

***Experiences and Trends of  
Manufacturing Technology of  
Advanced Nuclear Fuels***



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International Atomic Energy Agency

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EXPERIENCES AND TRENDS OF  
MANUFACTURING TECHNOLOGY OF  
ADVANCED NUCLEAR FUELS

INTERNATIONAL ATOMIC ENERGY AGENCY  
VIENNA, 2012

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## FOREWORD

The ‘Atoms for Peace’ mission initiated in the mid-1950s paved the way for the development and deployment of nuclear fission reactors as a source of heat energy for electricity generation in nuclear power reactors and as a source of neutrons in non-power reactors for research, materials irradiation, and testing and production of radioisotopes. The fuels for nuclear reactors are manufactured from natural uranium ( $\sim 99.3\%$   $^{238}\text{U}$  +  $\sim 0.7\%$   $^{235}\text{U}$ ) and natural thorium ( $\sim 100\%$   $^{232}\text{Th}$ ) resources. Currently, most power and research reactors use  $^{235}\text{U}$ , the only fissile isotope found in nature, as fuel. The fertile isotopes  $^{238}\text{U}$  and  $^{232}\text{Th}$  are transmuted in the reactor to human-made  $^{239}\text{Pu}$  and  $^{233}\text{U}$  fissile isotopes, respectively. Likewise, minor actinides (MA) (Np, Am and Cm) and other plutonium isotopes are also formed by a series of neutron capture reactions with  $^{238}\text{U}$  and  $^{235}\text{U}$ .

Long term sustainability of nuclear power will depend to a great extent on the efficient, safe and secure utilization of fissile and fertile materials. Light water reactors (LWRs) account for more than 82% of the operating reactors, followed by pressurized heavy water reactors (PHWRs), which constitute  $\sim 10\%$  of reactors. LWRs will continue to dominate the nuclear power market for several decades, as long as economically viable natural uranium resources are available. Currently, the plutonium obtained from spent nuclear fuel is subjected to mono recycling in LWRs as uranium–plutonium mixed oxide (MOX), containing up to 12%  $\text{PuO}_2$ , in a very limited way. The reprocessed uranium (RepU) is also re-enriched and recycled in LWRs in a few countries. Unfortunately, the utilization of natural uranium resources in thermal neutron reactors is  $<1\%$ , even after recycling of Pu and RepU.

$\text{UO}_2$  and MOX fuel technology has matured during the past five decades. These fuels are now being manufactured, used and reprocessed on an industrial scale. Mixed uranium–plutonium monocarbide (MC), mononitride (MN) and U-Pu-Zr alloys are recognized as advanced fuels for sodium cooled fast reactors (SFRs) on the basis of their higher breeding ratio and higher thermal conductivity. The advanced SFR fuels have so far been prepared only on a pilot plant scale in a very few countries, and MA bearing metal, oxide, carbide, nitride and inert matrix fuels are being prepared only on a laboratory scale for property evaluation and irradiation testing. Likewise, thorium based MOX has been manufactured on a pilot plant scale and utilized in power reactors in a few countries in a limited way, but there is no industrial facility for manufacturing these fuels.

Until the end of the 1970s, non-power research reactors and their fuels were mostly supplied worldwide by the USA and the former USSR. These reactors used high enriched uranium (HEU) fuel, containing  $>80\%$   $^{235}\text{U}$  in the form of aluminium matrix,  $\text{UAl}_x$  or  $\text{U}_3\text{O}_8$  dispersion fuel of low uranium density ( $1.3\text{--}1.7\text{ g/cm}^3$ ). In 1978, the USA launched the Reduced Enrichment for Research and Test Reactors (RERTR) Programme, with the objective of converting the HEU core to a low enriched uranium (LEU) core without affecting the operation and performance of the reactors. Later, the Russian Federation also joined this programme. As part of this programme, LEU based  $\text{Al-U}_3\text{Si}_2$  dispersion fuel with a uranium density of  $4.8\text{ g/cm}^3$  emerged and has been qualified. Efforts are under way to develop advanced fuels such as U–Mo alloy either as Al matrix dispersion fuel with a density of  $6\text{--}8.5\text{ g/cm}^3$  or as monolithic fuel with a uranium density of  $15\text{--}16\text{ g/cm}^3$ .

The IAEA has been fostering information exchange and collaborative R&D among Member States for the development, manufacture and performance evaluation of nuclear fuels for both nuclear power and research reactors, and has published a number of technical reports on nuclear fuels. The purpose of this report is to summarize the current status of nuclear fuel

manufacturing technology worldwide for both power reactors and research reactors, and to highlight the trends that are emerging for advanced fuels.

The IAEA would like to thank all the experts who participated in the Technical Meeting on Manufacturing of Nuclear Fuels held in Vienna from 18 to 20 May 2010 and the subsequent consultants meetings in June and December 2010. The IAEA officer responsible for this publication was U. Basak of the Division Nuclear Fuel Cycle and Waste Technology.

#### *EDITORIAL NOTE*

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# 1. INTRODUCTION

## 1.1. BACKGROUND

The historic ‘Atoms for Peace’ initiative announced at the United Nations General Assembly in December 1953 [1] and the first international conference on peaceful uses of atomic energy in August 1955 by the United Nations (UN) in Geneva [2] were the two major milestones that paved the way for the development and deployment of ‘nuclear fission reactors’ for generation of electricity and using non-power reactors as a source of neutrons for basic and materials research and production of radioisotopes.

Nuclear power reactors were commercially introduced for generation of electricity for the first time in Belgium, France, Russian Federation, Sweden, UK, and the USA during 1954–1957. The International Atomic Energy Agency (IAEA) was also formed around the same time, in 1957, as an independent and highly technical organization within the UN family, for facilitating safe, secure and peaceful uses of nuclear science and technology. The installed nuclear capacity rose relatively quickly from less than 1 GW(e) in 1960 to 100 GW(e) in the late 1970s, and 300 GW(e) in the late 1980s. Since the late 1980s, worldwide capacity has risen much more slowly, mainly because of the Three Mile Island and Chernobyl accidents. However, in recent years there is a rising expectation for nuclear energy worldwide as a viable option to meet the ever increasing demand of electricity economically and safely and with high plant availability factor, in a sustainable manner, without causing CO<sub>2</sub> and other greenhouse gas emissions that cause global warming or degradation of the environment. As of 31st October 2010, 441 nuclear power reactors are in operation in 30 countries with a total net installed capacity of ~375 GW(e), generating ~14% of global electricity. The USA has the maximum number of operating power reactors (104), followed by France (58), Japan (54), Russian Federation (32) and Republic of Korea (21). Sixty-one nuclear power reactors are under construction. Several new countries are planning to initiate nuclear power programmes for the first time and rapid expansion of nuclear power is underway in China and India. During the last 50 years, nuclear power reactors and associated fuel cycles have progressively developed into industrial activities. The IAEA low and high projections of installed nuclear power in 2030 are 546 GW(e) and 803 GW(e) respectively.

In addition, more than 650 research reactors have been constructed so far, of which some 237 are presently in operation in 56 countries [3]. The Russian Federation has the maximum number of operating research reactors (62), followed by the USA (54), Japan (18), France (15), Germany (14) and China (13). About 20 more reactors are planned or under construction. These reactors are being utilized for education and training and as a source of neutrons for basic research, materials analysis and characterization, studying neutron irradiation behavior of fuels and structural materials for nuclear power reactors and for production of radioisotopes for use in medical sector, industry and agriculture.

Uranium and thorium, the only two actinide heavy elements occurring in nature, are the basic raw materials for nuclear fuels. The earth’s crust contains ~ 2.7 mg/kg uranium and some 9.6 mg/kg thorium. Natural uranium (NU) contains 99.283% by weight <sup>238</sup>U, a ‘fertile’ isotope and 0.711% <sup>235</sup>U, the only ‘fissile’ isotope in nature and traces of <sup>234</sup>U. Thorium occurs in nature only as <sup>232</sup>Th, which is a ‘fertile’ isotope. The ‘fertile’ isotopes <sup>238</sup>U and <sup>232</sup>Th are transmuted to human-made ‘fissile’ isotopes <sup>239</sup>Pu and <sup>233</sup>U respectively by neutron capture reactions in a reactor. A series of such neutron capture reactions with <sup>235</sup>U, <sup>238</sup>U and <sup>239</sup>Pu also lead to the formation of other isotopes of plutonium, namely, <sup>240</sup>Pu, <sup>241</sup>Pu, <sup>242</sup>Pu and <sup>238</sup>Pu and Minor Actinides (MAs: Np, Am and Cm) which are either fertile or fissile

isotopes and do not occur in nature.  $^{241}\text{Pu}$  is also a fissile isotope of plutonium. Likewise,  $^{232}\text{U}$  is formed by (n, 2n) capture reaction with  $^{233}\text{U}$  in a reactor. The basic properties of these actinide isotopes are summarized in Table 1 [4]. Nuclear fuel materials consisting of uranium, plutonium, thorium and MAs, are radioactive and hazardous to health varying in extent. In addition, the critical mass of fissile materials are only in tens of kilograms and fissile and fertile isotopes are 'dual use materials', (can be used for peaceful and non-peaceful applications). Hence, dealing with radiological and criticality safety and non-proliferation of fissile and fertile materials are of paramount importance in nuclear fuel cycle activities, including manufacturing of nuclear fuels.

$^{235}\text{U}$ , the only fissile isotope in nature, is the fuel for nearly all operating nuclear power and research reactors in the world. Most of these reactors use slow or thermal neutrons (energy  $< 0.025$  e V) for fission of  $^{235}\text{U}$  and water as coolant and moderator.

TABLE 1. BASIC PROPERTY OF URANIUM, PLUTONIUM, THORIUM AND MINOR ACTINIDE ISOTOPES

Isotope	Half-life (y)	Gamma activity (MeV)	Neutron yield (neutrons/sec-kg)	Decay heat (W/kg)	Critical Mass (kg)
$^{231}\text{Pa}$	$32.8 \times 10^3$	0.30	nil	1.3	162
$^{232}\text{Th}$ (available in nature)	$14.1 \times 10^9$	0.06	nil	nil	infinite
$^{232}\text{U}$	76	(2.62)*	nil	nil	
$^{233}\text{U}$	$159 \times 10^3$		1.23	0.281	16.4
$^{235}\text{U}$ (available in nature)	$700 \times 10^6$	0.19	0.364	$6 \times 10^{-5}$	47.9
$^{238}\text{U}$ (available in nature)	$4.5 \times 10^9$	0.19	0.11	$8 \times 10^{-6}$	infinite
$^{237}\text{Np}$	$2.1 \times 10^6$	0.09	0.139	0.021	59
$^{238}\text{Pu}$	88	...( )	$2.67 \times 10^6$	570	10
$^{239}\text{Pu}$	$24 \times 10^3$	0.41	21.8	2.0	10.2
$^{240}\text{Pu}$	$6.54 \times 10^3$		$1.03 \times 10^6$	7.0	36.8
$^{241}\text{Pu}$	14.7	...(0.06)	49.3	6.4	12.9
$^{242}\text{Pu}$	$376 \times 10^3$		$1.73 \times 10^6$	0.12	89
$^{241}\text{Am}$	433	0.06	1540	115	57
$^{243}\text{Am}$	$7.38 \times 10^3$	0.08	900	6.4	155
$^{244}\text{Cm}$	18.1	...(0.99)	$11 \times 10^9$	$2.8 \times 10^3$	28
$^{245}\text{Cm}$	$8.5 \times 10^3$	0.18	$147 \times 10^3$	5.7	13
$^{246}\text{Cm}$	$4.7 \times 10^3$		$9 \times 10^9$	10	84

\* $^{212}\text{Bi}$  (1.6 MeV gamma) and  $^{208}\text{Tl}$  (2.6 MeV gamma) are daughter products of  $^{232}\text{U}$ .

