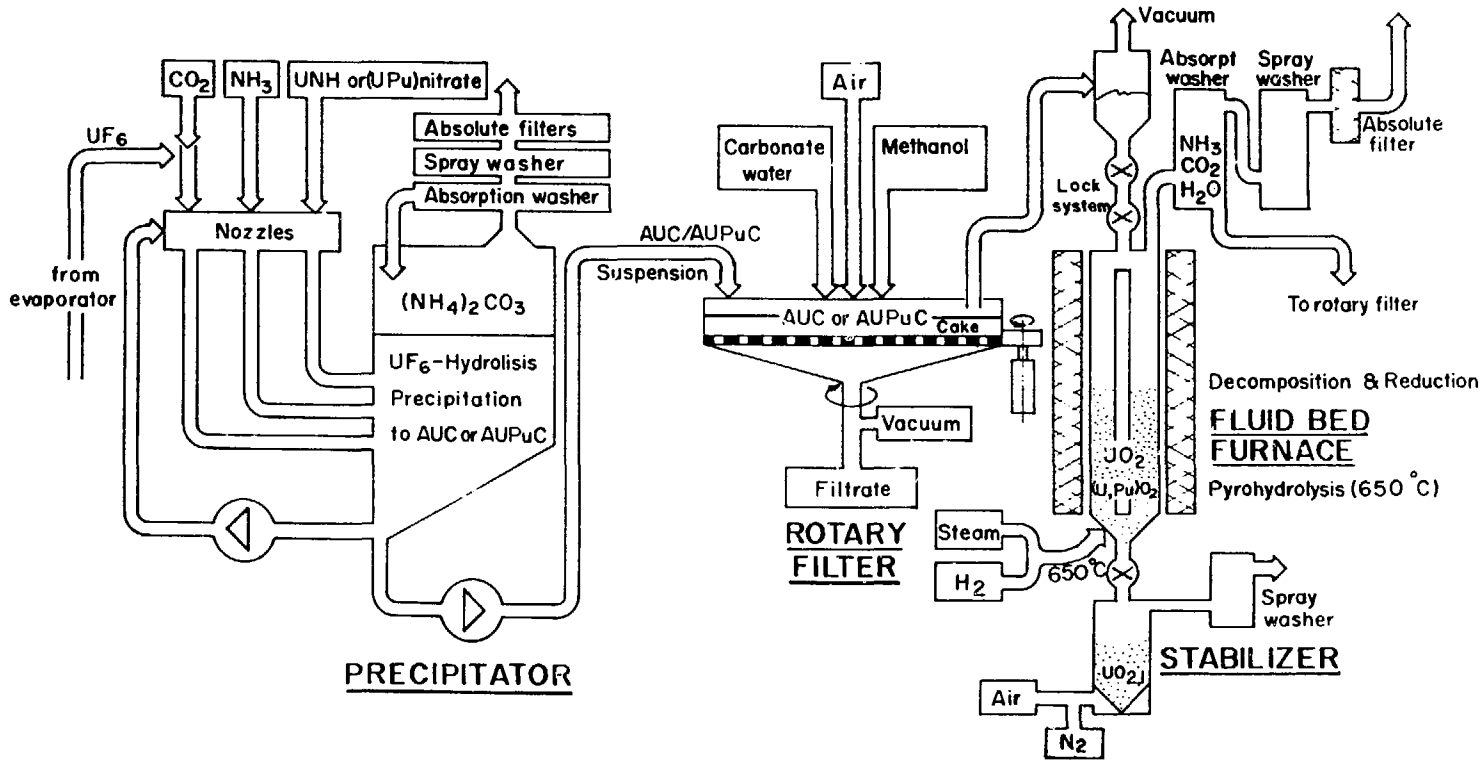
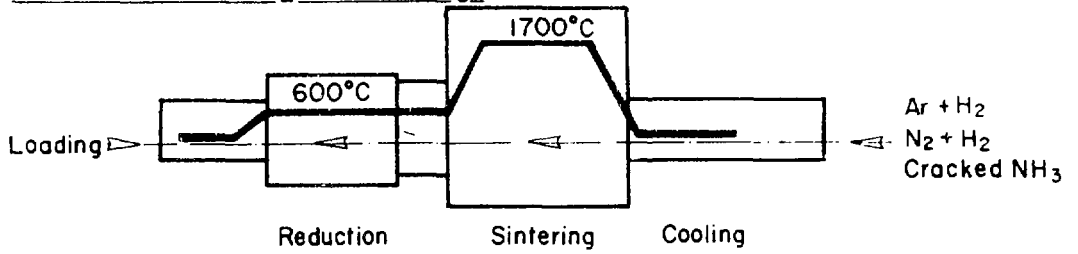