## 1.2. CONVENTIONAL AND ADVANCED FUELS FOR POWER REACTORS

Amongst the power reactors, some 82% are light water cooled and moderated reactors (LWRs), consisting of pressurized water reactors (PWRs) of western design and Russian design (WWERs) and boiling water reactors (BWRs) and ~10% are pressurized heavy water cooled and moderated reactors (PHWRs), also known as CANDU. The LWRs began commercial operation in the USA during the late 1950s and by early 1960s and became the prototypes of the current generation of PWRs and BWRs used throughout the world today. These nuclear plants are not only the most widely used, but also the most technologically advanced with Generation III+ of both the BWRs and PWRs having come online within the

past decade. Advanced designs of the Russian PWRs (WWER-440 and WWER-1000) have also developed in parallel. All three types of LWRs have been developed to a very high degree of maturity and have demonstrated a high level of safety and reliability. The current trends indicate that LWRs mainly, and to a limited extent PHWRs, will dominate the nuclear power market up to 2050 and beyond, as long as natural uranium resources are economically available. Graphite moderated water cooled reactors (RBMK), are in operation in the Russian Federation and in a few Commonwealth of Independent States (CIS) countries. The MAGNOX and advanced gas cooled reactors (AGR) are in operation only in the UK and are being phased out. Amongst the fast neutron reactors, only sodium cooled fast reactor (SFR) has been developed and deployed commercially in a very limited way. Presently, the BN 600, in the Russian Federation, is the only operating commercial SFR in the world. The Japanese prototype SFR, MONJU, was restarted in 2010. A few demonstration and test type SFRs are in operation in China (CEFR), India (FBTR), Japan (JOYO) and the Russian Federation (BOR 60). A commercial SFR, BN 800 in the Russian Federation and prototype sodium cooled faster breeder reactor (PFBR) of 500 MW(e) in India are under construction. The SFRs are likely to play an important role in long term sustainability of nuclear power. However, their capital and fuel cycle costs are higher compared to LWRs and PHWRs. The transitions from thermal reactors to SFRs are likely to start only from the middle of the 21st century.

The PHWRs and MAGNOX use natural uranium ( $0.711\% \text{ }^{235}\text{U}$ ) fuel in the form of high density, cylindrical oxide pellets and metallic uranium respectively. The conventional fuel for LWRs, RBMKs and AGRs is low enriched uranium (LEU:  $<20\% \text{ }^{235}\text{U}$ ) containing up to  $5\% \text{ }^{235}\text{U}$  in the form of high density cylindrical uranium oxide pellets. In a limited number of LWRs in Europe and Japan, mixed uranium plutonium oxide (MOX) is being used up to one third of the fuel core and advanced LWRs have been designed and are being constructed which could accommodate 100 % MOX fuel in core. The reference fuel for SFRs is MOX containing 15–25%  $\text{PuO}_2$  in combination with depleted uranium oxide. Mixed uranium plutonium monocarbide (MC), mononitride (MN) and U-Pu-Zr alloys are recognized as advanced SFR fuels mainly based on their higher breeding ratio and better thermal conductivity compared to oxide fuel.

The fuel pellets are stacked and encapsulated in cladding tubes to form fuel pins. A cluster of fuel pins is then arranged in a structure called the fuel assembly. The PHWRs, LWRs (PWRs, ERs and BWRs) and RBMKs use zirconium alloy as cladding tube, end plugs and spacer material. The AGRs and MAGNOX use stainless steel and magnesium alloy respectively as cladding material. Austenitic stainless steel is the conventional cladding, end cap, hexcan material for SFR fuel. The cladding tubes act as the primary containment of the radiotoxic fuel and fission products and is also responsible for transferring fission heat energy from fuel to coolant.

The ceramic nuclear fuels, namely oxide, carbide and nitride are mostly manufactured in the form of “fuel pellets” formed by compaction and sintering of “powder” or “fuel microspheres” in the diameter range of 10–1000  $\mu\text{m}$ . The fine fuel powder is granulated and subjected to cold-compaction followed by high temperature sintering in hydrogen atmosphere to form fuel pellets, which are then ground, inspected and loaded in cladding tubes and encapsulated. Alternatively, microspheres of different size fraction could be subjected to vibratory compaction in a one-end welded cladding tube and encapsulated to form ‘sphere-pac’ fuel pins. The microspheres could also be compacted in the form of fuel pellets, loaded in cladding tube and encapsulated. Figure 1 shows the fuels for operating nuclear power reactors and Table 2 summarizes the conventional and advanced fuels for LWRs, PHWRs and SFRs [5].

For fabrication of fuel assembly for high temperature gas cooled reactors (HTGRs), the fuel microspheres are further processed to have multi-layer coated fuel particles, which are embedded in graphite matrix in the form of spherical shells or prismatic blocks. A few experimental and prototype HTGR have been built and operated successfully but HTGR has not been deployed for commercial use so far. Two experimental HTGRs are currently operating in China and Japan. The HTGR is being revived as very high temperature gas cooled reactor (VHTR) for the dual purpose of generating electricity and supplying high temperature process heat for producing hydrogen fuel from water. These reactors are also being proposed for district heating and desalination of sea water.

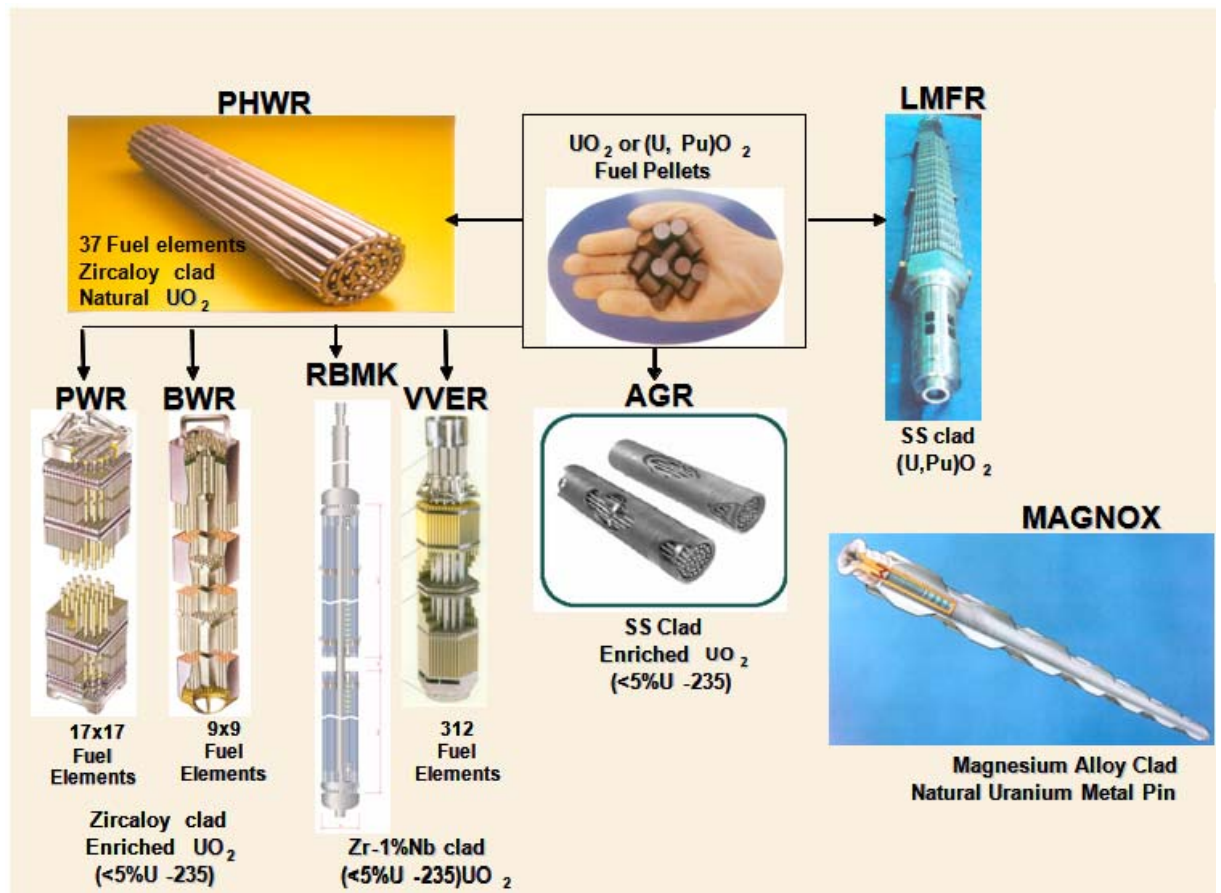


FIG. 1. Fuel pellets, fuel elements and fuel assemblies for nuclear power reactors.

TABLE 2. CONVENTIONAL AND ADVANCED FUELS FOR LWRs, PHWRs AND SFRs [5]

Reactors	Conventional fuels	Advanced/alternative fuels
<p>Light water reactor(LWR): BWR, PWR, WWER</p> <p>- Fuel</p> <p>- Cladding</p> <p>- Burnup (GW d/t HM)</p>	<p>UO<sub>2</sub> (U-235≤5%) up to 9–10% Gd<sub>2</sub>O<sub>3</sub> + UOX (burnable poison)</p> <p>Zircaloy 2 (BWR) Zircaloy 4 (PWR) Zr-Nb-Sn</p> <p>40–50</p>	<p>-Low enriched UOX (&gt; 5 % U-235 )</p> <p>-Mixed uranium plutonium oxide (≤12% PuO<sub>2</sub>)</p> <p>Zr-Sn-Nb-Fe &amp; Zr-Nb-O</p> <p>High : up to 60 Ultra High : up to 80 Cr/Cr+Si/ Al/Al+Si dopant as oxide in UOX or MOX for large grain (≥ 40 μ )</p>
<p>Pressurized heavy water reactor (PHWR) Fuel pellets</p> <p>Cladding</p> <p>Burnup (GW·d/ton HM)</p>	<p>Natural UO<sub>2</sub></p> <p>Zircaloy 4</p> <p>6.7</p>	<p>- REPU or SEU in the form of UO<sub>2</sub></p> <p>- (U,Pu)O<sub>2</sub> (Th, Pu)O<sub>2</sub> &amp; (Th, <sup>233</sup>U)O<sub>2</sub>, containing up to 2% fissile material.</p> <p>- PuO<sub>2</sub> in Inert Matrix (SiC) for burning ‘Pu’ Zircaloy 4</p> <p>15–20</p>
<p>Sodium cooled fast reactors (SFRs) Fuel (pellets/particles/pins)</p> <p>Cladding</p> <p>Burnup (GW d/t HM)</p> <p>Breeding ratio</p>	<p>HEU in the form of UO<sub>2</sub> &amp; (U, Pu)O<sub>2</sub> (≤25% Pu) pellets He-filled pins containing fuel pellets</p> <p>Stainless steel D-9</p> <p>100</p> <p>1.0–1.2</p>	<p>- Na-bonded and He-bonded (U, Pu)C, (U, Pu)N &amp; Na-bonded U– Pu–Zr, (≤25% Pu) fuel with/without MA</p> <p>- He-filled carbide/nitride pins containing pellets</p> <p>- (PuO<sub>2</sub>-ThO<sub>2</sub>) for burning ‘Pu’</p> <p>- He-filled vibratory compacted oxide, carbide and nitride fuel pins</p> <p>- ‘Pu’ and (Pu, MA) in inert matrix for burning</p> <p>- (U/Th + MA) in blanket for ‘proliferation resistance’ in irradiated blanket</p> <p>Oxide dispersion strengthened (ODS) steel</p> <p>200</p> <p>1.2–1.5</p>

### 1.3. CONVENTIONAL AND ADVANCED FUELS FOR RESEARCH REACTORS

Most of the non-power research reactors are materials test reactors (MTRs), pool or tank type, and some are TRIGA (testing, research and isotope production reactors of General Atomics, USA). These reactors are much simpler and compact than power reactors, have much higher fissile material enrichment and are usually cooled and moderated by light water. The research reactors need far less fuel compared to a power reactor, operate at lower temperatures (coolant temperature:  $<100^{\circ}\text{C}$ ) and use aluminium alloy as cladding and core structural materials. Till the late 1970s, most research reactors used high enriched uranium (HEU:  $>20\%$   $^{235}\text{U}$ ) with as high as 90% and beyond  $^{235}\text{U}$  enrichment in order to have more compact cores, with high neutron fluxes and also longer times between refueling. These reactors used Al clad Al-U alloy with uranium density in the fuel in the range of 1.3–1.7  $\text{g/cm}^3$ . Lowering of the  $^{235}\text{U}$  enrichment to the level of some 35% meant that the uranium density had to be increased. Initially this was raised to 2.3–3.2  $\text{g/cm}^3$  with higher uranium content in existing Al-U alloy and with Al- $\text{U}_3\text{O}_8$  dispersion type fuels. In 1978, the USA launched an international programme, titled, reduced enrichment for research and test reactors (RERTR) and restricted  $^{235}\text{U}$  enrichment to less than 20% to guard against weapons proliferation from the HEU fuel. Later, the Russian Federation and other CIS countries and China joined the RERTR programme. As uranium enrichment is decreased, uranium density in the fuel had to be increased in order to maintain the net fissile ( $^{235}\text{U}$ ) atom density of the fuel. Over the last two decades, fuels with increasing uranium density have been developed to allow conversion of HEU to LEU cores. Proceedings of the annual meetings on research reactor fuel management (RRFM) and RERTR have been reporting the development of LEU fuels for non-power reactors [6–8]. The highest uranium density fuel currently licensed by the US Nuclear Regulatory Commission is based on a dispersion of uranium silicide ( $\text{U}_3\text{Si}_2$ ) particles in aluminium matrix with uranium density of 4.8  $\text{g/cm}^3$ . Efforts are underway to develop and qualify aluminium matrix, U-Mo dispersion fuel ( $\gamma$  U) as dispersoid phase) with uranium density 8.0–9.0  $\text{g/cm}^3$  and monolithic U-Mo alloy with density 14–16  $\text{g/cm}^3$ . Table 3 gives a list of the conventional and advanced fuels for research reactors.

TABLE 3. CONVENTIONAL AND ADVANCED FUELS FOR NUCLEAR RESEARCH REACTORS

Reactors	Conventional fuels	Advanced fuels
Mostly MTRs (tank or pool types) and TRIGA.	Aluminum alloy clad: (i) Natural U metal rod,  (ii) Al-matrix dispersion fuel with $\text{UAl}_x$ , $\text{U}_3\text{O}_8$ , $\text{U}_3\text{Si}_2$ dispersoid in the form of fuel pins and fuel plates (‘U’ density in fuel: $\leq 4.8 \text{ g/cm}^3$ )	Aluminum alloy clad: (i) Al alloy matrix - $\text{U}_3\text{Si}$ dispersion fuel (with small addition of Al), (ii) Al alloy matrix U-Mo dispersion fuel ( $\gamma$ U phase) with U-density in fuel 8–9 $\text{g/cm}^3$ in plate form (iii) Monolithic U-Mo alloy fuel with U-density 14–16 $\text{g/cm}^3$ in plate form

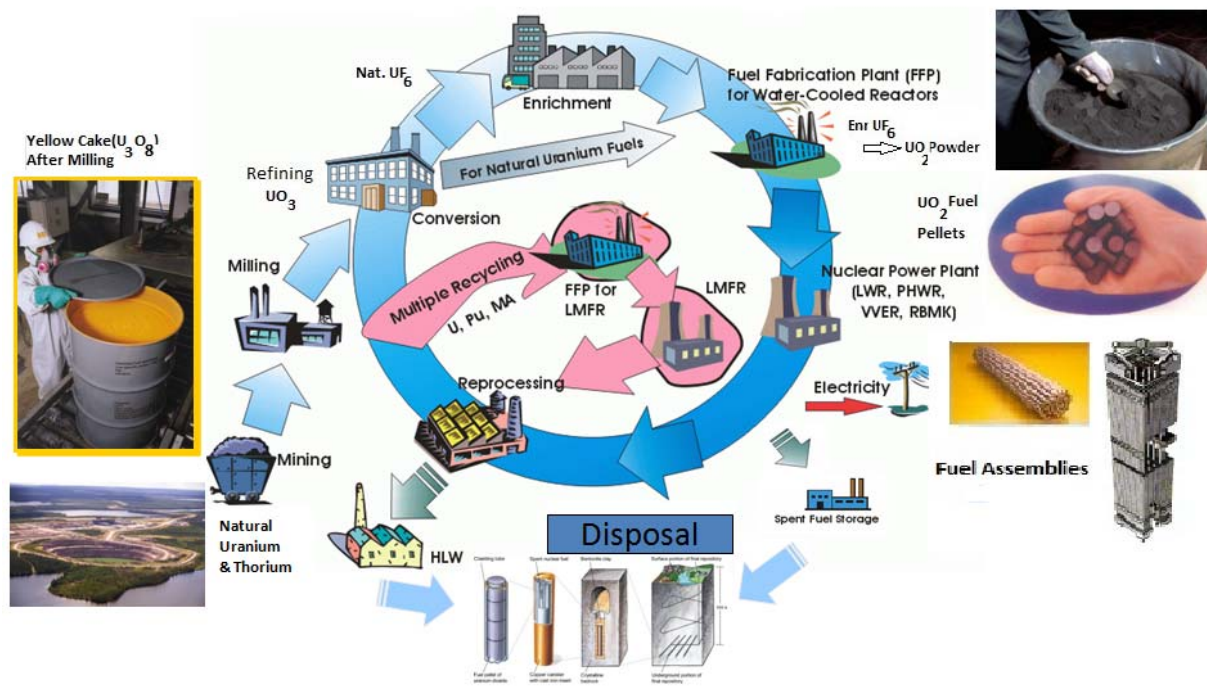


FIG. 2. Nuclear fuel cycles showing open and close fuel cycles.

#### 1.4. NUCLEAR FUEL CYCLE

Figure 2 shows the major steps in the front and back ends of nuclear fuel cycle. The front end includes all activities from the ‘ore to core’ of the reactor, namely, exploration for discovering uranium and thorium deposits, mining and milling of U and Th ores, refining, conversion, isotopic enrichment (only for  $^{235}\text{U}$ ) and fuel fabrication. All activities related to the spent nuclear fuel (SNF) management, including storage, reprocessing, re-fabrication of fuel and waste management form a part of the back-end. In the ‘once-through’, open-ended fuel cycle, the spent uranium fuel is considered to be a waste. It is subjected to underwater wet storage initially followed by long-term ‘away from reactor’ (AFR) wet or dry storage before permanent disposal in repository. In the ‘closed’ fuel cycle, SNF is considered as a source of energy. The SNF is reprocessed to recover and recycle fertile and fissile materials. The radioactive fission products are immobilized in glass and sent to geologically stable, underground repository for permanent disposal.

Presently, only the uranium fuel cycle activities are carried out on an industrial scale all over the world and very little work is being pursued in thorium fuel cycle. The total identified uranium resources is 6.30 million tons (at <260 US\$/kg U) and the total undiscovered resources amount to another 10.40 million tons [9]. In addition, the unconventional uranium resources, mostly as phosphate rocks, add to more than 9 million ton U and could be as high as 22 million tons U. The current annual uranium demand is in the range of 60 000–65 000 tons U and the annual production is in the range of 43 000–50 000 tons. The gap between uranium demand and supply is being met from secondary supplies of already mined uranium. The annual demand of uranium is likely to increase to the level of 90 000–140 000 tons U by



2035, based on low and high growth scenarios of nuclear power. Hence, there is adequate natural uranium resources to meet the fuel requirement of the operating water cooled reactors up to 2050 and beyond for any foreseeable growth scenario of nuclear power. However, a sustained strong market for uranium will be needed to bridge the gap between uranium in the ground and uranium concentrate in the can and also to increase uranium resources through brown and green field explorations.

In the currently operating thermal power reactors,  $^{235}\text{U}$  undergoes fission and generates heat energy, whereas  $^{238}\text{U}$  is partially transmuted to plutonium by neutron capture reaction. The fissile plutonium isotopes ( $^{239}\text{Pu}$  and  $^{241}\text{Pu}$ ) undergo in situ fission and contribute to some 30% of fission heat energy. The ratio of fissile Pu formed from fertile  $^{238}\text{U}$  to the fissile  $^{235}\text{U}$  consumed, known as conversion ratio, is between 0.4–0.6 in these reactors. As a result, the natural uranium utilization is <1% in thermal reactors even after recycling of U and Pu. In fact, more than 99% of uranium mined and used for fabricating fuels for thermal reactors, including LWRs and PHWRs, is locked as  $^{238}\text{U}$  in Depleted U (DU: <0.7%  $^{235}\text{U}$ ) tailings of the enrichment plants (for LWRs), in REP U and in spent fuel. The spent fuel from currently operating thermal reactors contain 95–96% U (mostly as  $^{238}\text{U}$ ), 3–4% fission products, < 1% Pu (of which 50–60% as  $^{239}\text{Pu}$  the balance being other isotopes:  $^{240}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{242}\text{Pu}$  and  $^{238}\text{Pu}$ ) and ~0.1% MA. Presently, only France, Japan and UK are reprocessing spent fuel from thermal reactors on an industrial scale, recovering the plutonium and manufacturing MOX fuel, containing up to 12%  $\text{PuO}_2$ , for use in LWRs. Semi-industrial/pilot scale reprocessing and MOX fuel fabrication plants are also in operation in India and the Russian Federation. MOX fuel is being used in some 30–40 PWRs in Belgium, France, Germany and Switzerland for nearly 3 decades and has recently been introduced in the LWRs in Japan. Nearly one third of the core of these LWRs is made up of MOX fuel. Presently, the trend is mono recycling of plutonium in LWRs and storing the spent MOX fuel for reprocessing at a later date when the SFR technology matures. All aspects of nuclear fuel cycle including the front and back ends are updated in recent IAEA publications [10–11].

Enrichment of  $^{235}\text{U}$  and reprocessing of spent fuel are the two main steps in uranium fuel cycle that are highly sensitive. In the mid-1940s, the first uranium enrichment plants were built to produce HEU and the first reactors were built to produce plutonium — both for weapons. The civil and military nuclear fuel cycles have many materials, processes and products in common and a capability to produce HEU and plutonium for weapons is inherent in the civilian nuclear fuel cycle. This raises the possibility of the diversion of materials from civil to military programmes and of covert production of weapon usable materials. Proliferation resistance of fissile and fertile materials is, therefore, of paramount importance in nuclear fuel cycle for peaceful and civilian application. According to weapon designers, the construction of a  $^{235}\text{U}$  based nuclear device becomes impractical for enrichment levels below 20% because of the very high critical mass as shown in Fig. 3 [12]. In fact, the critical mass is nearly infinite if  $^{235}\text{U}$  enrichment level is 6% and below. Thus, the present generations of LWR and PHWR fuels, with maximum  $^{235}\text{U}$  enrichment level of 5% have inherent proliferation resistance.

Hence, <20%  $^{235}\text{U}$  has been set as the upper limit of enriched uranium for civilian application. The IAEA considers HEU (>20%  $^{235}\text{U}$ ) as a ‘direct use’ weapon material, though in actual weapon  $^{235}\text{U}$  enrichment is >90% and this is known as ‘weapon grade’ uranium. In the back end of fuel cycle, while  $^{239}\text{Pu}$  is the only fissile material known to be used in nuclear weapons,  $^{233}\text{U}$ ,  $^{237}\text{Np}$  and  $^{241}\text{Am}$  have reasonably low bare critical masses (Table 1) and could be used for nuclear weapons.

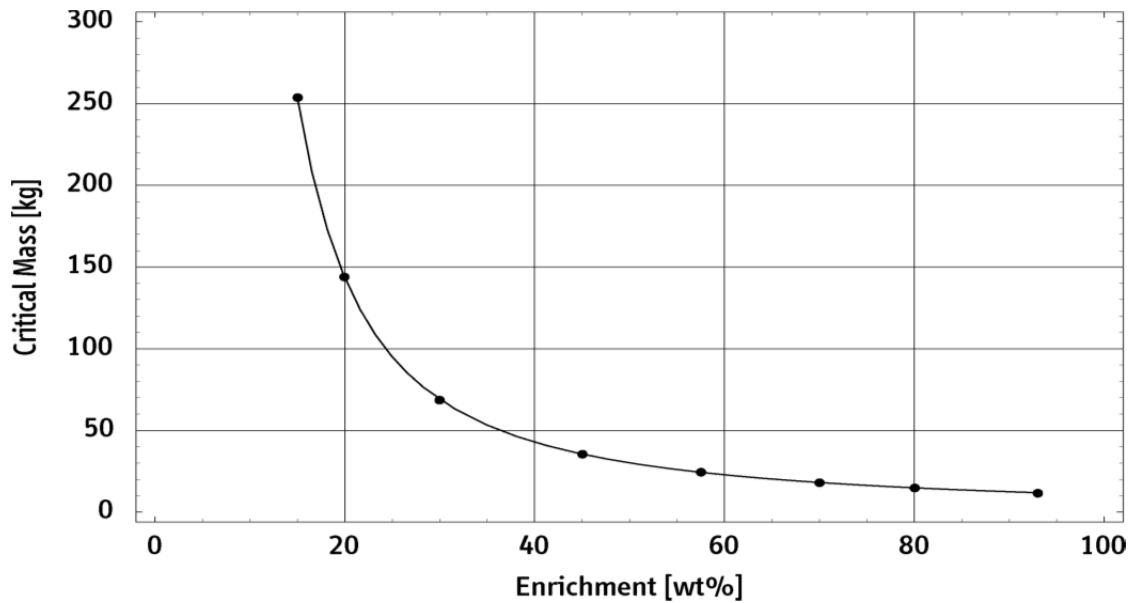


FIG. 3. Fast critical mass of uranium ( $^{235}\text{U} + ^{238}\text{U}$ ) with different levels of  $^{235}\text{U}$  enrichment (critical mass is for a uranium sphere enclosed in a 5 cm Be reflector) [12].