Fig. 4 : Ammonium uranyl carbonate (AUC) and ammonium uranyl plutonyl carbonate (AUPuC) processes of FRG

Conventional (H_2) Sintering



Oxidative (CO_2) Sintering

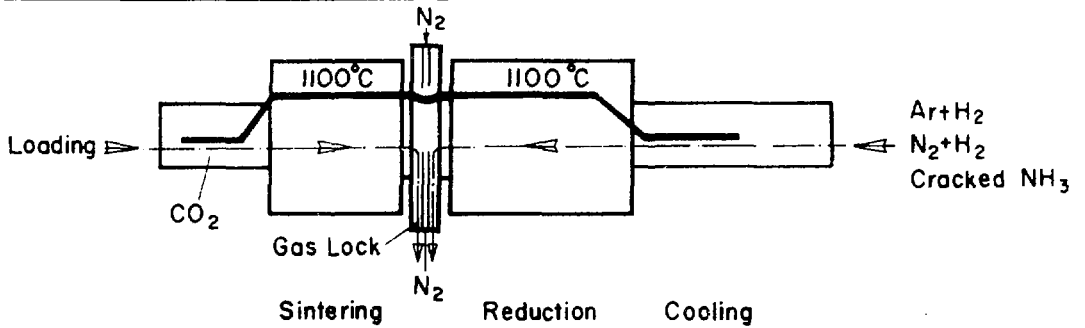


Fig. 5 : Low temperature sintering - NIKUSI furnace of FRG

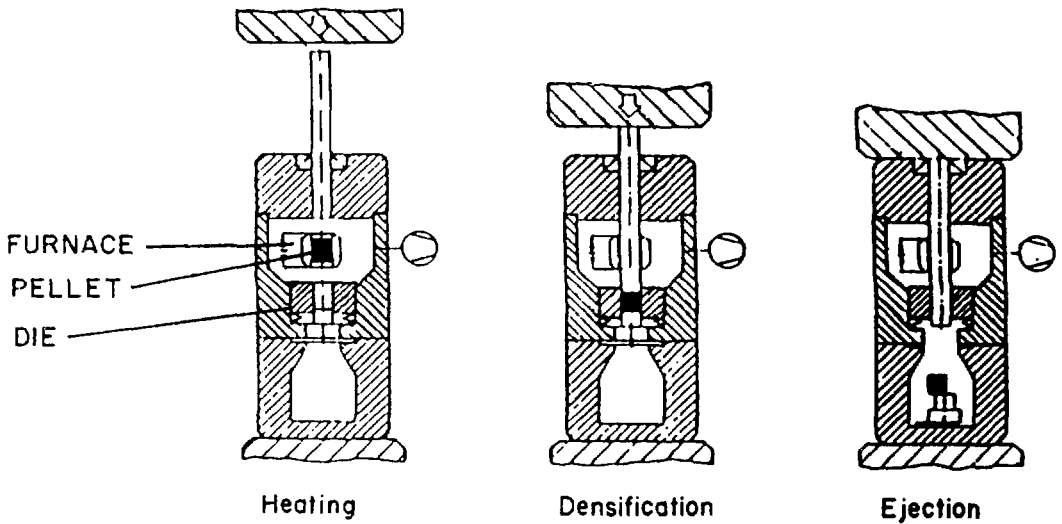


Fig. 6 : Principal stages of hot impact densification (HID) process - heating, densification and ejection

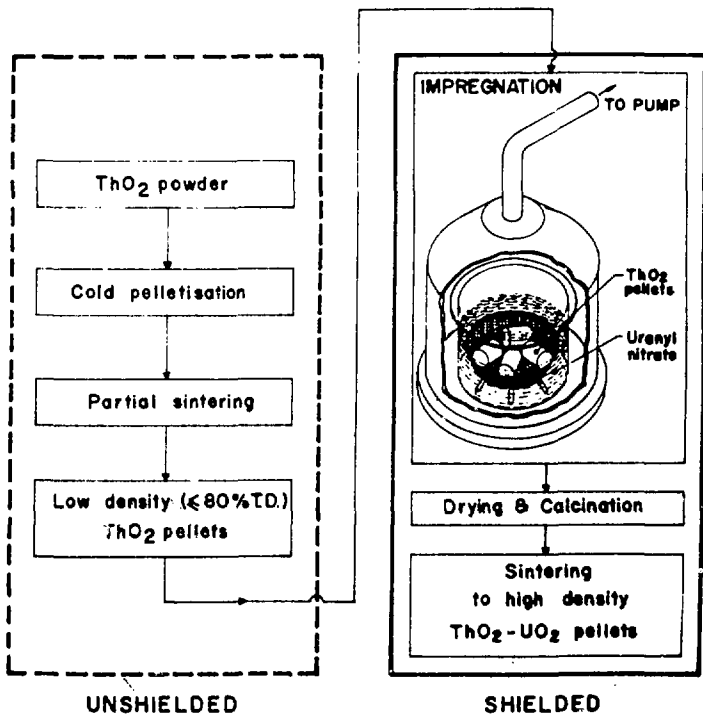


Fig. 7 : Process flowsheet for the pellet impregnation method developed in BARC