Hence, the general guideline to ensure ‘intrinsic proliferation resistance’ in operating and upcoming spent fuel reprocessing plants is to avoid separated plutonium, neptunium or americium streams and uranium ( $^{233}\text{U}$ ) stream in spent  $^{232}\text{Th}$ - $^{233}\text{U}$  fuel. The other alternative suggested to ensure intrinsic proliferation resistance in fuel cycle is to spike the transuranium actinides with  $^{238}\text{Pu}$  and  $^{233}\text{U}$  with  $^{232}\text{U}$  isotopic barriers. Reactor plutonium containing  $>6\%$   $^{238}\text{Pu}$  is considered to be denatured and proliferation resistant owing to the high decay heat and high spontaneous neutron associated with  $^{238}\text{Pu}$ . Likewise,  $^{232}\text{U}$  has a relatively short half-life and strong gamma emitting daughter products that facilitate intrinsic proliferation resistance.

$^{239}\text{Pu}$  is the best fissile material in SFRs, where in combination with  $^{238}\text{U}$  it is possible to breed more  $^{239}\text{Pu}$  from  $^{238}\text{U}$  than consumed or in other words have a breeding ratio  $>1.0$ . Multiple recycling of Pu with  $^{238}\text{U}$  in SFRs will increase the natural uranium utilization at least sixty times more as compared to once-through cycle. In addition, SFR could be used for transmutation or burning of MA, thereby minimizing the long term radio toxicity and decay heat in spent fuel. The fast reactor could also be utilized to breed fissile  $^{233}\text{U}$  from natural thorium. It is possible to have self-sustaining  $^{232}\text{Th}$ - $^{233}\text{U}$  fuel cycle in both thermal and fast neutron spectrums. For long term sustainability of nuclear power, SFRs and closed fuel cycle are inevitable. However, the economics of fast reactor technology and the related fuel cycle is yet to be established, though a few prototype and commercial SFRs have been built and successfully operated.

## 1.5. OBJECTIVE OF THE REPORT

The present publication is a compilation of updated information on experiences and trends in manufacturing technology of nuclear fuels for power reactors and research reactors. Though the fuel cladding and other structural components of fuel element and fuel assembly are integral part of the fuel, the report does not cover the manufacturing of these non-fissile and non-fertile components. The publication focuses on fabrication processes of matured fuels like  $\text{UO}_2$  and MOX for water cooled power reactors and SFRs, emerging SFR fuels like mixed uranium plutonium mono-carbide, mono-nitride, U-Pu-Zr, MA bearing fuels and thoria-based mixed oxide fuels for power reactors and aluminum matrix dispersion type fuels

and monolithic fuels for research reactors. This report has six sections. Section 1 gives a brief historical review of nuclear fuels and fuel cycle options, highlighting the unique features of nuclear fuels and the conventional and advanced fuels for power reactors and non-power reactors. Section 2 summarizes the experiences of fabrication of oxide fuels for power reactors, highlighting  $\text{UO}_2$  and mixed uranium plutonium oxide (MOX) fuels.  $\text{UO}_2$  is the universal fuel for most of the operating thermal reactors (except the Magnox reactor) and is being manufactured in the form of high density pellets by the classical powder-pellet route, on an industrial scale, for over three decades, in several countries. Mixed uranium plutonium oxide (MOX) is the reference fuel for SFR but is also being used in the interim period in one third of the cores of several LWRs in Europe and Japan. MOX fuel has also achieved industrial maturity but only in very few countries. The emphasis on MOX fuel fabrication is to develop process flow sheet with due consideration for coping with radiotoxic dust and personal exposure hazards and to properly safeguard plutonium streams in the manufacturing process in order to ensure proliferation resistance of the process. This section covers challenges associated with manufacturing of highly radiotoxic minor actinide bearing oxide fuel for burning MA in SFRs. Section 3 summarizes the experiences of fabrication of thorium-based oxide fuels and the challenges of manufacturing these fuels. Section 4 deals with the manufacturing processes of mixed uranium plutonium mono-carbide and mono-nitride fuels, which are advanced fuels for SFR. The MC and MN fuels are pyrophoric and have so far been fabricated on a laboratory or pilot plant scale, under inert cover gas, in very few countries for use as driver fuel in small test reactors and for irradiation testing experiments. In recent years, MA bearing oxide, mono-carbide and mono-nitride fuels have been manufactured on a laboratory scale for irradiation testing. Section 5 describes the fabrication of U–Zr and U–Pu–Zr metallic fuels for advanced SFRs. The section also includes the limited laboratory scale experience in manufacturing MA based metallic fuel for burning MA in SFRs. Section 6 summarizes the manufacturing experience of a wide variety of dispersion and monolithic fuels for non-power reactors for research, materials testing and isotope production, where the basic objective is to develop LEU based, high uranium density dispersion and monolithic fuels. The main contents of this chapter is the manufacturing experience of aluminum matrix Al– $\text{U}_3\text{Si}_2$  dispersion fuel, which is the certified fuel for LEU based MTR, and the recent developments on high density U–Mo dispersion and monolithic fuels report. The summary of the experiences of manufacturing technology of nuclear fuel is presented in Section 7, identifying the gaps in information and the areas of future research and development.

## **2. MANUFACTURING TECHNOLOGY OF URANIUM AND MIXED URANIUM PLUTONIUM OXIDE FUELS**

### **2.1. INTRODUCTION**

Since the inception of nuclear power programme in the mid-1950s, uranium dioxide (UOX) has been the reference fuel for water cooled thermal reactors on the basis of favorable properties like high melting point ( $\sim 3073$  K), stable single phase structure up to the melting point, high chemical and irradiation stability, low chemical activity towards coolant and cladding material and relatively simple fabrication methods. The uranium oxide fuels for LWRs and RBMKs have up to 5%  $^{235}\text{U}$  enrichment. The CANDU/PHWRs use natural uranium oxide as conventional fuel. LEU oxide with up to 5%  $^{235}\text{U}$  is also the driver fuel for AGRs. In the Russian Federation, HEU oxide has been used as fuel for prototype and commercial SFRs and in China, HEU oxide is the fuel for the experimental SFR. Depleted

UO<sub>2</sub> has been the standard blanket material for SFRs and also used in CANDU/PHWRs for neutron flux flattening of the startup cores. The UO<sub>2</sub> fuel has demonstrated excellent chemical compatibility with zirconium alloy cladding and high temperature pressurized water and steam in LWRs, PHWRs and RBMK, with liquid sodium coolant and stainless steel cladding in SFRs and with CO<sub>2</sub> coolant and stainless steel cladding in AGRs. The basic information on UO<sub>2</sub> fuel, highlighting manufacturing has been covered in details by several authors [13–17]. Proceedings of international conferences on LWR fuels and CANDU fuels have also been highlighting the state of the art information on all aspects of natural and enriched uranium oxide fuels [18–22].

The oxide fuel performance has improved significantly over the years, particularly in water cooled reactors which account for nearly 95% of the operating reactors. Major problems like external and internal hydriding of zirconium alloy cladding, pellet cladding interaction (PCI) failure due to stress corrosion cracking (SCC) during power ramp, debris related failures and crud induced localized corrosion have been resolved with: (i) tighter fuel pellet specification in terms of hydrogen content, pellet geometry (optimizing chamber, landing, dishing and length to diameter ratio) and microstructure (grain size and pore size, shape and distribution), (ii) using graphite coating on inner surface of zirconium alloy cladding tube of PHWR / CANDU fuel to act as a lubricant and also a diffusion barrier, (iii) using helium pre-pressurization of LWR cladding tube, (iv) introducing new zirconium alloys with better corrosion resistance and irradiation behavior, (v) controlling coolant chemistry and (vi) optimizing in-core fuel management. The present trend in water cooled reactor fuels is better performance and higher burnup, zero manufacturing defects and zero in-core failure. A lot of emphasis is now being given on microstructure of fuel pellet. Large grain size (>40 µm) is recommended for LWR and PHWR fuels for which dopants like Al, Cr, Si, Ti and their combination are being tried [23–28].

Mixed uranium plutonium oxide (MOX) containing 15–32% PuO<sub>2</sub> and depleted uranium has been the driver fuel for the first generation of experimental and prototype SFRs in France, Germany, Japan, the UK and USA and in one commercial SFR in France. In the 1960s and 1970s, pilot and semi industrial plants were set up in Belgium, France, Germany, Japan, UK and USA for manufacturing MOX fuel for initial and reload cores of Rapsodie, Phenix and Super Phenix reactors in France, KNK II in Germany, JOYO in Japan, PFR in the UK and FFTF in the USA. These facilities were also used for manufacturing MOX fuel containing up to 10% PuO<sub>2</sub> for irradiation testing in LWRs in Belgium, the USA, Germany, France and Italy. In the 1970s, MOX fuel was introduced in industrial scale in two BWRs and one PWR in Germany. In the 1980s, since the commercial deployment of SFRs was delayed, the stocks of separated Pu were diverted for manufacturing MOX fuels on an industrial scale for utilization in progressively more than 30 LWRs in Belgium, France, Germany and Switzerland. Five pilot facilities in the USA with cumulative capacity of 50–70t HM/year were in operation till mid-1970s after which they were shut down for political reasons. However, the USA has started constructing the mixed oxide fuel fabrication facility (MFFF) at the Savannah River Site in August 2007 with a capacity to process 35 t/year of weapons-grade plutonium into MOX fuel for utilization in LWRs. MFFF is expected to begin operations in 2016 [29]. The semi-industrial MOX fuel fabrication plant in Germany with annual capacity of 20–25t HM for LWRs and SFRs was shut down in 1992 after twenty years of operation. A larger plant of 120t HM/year in Germany was almost ready to start operation but was also shut down. In Belgium, semi-industrial plant started operation in 1972 for manufacturing both LWR and SFR fuels. In the mid-1980s, it was converted into a commercial plant, which produced yearly 40t HM LWR fuel until 2006, when it was shut down due to reduced demand for MOX fuel. The MOX plant in Cadarache, France was

extensively utilized for manufacturing MOX fuel for Phenix and Super-Phenix prototype and commercial SFRs respectively [30–31]. Later, a portion of the plant was dedicated for manufacturing MOX fuels for LWRs. The MOX plant at Cadarache was shut down in 2003, since it did not meet the new seismic regulation. Since, all SFRs in France have been shut down, MELOX, the large scale industrial MOX facility in France, which started operation in 1995, was designed and engineered exclusively for LWR fuel fabrication [32]. In Japan, the manufacturing of MOX fuel was initiated in early 1970s in a pilot plant named plutonium fuel fabrication facility (PFFF) with capacity 10t HM/year [33]. Later, a semi-industrial plutonium fuel production facility (PFPP) was set up at Tokai where the reload MOX fuel for JOYO and initial and reload fuels for MONJU was started in 1988 [34–35]. Japan has started constructing the MOX fuel fabrication plant, named J-MOX, adjacent to Rokkasho reprocessing plant in October 2010 with a capacity of 130t HM/y for LWRs [36]. It is expected that the J-MOX will be completed in March 2016. The information on fabrication, performance and reprocessing of MOX fuel has been reported in detail earlier [37–38].

The fabrication of  $\text{UO}_2$  fuel is being carried out on an industrial scale for over four decades and the technology has attained a high level of maturity in several countries. Likewise, MOX fuel technology has also reached a high level of maturity, though in a limited number of countries. Table 4 summarizes the manufacturing facilities of natural and enriched  $\text{UO}_2$  and MOX fuels, in operation and their capacities, all over the world for PHWRs, LWRs, AGRs and SFRs [39].

The current trend in LWRs and to some extent in PHWRs is to increase fuel burnup to high or ultrahigh levels and achieve zero fuel failure. The target burnup for LWR and PHWR fuel is 60 000–80 000 MW d/t HM and 15 000–20 000 MW d/t HM respectively. For this it is essential to:

- (i) Use LEU beyond 5%  $^{235}\text{U}$  for LWR fuel and in the range of 1%  $^{235}\text{U}$  enrichment for PHWR fuel;
- (ii) Use higher percentage of Gd as burnable poison in LWRs with  $\text{UO}_2\text{--Gd}_2\text{O}_3$  containing 9–10%  $\text{Gd}_2\text{O}_3$ ;
- (iii) Produce uranium oxide (UOX) and mixed uranium plutonium oxide (MOX) fuel pellets of large grain size ( $\geq 40\text{ }\mu\text{m}$ ) in order to minimize fission gas release and enhance fuel creep to avoid pellet cladding interaction (PCI) failure at high burnup.

Doping  $\sim 1000\text{ppm}$  ‘sintering aid’ like Cr, Al, Cr + Si and Al + Si by admixing  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3 + \text{SiO}_2$  and mullite respectively to the oxide fuel powder during co-milling, prior to pelletization was found to be effective for homogeneous blending. The sintering of fuel pellets is required to be carried out in tighter specified atmosphere by proper adjustment of oxygen potential and scrap recycling strategy, by wet and dry methods, need to be revisited.

TABLE 4. INDUSTRIAL FACILITIES WORLDWIDE FOR MANUFACTURING  $\text{UO}_2$  AND  $(\text{U}, \text{Pu})\text{O}_2$  FUELS [39]

S.No.	Country	Natural $\text{UO}_2$ (PHWR Fuel) Capacity: t HM/a	Low enriched $\text{UO}_2$ (LWR mainly) Capacity: t HM/a	MOX (LWR/PHWR/SFR) Capacity: t HM/a	Manufacturing technique of MOX fuel
1.	Argentina	160 (0.9% $^{235}\text{U}$ )	Nil	Nil	
2	Belgium	Nil	750	Nil (shut down)	MIMAS
3	Brazil	Nil	100	Nil	
4	Canada	2700	Nil	Nil	
5	China	200	400	Nil	
6	France	Nil	820	195	COCA and MIMAS
7	Germany	Nil	650	Nil (shut down)	OCOM and AUPuC
8	India	600	25	10	Adaptation of SBR
9	Japan	Nil	1724	5.7(8 <sup>+</sup> )	Conventional and MH de-nitration
10	Republic of Korea	400	550	Nil	
11	Pakistan	20	Nil	Nil	
12	Russian Federation	Nil	2020 (includes $\text{UO}_2$ with HEU for SFR)	1.3 (only SFRs)	Conventional and Vi-pack
13	Romania	240	Nil	Nil	
14	Spain	Nil	300	Nil	
15	Sweden	Nil	600	Nil	
16	UK	Nil	330 (AGR)	48	SBR
17	USA	Nil	3900	Nil (Shut down — a new plant under construction)	Conventional
18	TOTAL(Rounded):	4160 t HM/a	10 000 t HM/a	350 t HM/a	

\* Licensed annual capacity only for scrap processing in PFFF.

The manufacturing processes of  $\text{UO}_2$  and MOX fuels are more or less similar because  $\text{UO}_2$  and  $\text{PuO}_2$  are iso-structural (FCC,  $\text{CaF}_2$  type), completely solid soluble and have quite similar thermodynamic and thermo-physical properties. The two main steps in the fabrication are:

- (i) Preparation of oxide in the form of powder, granules or micro-spheres starting from suitable compounds of uranium and plutonium;
- (ii) Consolidation of the fuel powder, granules or micro-spheres and encapsulation in cladding tubes.

Figure 4 summarizes the viable techniques for preparation of  $\text{UO}_2$ ,  $\text{PuO}_2$  and MOX powder and microspheres using uranyl nitrate, uranium hexafluoride and plutonium nitrate as feed materials. Figure 5 shows the major steps and options in preparation of  $\text{UO}_2$  and MOX powder, microspheres, granules and fuel pins.

## 2.2. INDUSTRIAL METHODS FOR PREPARATION OF $\text{UO}_2$ POWDER

The industrial methods followed worldwide for preparation of  $\text{UO}_2$  powders are the ammonium diuranate (ADU) process, the ammonium uranyl carbonate (AUC) process, the dry conversion (DC) process including the integrated dry route (IDR). The ADU, AUC and DC processes are described in details in several publications [40–42].

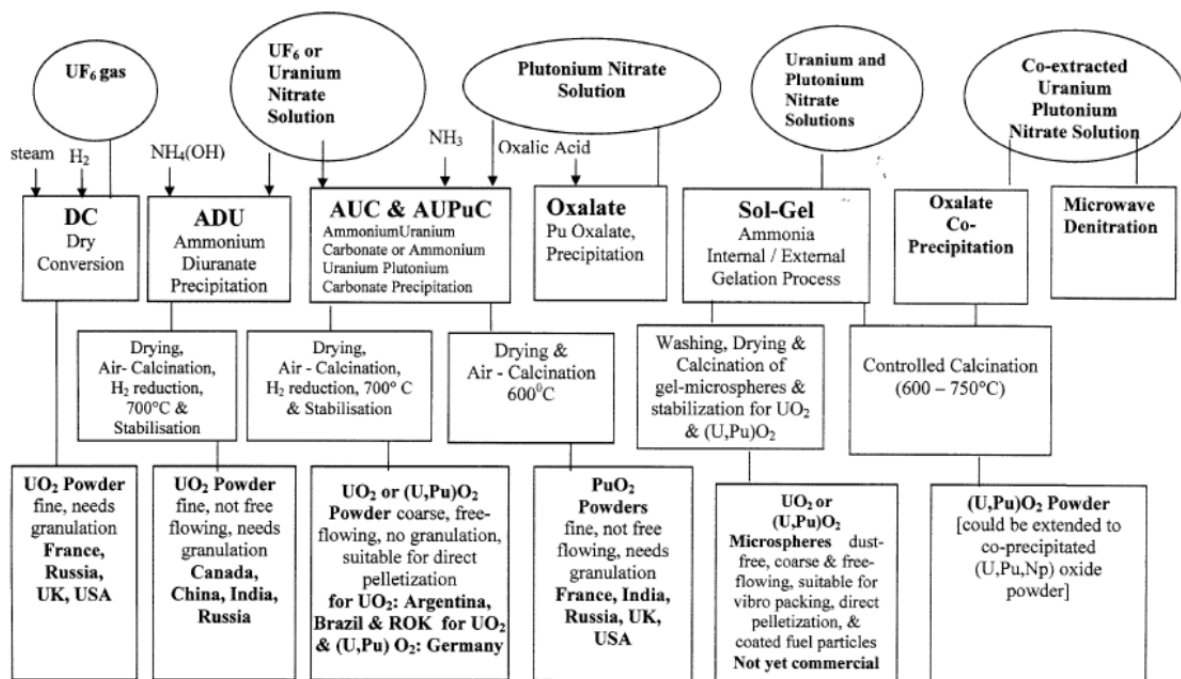


FIG. 4. Industrial methods for manufacturing UO<sub>2</sub> and (UPu)O<sub>2</sub> powders and microspheres.

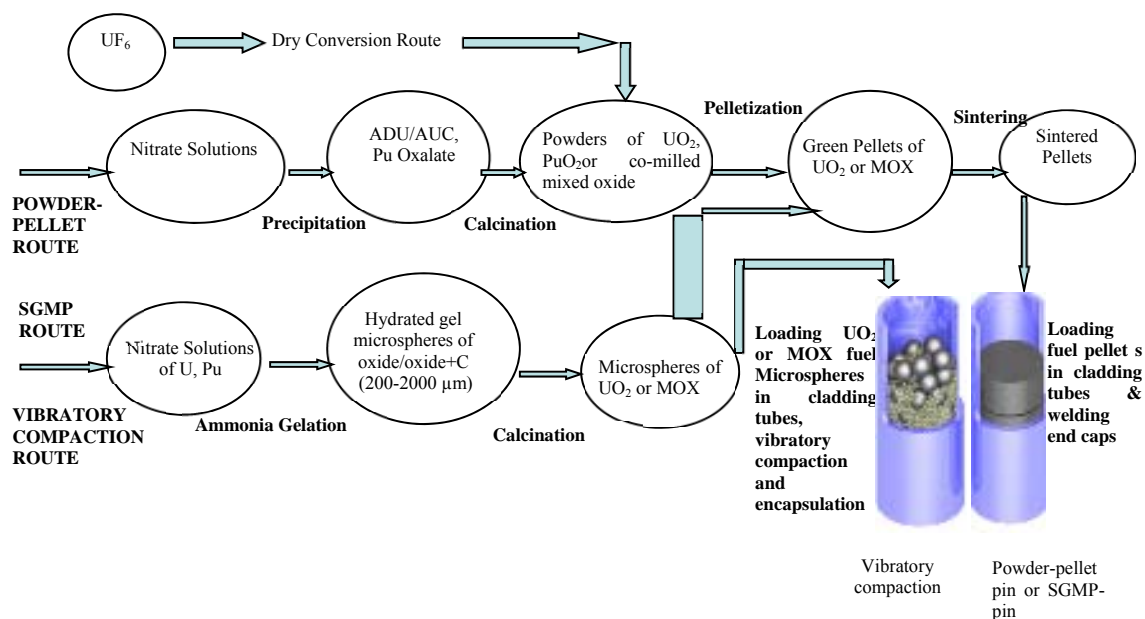


FIG. 5. Manufacturing processes of UO<sub>2</sub>, (U,Pu)O<sub>2</sub> fuel pellets and microspheres and their encapsulation.

The ADU and AUC are wet chemical processes that use uranyl nitrate or UF<sub>6</sub> as starting materials for preparation of both natural and enriched UO<sub>2</sub> powder. The DC processes use UF<sub>6</sub> as feed material and are the most common processes nowadays for manufacturing enriched UO<sub>2</sub> powder.

### 2.2.1. ADU process

The ADU process is mainly followed in Canada and India for preparation of natural  $\text{UO}_2$  powder for manufacturing very high density  $\text{UO}_2$  fuel pellets ( $> 96\%$  T. D.) for CANDU/PHWRs. The pure uranyl nitrate solution, obtained after the refining process based on solvent extraction, is reacted with ammonium hydroxide solution to obtain the precipitates of ammonium di uranate (ADU) as per the following reaction:



The process flow sheet followed in Canada is shown in Fig. 6 [40]. The ADU derived  $\text{UO}_2$  powder is extremely fine ( $< 1 \mu\text{m}$ , has specific surface area in the range  $2.5\text{--}6.0 \text{ m}^2/\text{g}$  and has poor flowability. Additional process steps, namely pre-compaction or roll-compaction followed by granulation, are needed for producing coarse and free-flowing  $\text{UO}_2$  granules suitable for pelletization at  $300\text{--}400 \text{ MPa}$  in high speed automatic hydraulic, mechanical and rotary compaction presses. A major disadvantage of the ADU route is radiotoxic aerosol associated with fine powder of  $\text{UO}_2$ .