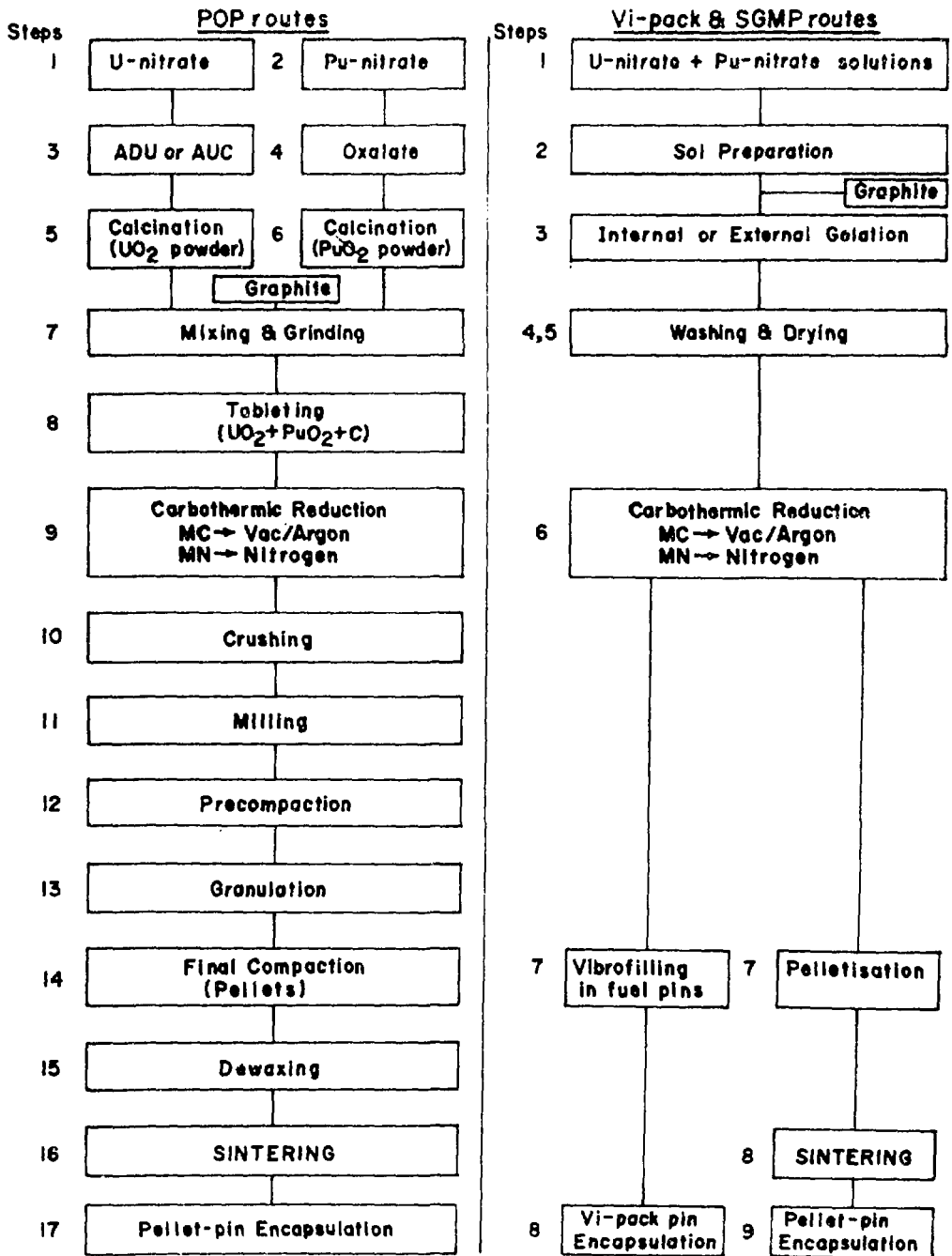


Fig. 8 : Vibrosol, SGMP and POP flowsheets for fabrication of oxide, carbide and nitride fuel pins