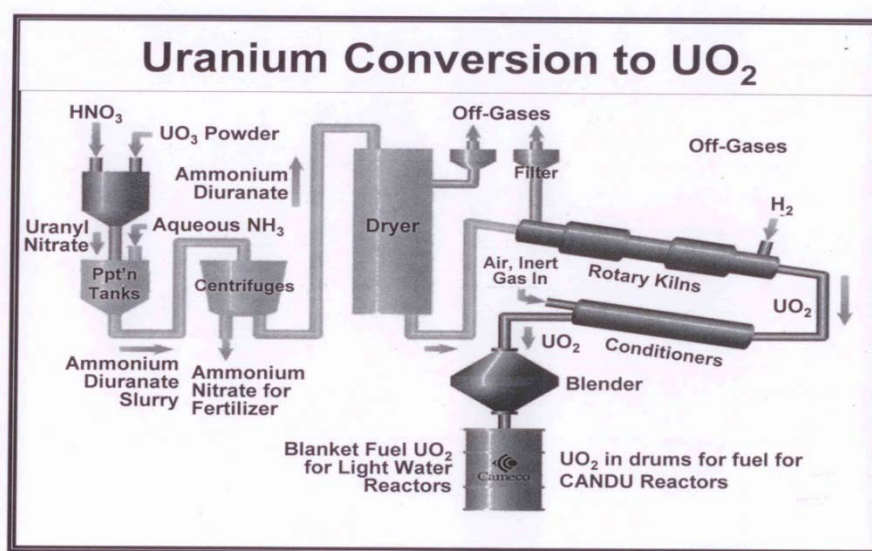
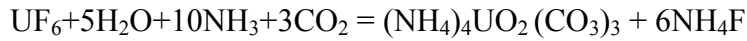
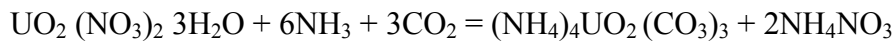


FIG. 6. Ammonium di-uranate (ADU) process followed in Canada for preparation of sinterable grade  $\text{UO}_2$  powder [40].

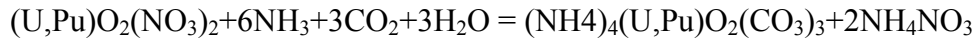
### 2.2.2. AUC process

The AUC process was developed and followed in Germany and has been extended to Sweden, Brazil and the Republic of Korea. With shutdown of the Hanau plant, the process is not used in Germany anymore. The starting material could be either uranyl nitrate or  $\text{UF}_6$  though the latter is more commonly used. Figure 7 [41] shows the schematic diagram of AUC process developed in Germany. The chemical equations involved in the AUC process are as follows:





The uranium dioxide powder, obtained after controlled calcinations of AUC at  $\sim 650^\circ\text{C}$  in reducing atmosphere, is coarse ( $10\text{--}20\ \mu\text{m}$ ) and free flowing, has a relatively high specific surface area ( $5\text{--}7\ \text{m}^2/\text{g}$ ) and is suitable for direct pelletization. The process has been extended in Germany for co-precipitation of ammonium uranyl plutonyl carbonate (AUPuC) as per the following equations:



The ex-AUPuC mixed oxide powder is suitable for direct pelletization for production of mixed oxide pellets of excellent plutonium micro-homogeneity. The AUPuC process has been utilized for preparation of  $(\text{U,Pu})\text{O}_2$  powder, containing up to 30 %  $\text{PuO}_2$  for use in SFR fuel fabrication.

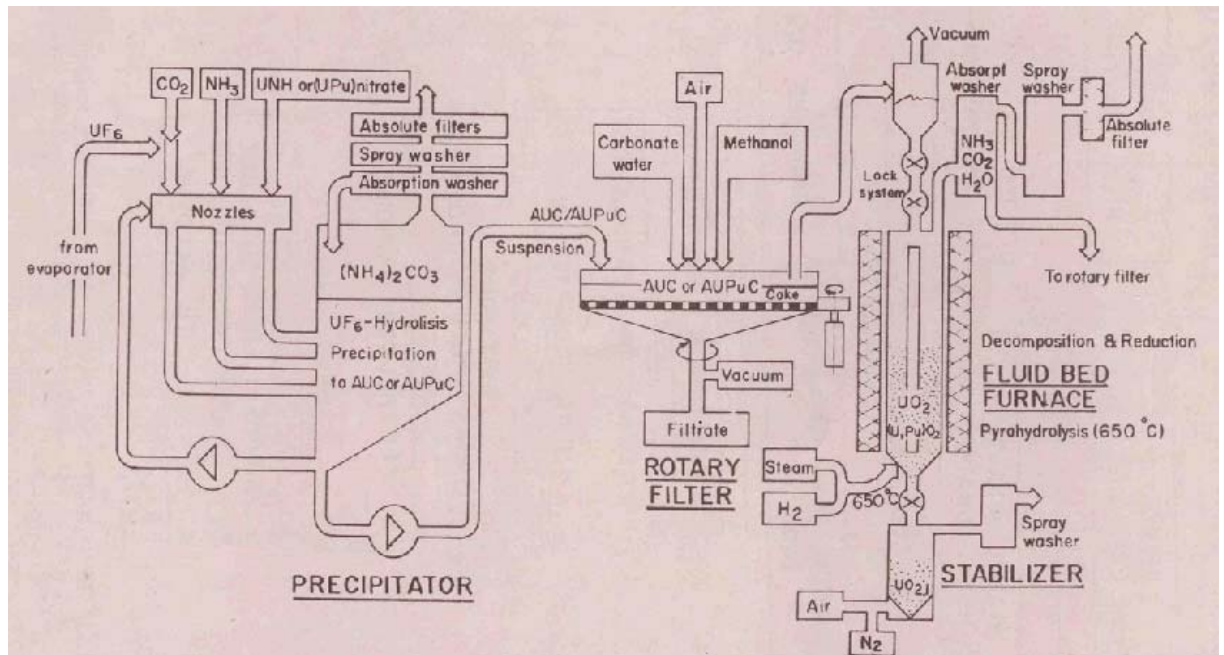
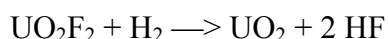
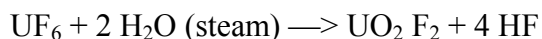


FIG. 7. Ammonium uranyl carbonate (AUC) and ammonium uranyl plutonyl carbonate (AUPuC) processes of Germany [41].

### 2.2.3. Dry processes

The dry processes involving direct steam pyro-hydrolysis of  $\text{UF}_6$  are widely practiced in France, Germany, Republic of Korea, Russian Federation and the USA and have been summarized by Peehs et.al [42]. These processes aim at producing sinterable  $\text{UO}_2$  powder with low fluorine content. Unlike the ADU and AUC processes, the dry processes accept only  $\text{UF}_6$  as feed material. The dry conversion (DC) process of Germany [43–44] and General

Electric Company (GECO) are utilized for preparation of enriched  $\text{UO}_2$  powder for fabrication of LWR fuel pellets involving the following two reactions:



In the two step DC process,  $\text{UO}_2$  is formed together with minor amounts of  $\text{UO}_2\text{F}_2$  in a fluidized-bed reactor. In a subsequent rotary kiln, the  $\text{UO}_2$ - $\text{UO}_2\text{F}_2$  mixture is converted to  $\text{UO}_2$  powder with negligible impurities of fluorine. The DC process, shown in Fig. 8, comprises the following 4 stages.

- A gas phase reaction of vaporized  $\text{UF}_6$  with superheated steam which produces uranyl fluoride ( $\text{UO}_2\text{F}_2$ ) at the nozzle inside the fluidized bed reactor;
- Conversion of  $\text{UO}_2\text{F}_2$  to uranium oxide ( $\text{UO}_{2+x}$ ) powder and de-fluorination in the fluidized bed by steam and hydrogen;
- Final de-fluorination of the  $\text{UO}_2$  powder in the rotary kiln;
- Stabilization of the  $\text{UO}_2$  powder with air in the stabilizer.

The two reaction steps in the DC and GECO processes have been combined in one step in the integrated dry route (IDR) in UK [45], for manufacturing enriched  $\text{UO}_2$  powder for fabrication of AGR fuel pellets. The dominant feature of the DC process and IDR is that these processes involve only the gas–gas and gas–solid reactions. Figure 8 shows the schematic diagram of the IDR and DC process followed respectively in UK and Germany. The only by-product of the process is HF, which is of high purity and could be recovered and sold. The specific surface area of  $\text{UO}_2$  powder derived from dry processes is relatively low and in the range of  $2.0 \text{ m}^2/\text{g}$ . The stability of the powder is excellent and no passivation treatment is required.

The DC process utilized in the USA, Germany and the Russian Federation has an additional fluidized bed in the lower part of the reactor vessel where, reduction of  $\text{UO}_2\text{F}_2$ , removal of fluorine and shaping and sizing of  $\text{UO}_2$  powder takes place. Thus, partial flowability is induced to the powder, which is important for further application. In the rotating kiln at higher temperature ( $700^\circ\text{C}$ ), the reduction and calcination is completed.  $\text{UO}_2$  powder thus produced is utilized for MOX fuel fabrication as described in subsequent section.

The uranium and plutonium are extracted to the organic phase, leaving the fission products and MA in aqueous phase. Next, the U and Pu are stripped back from organic to aqueous phase by adding nitric acid of very low concentration to obtain pure solution of mixed uranyl plutonyl nitrate. The plutonium is separated from uranium by redox stripping in which the oxidation state of the plutonium is lowered by the action of a reducing agent. The pure plutonium nitrate solution thus obtained is subjected to oxalic acid treatment followed by air calcination at around  $600^\circ\text{C}$  to obtain  $\text{PuO}_2$  powder.

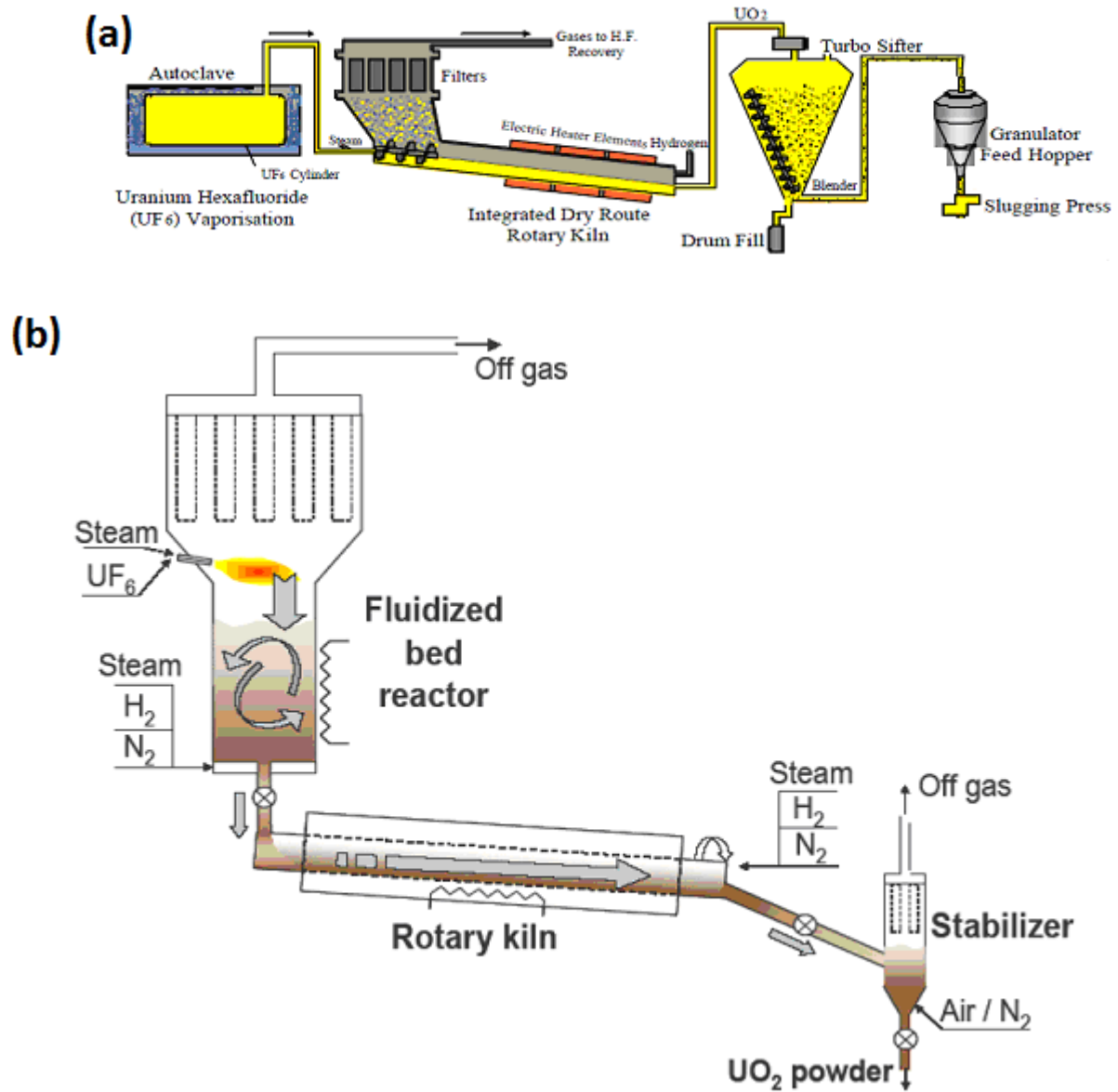


FIG. 8. Schematic representation of: (a) Integrated Dry Route (IDR) in UK [45] and (b) Dry Conversion (DC) process at Advanced Nuclear Fuels, GmbH, Lingen, Germany [43].

PUREX technology has attained a high level of industrial maturity and has been adapted in several countries during the last five decades. Presently, two large facilities, one in France [46], namely the La Hague plant (UP-2 and UP-3 of 1000 tonnes/a each, now coupled together into a single consolidated plant of nominal 1700 t HM/a licensed capacity), and the other in UK [47] namely the Sellafield plants (Magnox fuel: 1500 tons spent fuel/year and Thorp 900 tons spent fuel/year) are in operation. A reprocessing plant with a capacity of 800 tons per year has been set up in Rokkasho-mura, Japan [48]. The Rokkasho reprocessing plant is now in the final stage of its pre-operation test commencing commercial operation in October 2012. Japan has also an operating pilot plant in Tokai-mura with a capacity of 210 t/a. Reprocessing plants based on PUREX process were also in operation in Germany and the USA but these have been closed. Semi industrial scale PUREX plants are in operation in India and in the Russian Federation [49].

The alternative dry pyro electro chemical routes for reprocessing spent fuel have been developed in USA for metallic fuel and in the Russian Federation for spent UOX and MOX fuels. The end products are the co-deposited actinides in the form of metal and oxide granulates. The dry routes are suitable for integrated SFRs, where the fuel reprocessing and re-fabrication plants are co-located with the reactor.

#### **2.2.4. Modified PUREX route for MOX and MA bearing oxide powders**

PUREX technology is being modified in recent years with the objective of making it more proliferation resistant and recovering all actinides, including MAs. The Pu is recycled as MOX for efficient utilization of U resources and MAs would be recycled mainly to reduce the volume, radio-toxicity and decay heat of the high level waste, containing fission products for disposal in repositories. Accordingly, R&D activities on ‘partitioning’ processes [50–52] are underway to co-extract uranium with Np first and then uranium with Pu, in the form of mixed nitrate solutions and to obtain MOX powder by:

- (i) Direct de-nitration by microwave heating (MH) followed by calcination and reduction as developed in Japan [53–54];
- (ii) Co-precipitation as mixed oxalate followed by controlled calcination and reduction as demonstrated in France [55];
- (iii) Co-precipitation as uranium plutonium carbonate (AUPuC) followed by controlled calcination in moist air and hydrogen atmosphere as demonstrated in the past in Germany [56].

These processes, based on co-extraction and co-precipitation, enhance the proliferation resistance of fissile material by avoiding separate plutonium streams in spent fuel reprocessing plants. The alternative option being studied is group separation of all actinides in the spent fuel nitrate solution, including Pu, U and MAs, leaving the fission products in the raffinate, followed by co-precipitation as mixed actinide oxalate and controlled calcination and reduction to MOX powder containing all MAs. This route is also very attractive from the point of view of proliferation resistance as it avoids separate streams of plutonium and MAs.

The other option is to have separate nitrate streams of plutonium and individual MAs [57–58]. The individual actinide oxide powders could be obtained by the oxalate route as shown in Fig. 9. This option is suitable for inert matrix fuel (IMF) containing Pu or MAs or both for burning plutonium and MAs in SFRs or in accelerator driven system (ADS). The preferred inert matrixes are  $\text{ZrO}_2$ ,  $\text{MgO}$ , Spinel,  $\text{Al}_2\text{O}_3$ , SiC etc. IMF has the advantage that it burns Pu and MAs and avoids plutonium breeding. However, in such cases, the separate streams of fissile materials needed in reprocessing the plant make it less attractive from the point of view of proliferation resistance.

#### **2.2.5. Preparation of $\text{UO}_2$ , MOX and MA bearing oxide microspheres by sol gel processes**

Sol gel process is a wet chemical route for preparation of hydrated gel-microspheres of uranium oxide, plutonium oxide and MOX which after controlled calcination produce dust-free and free-flowing microspheres in the diameter range of 10–1000  $\mu\text{m}$ .

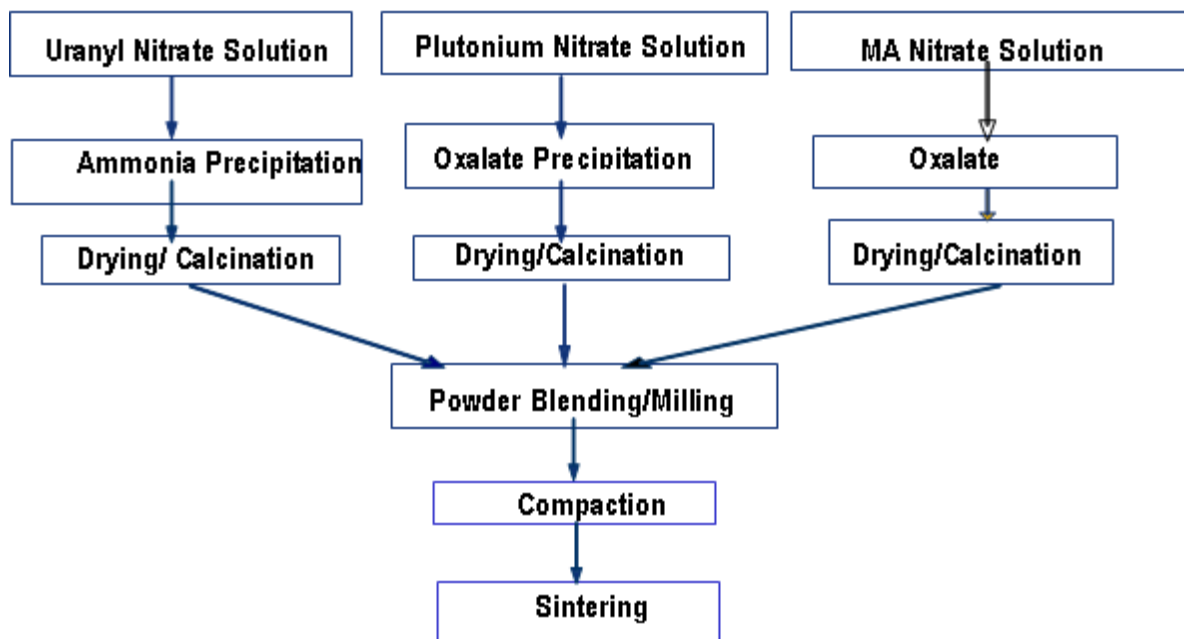


FIG. 9. Co-extraction and oxalate co-precipitation of MOX from nitrate solutions with and without minor actinides.

The hydrated gel-microspheres are prepared by ‘ammonia gelation process’, using nitrate solutions of uranium, plutonium, their mixture and MAs as feed material. The ammonia gelation is achieved ‘externally’ via  $\text{NH}_3$  gas and  $\text{NH}_4\text{OH}$  or ‘internally’ via an added ammonia generator, namely hexa methylene tetra amine (HMTA). The ammonia gelation processes have been described in details elsewhere and in several IAEA publications. The essential steps in sol gel processes are:

- Preparation of sol or broth from heavy metal (U, Pu) nitrate solutions;
- Droplet formation by vibrating nozzle;
- Droplet gelation in  $\text{NH}_3$  and  $\text{NH}_4\text{OH}$  bath (for external gelation) or silicone oil bath at  $\sim 90^\circ\text{C}$  (for internal gelation);
- Washing of gel-microspheres;
- Drying of gel-microspheres;
- Controlled calcination.

The end product of sol gel process is dust free and free flowing spherical oxide or mixed oxide fuel of high specific surface area, high sinterability and excellent micro-homogeneity.

The external gelation of uranium (EGU) and internal gelation of uranium (IGU) processes have been utilized in several pilot plant or R&D facilities for preparation of spherical fuel particles of  $\text{UO}_2$  and MOX [59–64] in particular to fabricate HTGR coated particle fuels.

In the EGU process, uranium and mixed uranium plutonium broths are first prepared by mixing heavy metal nitrate solution (1 mole/liter) with urea (4 moles/liter) and  $\text{NH}_4\text{NO}_3$  (2.5 moles/liter) and boiling the mixture for 30 minutes. A small amount of polyvinyl alcohol (5 g/L) is also added to the mixed solution for mechanical stability of the gel.



The broth/sol is dispersed into droplets which pass through a curtain of  $\text{NH}_3$  gas and fall into 10 wt% aqueous ammonia gelation bath. In the gelation bath, the droplet gel within seconds to rigid gel-particles which are then washed in 1% ammonia solution for removal of  $\text{NH}_4\text{NO}_3$  and dried on a continuous belt drier at 200–250°C.

In the IGU process, the uranium nitrate or mixed uranium plutonium nitrate solution, HMTA (ammonia generator) and urea are mixed in mole proportions of 1.25, 1.50 and 1.75 respectively and cooled to 0°C. Urea prevents premature gelation of solution. Droplets of the sol or broth fall into silicone oil gelation bath at  $90 \pm 1^\circ\text{C}$  which decomposes HMTA to release ammonia for conversion of the droplets into hydrous gel particles. The gel particles are washed with carbon tetrachloride to remove oil and 3M  $\text{NH}_4\text{OH}$  solution to remove ammonium nitrate. The hot silicone oil bath could be replaced by microwave heating, for decomposition of HMTA as shown in Fig. 10 [65]. Thus, the additional step of washing and silicone oil waste stream are avoided.

In recent years, the sol-gel process [66–67] has been used on a laboratory scale for preparation of MA bearing oxide and mixed oxide particles according to the process flow sheet shown in Fig. 11 at TUI, Karlsruhe, Germany and PSI, Switzerland.

For preparation of hydrated gel microspheres of the oxide or mixed oxides, suitable for manufacturing oxide or mixed oxide pellets of high density, the following modifications of the gelation process were found to be successful:

- Using a heavy metal nitrate feed solution of lower concentration (molarity <1);
- Addition of carbon black pore former to sol or broth prior to gelation and later removing the same from gel-microspheres by controlled air calcinations at 700°C to form ‘porous’ microspheres;
- Addition of dopants to the heavy metal nitrate feed solutions which enhance densification and/or grain growth during sintering of pellets;
- Controlled calcination for removal of carbon black pore former followed by hydrogen reduction (for  $\text{UO}_2$  bearing oxide and mixed oxides).

The soft and porous microspheres thus produced have excellent flowability, low crushing strength, high specific surface area ( $10 \pm 5 \text{ m}^2/\text{g}$ ), excellent compactibility and sinterability.

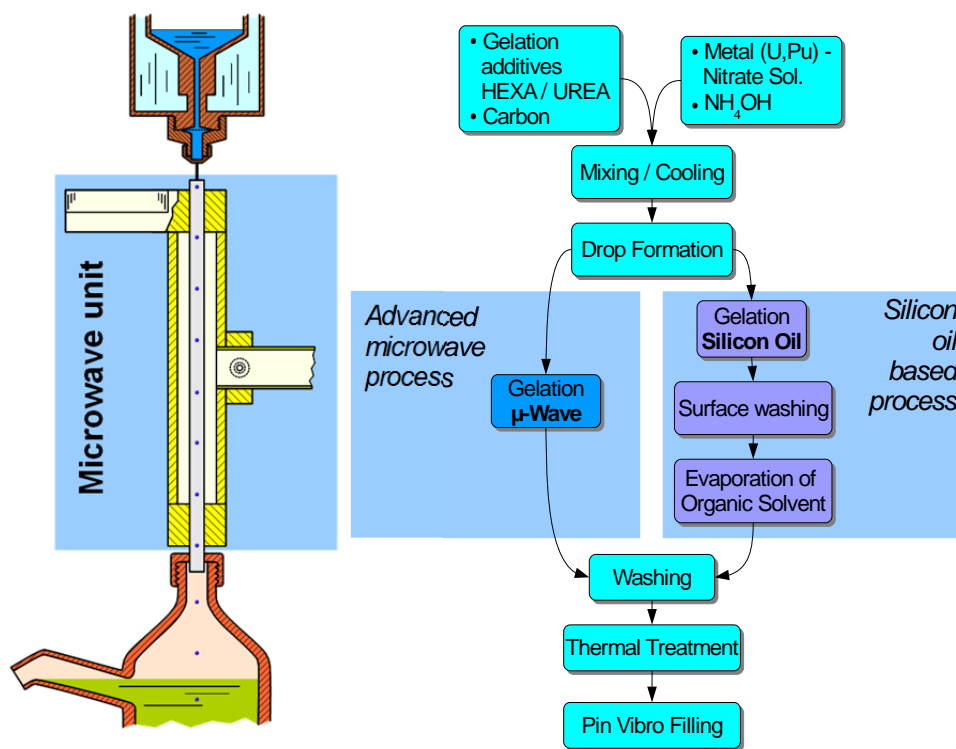


FIG. 10. Internal gelation processes utilizing microwave heating [65].