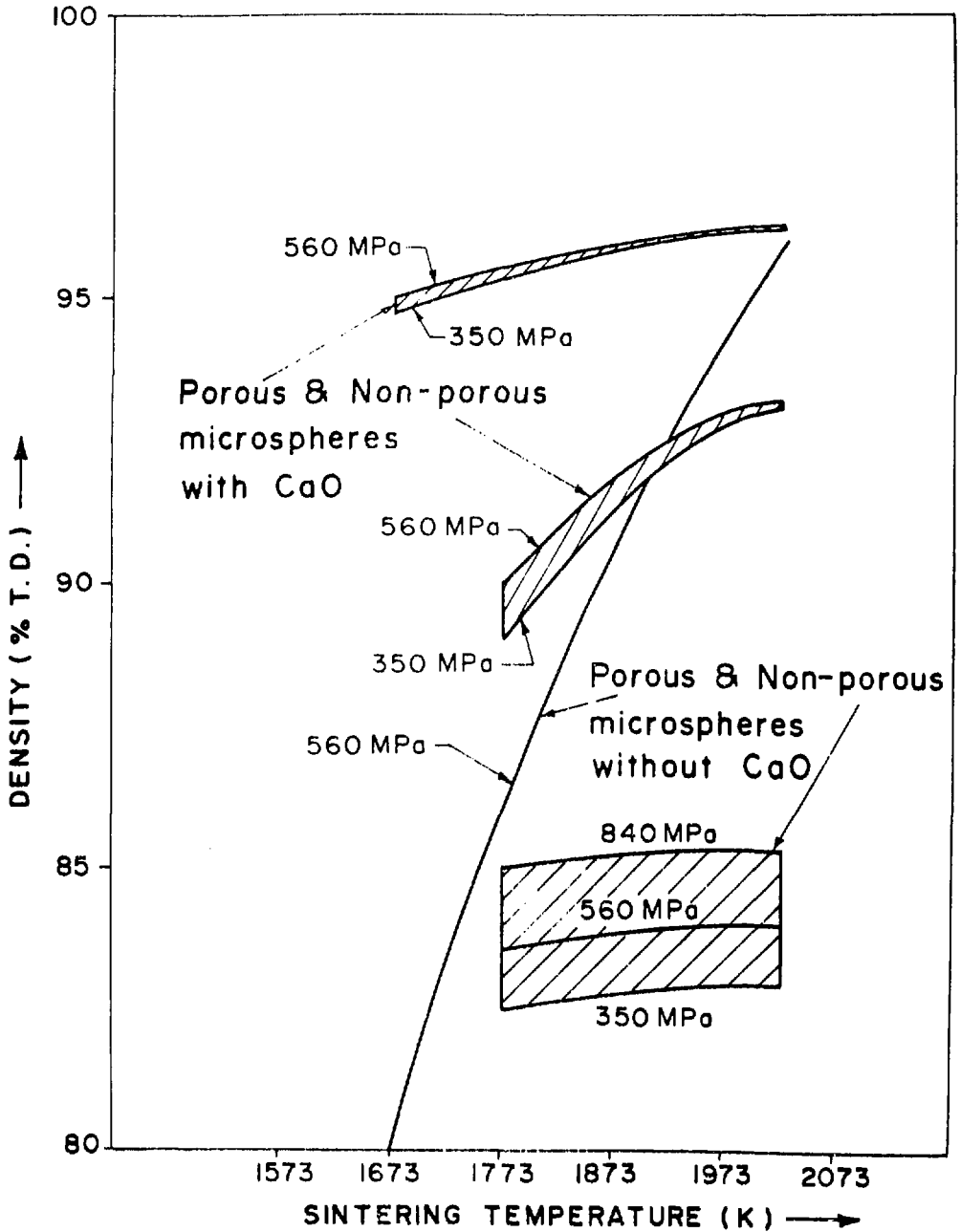


Fig. 9 : Density of sintered $\text{ThO}_2\text{-2\% UO}_2$ pellets prepared from "porous" and "non-porous" microspheres with or without CaO sintering aid

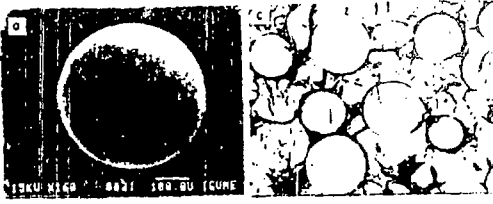


Fig. 10: Microstructure of calcined microspheres and sintered ThO_2 -2% UO_2 pellets

- (a) non-porous microsphere
- (b) porous microsphere
- (c) sintered pellets prepared from non-porous microspheres showing blackberry structure (BS)
- (d) sintered pellet prepared from porous microspheres showing no microsphere boundary



Fig. 12: Microstructure of UO_2 and UO_2 - Gd_2O_3 sintered pellets prepared by the SCMP route

- (a) UO_2 pellets prepared from non-porous microspheres showing BS.
- (b) UO_2 pellets prepared from porous microspheres
- (c) UO_2 - Gd_2O_3 pellets prepared from porous microspheres
- (d) UO_2 pellet prepared from porous microspheres (gel microspheres prepared by the internal gelation process of BARC)

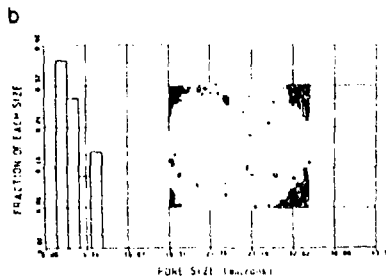
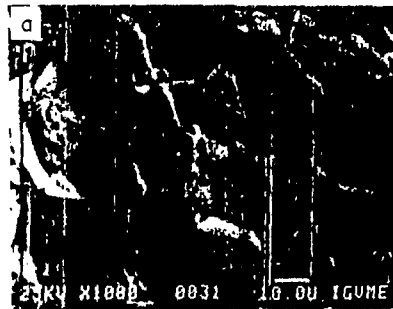


Fig. 11: Pore size and distribution in sintered ThO_2 -2% UO_2 fuel pellets prepared from porous microspheres

- (a) SEM picture of fractured surface of sintered pellets
- (b) distribution of pore as obtained by image analysis

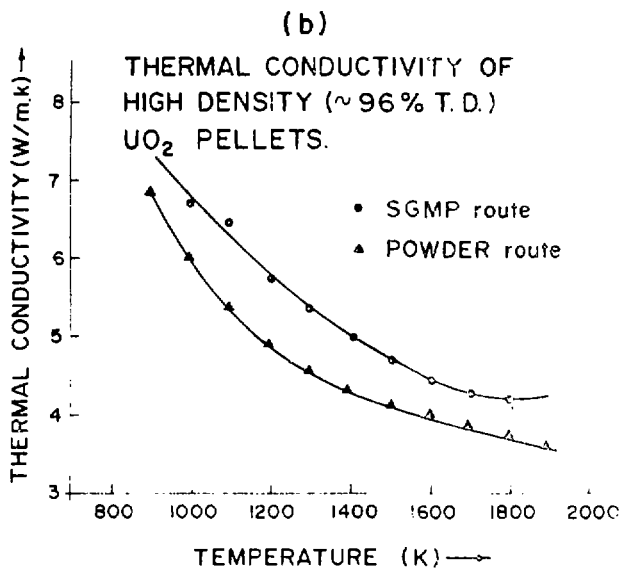
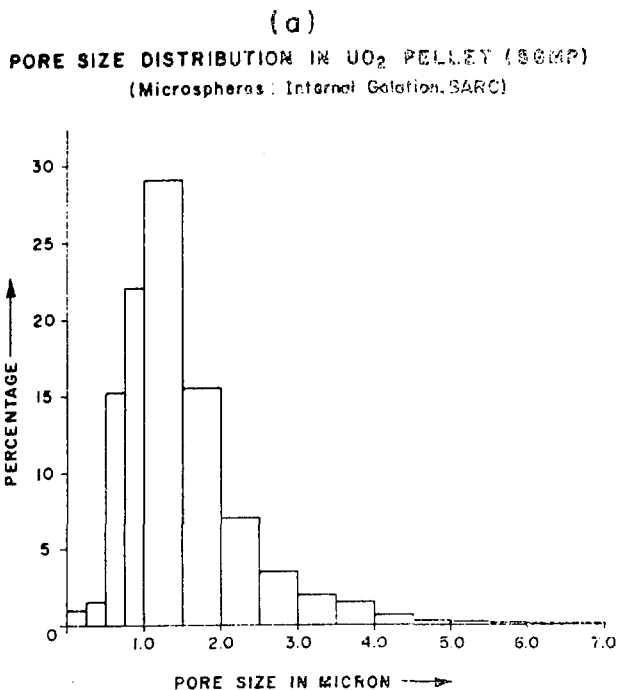


Fig. 13 : Pore size distribution in sintered UO_2 pellet prepared by the SGMP route and its effect on thermal conductivity
 (a) pore size distribution by image analysis
 (b) thermal conductivity by laser flash technique

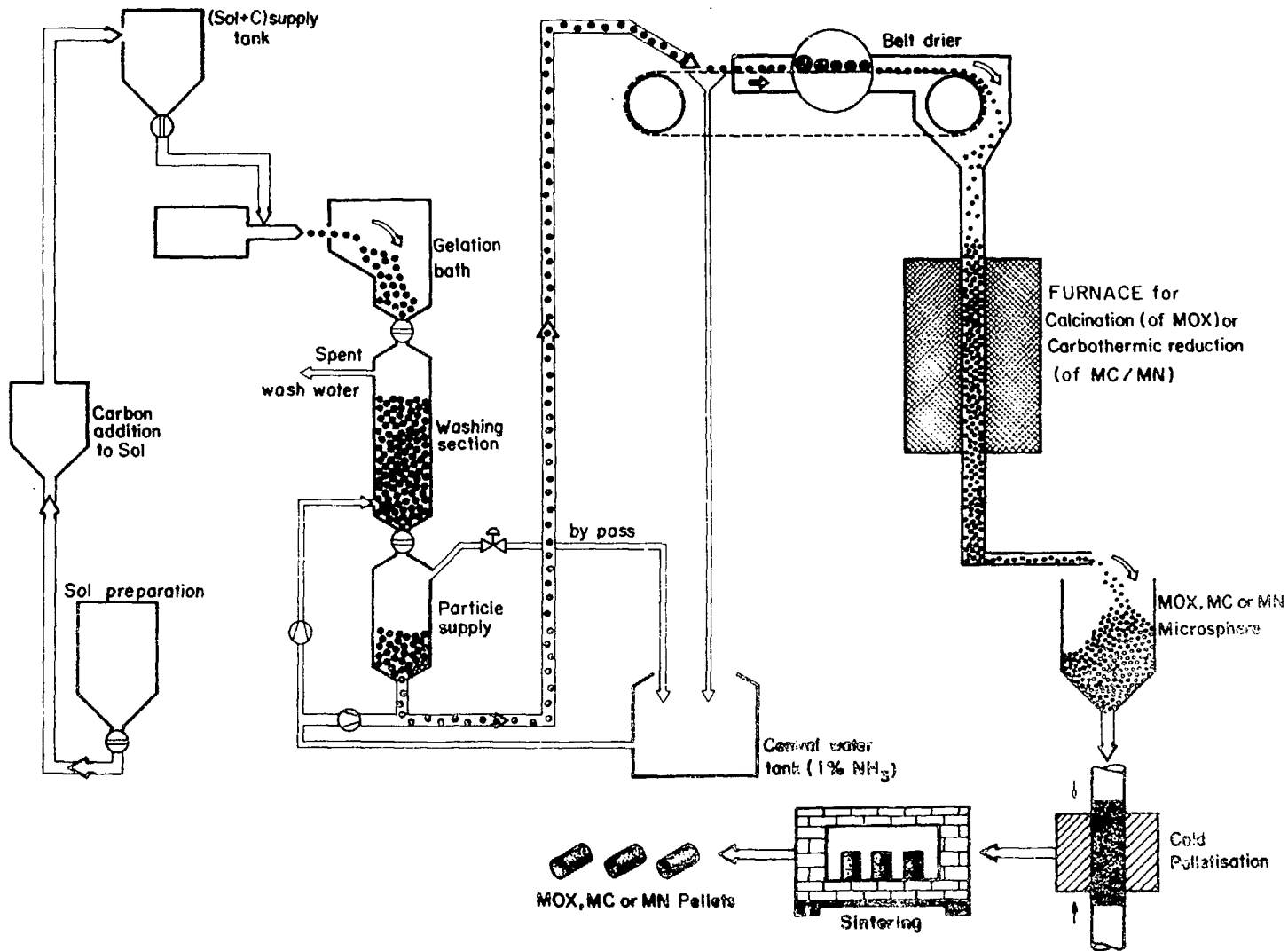


Fig. 14 : Sol gel microsphere pelletisation (SGMP) of MOX, MC & MN fuels