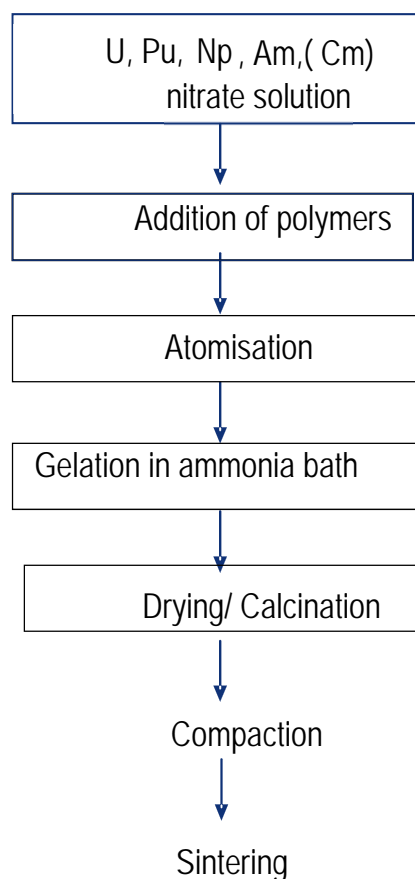


FIG. 11. External gelation process followed for preparation of MA bearing oxide pellets.

## 2.2.6. Pyro-processing for preparation of $\text{PuO}_2$ , MOX, MA bearing oxide granulates from spent fuel

The Research Institute of Atomic Reactors (RIAR) at Dimitrovgrad in the Russian Federation had initiated in the early 1990s a programme named DOVITA (dry reprocessing, oxide fuel, vibro-pack, integral, transmutation of actinides) for demonstrating new fuel cycle technologies for the transmutation of MA [68–71]. A pilot plant has been set up based on dry pyro-electrolytic technique, for reprocessing of spent  $\text{UO}_2$  or MOX fuel, using combined chlorinator and electrolyser equipment. The pilot plant has been operating for more than three decades in RIAR for preparation of  $\text{PuO}_2$  and MOX granules which have been vibro-packed in stainless steel cladding tube for irradiation — testing in BOR 60 and BN 600 SFRs. The Dimitrovgrad dry process (DDP) has been extended to preparation of MA bearing experimental mixed oxide pins like  $(\text{U}, \text{Np})\text{O}_2$ ,  $(\text{U}, \text{Np})\text{O}_2\text{--PuO}_2$  and  $(\text{U}, \text{Pu}, \text{Am})\text{O}_2$  containing varying amounts of  $\text{NpO}_2$  and  $\text{AmO}_2$ .

The DDP flow sheet, shown schematically in Fig. 12, consists of the following main steps:

- Dissolution of spent nuclear fuel in molten salts of mixed chlorides;
- Deposition of  $\text{PuO}_2$  and  $(\text{U}, \text{Pu})\text{O}_2$  on the cathode;
- Processing of the cathode deposit and production of oxide and mixed oxide granulates

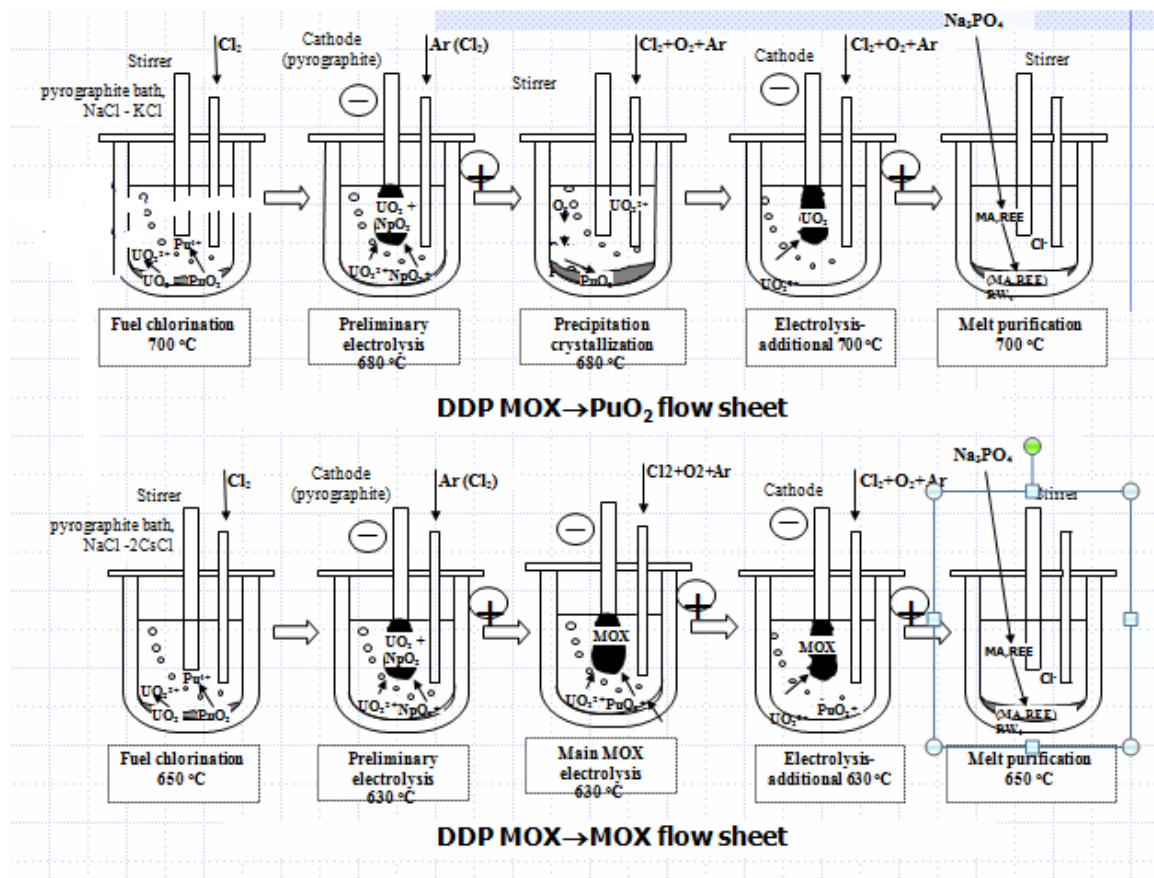
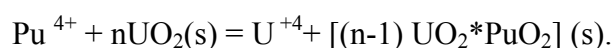
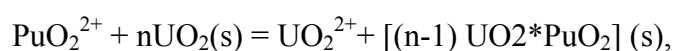


FIG. 12. Dry pyro electrolytic process for reprocessing spent Oxide fuel for preparation of oxide fuel granulates suitable for vibro-packing (DOVITA)[73].



The pyro electro chemical technology being used is based on the production of pure and mixed actinide oxides from molten alkali chloride bath [72–75]. In molten chlorides, uranium, plutonium and neptunium form complex oxygen containing ions of  $\text{MeO}^{2n}$  which are recovered as dioxides during electrolysis. Increasing oxygen content in molten salt causes decomposition of Np and Pu chlorides into insoluble dioxides that undergo an exchange reaction with  $\text{UO}_2$  and form solid solutions. Since uranium dioxide is a conductor at temperatures above  $400^\circ\text{C}$ , during electrolysis of the melt containing  $\text{UO}_2$  ions, crystals form and grow. Since the electric conductivity of  $\text{UO}_2$  is less than that of molten salt, electrolysis results in stable plane crystallization and formation of compact deposits on cathode. The process of mixed uranium plutonium oxide production is based on cathode collection of  $\text{UO}_2^{2+}$ ,  $\text{PuO}_2$  and  $\text{PuO}_2^{2+}$  in a molten  $\text{NaCl-2Cs}$  bath. During electrolysis, the  $\text{UO}_2$  deposition rate is controlled by current density. The  $\text{PuO}_2$  deposition rate is limited by diffusion of  $\text{PuO}_2$  and  $\text{PuO}_2^{2+}$  to the cathode surface. The content of plutonyl ions in the melt is regulated by varying the oxygen potential of the melt using a  $\text{Cl}_2\text{-O}_2$  gas mixture. Along with the direct electrochemical reduction of plutonyl ions,  $\text{PuO}_2$  can be deposited on  $\text{UO}_2$  substrate according to the exchange reactions:



Np is close to Pu in its physical and chemical behavior in molten chlorides. Based on the deposition potentials of  $\text{NpO}_2$  in  $\text{NaCl-KCl}$  and  $\text{NaCl-2CsCl}$  molten bath, granules of  $(\text{U}, 5\%\text{Np})\text{O}_2$ ,  $(\text{U}, 3\%\text{Np})\text{O}_2 + 20\% \text{PuO}_2$  and  $(\text{U}, 6\%\text{Np})\text{O}_2 + 20\% \text{PuO}_2$  have been prepared. Likewise, Am has been co-deposited in  $\text{UO}_2$  and  $(\text{U}, \text{Pu})\text{O}_2$  matrix and granules of compositions  $(\text{U}, \text{Pu}, \text{Am})\text{O}_2$  containing 49% Pu and 2% Am, 8% Pu and 5% Am and 2% Pu and 3.5% Am have been prepared on a laboratory scale.

Figures 13 and 14 show the photographs of mixed uranium plutonium oxide (MOX) fuel fabrication facility, co-deposited MOX granulates prepared on a semi industrial scale at RIAR adapting the DDP and the characteristic & microstructure of the MOX granulates.

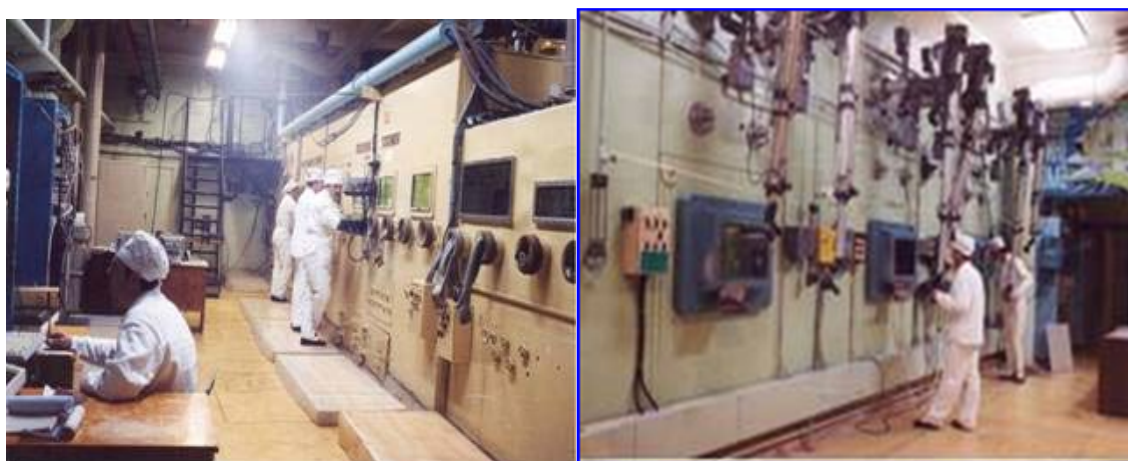
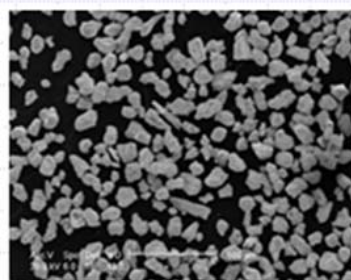
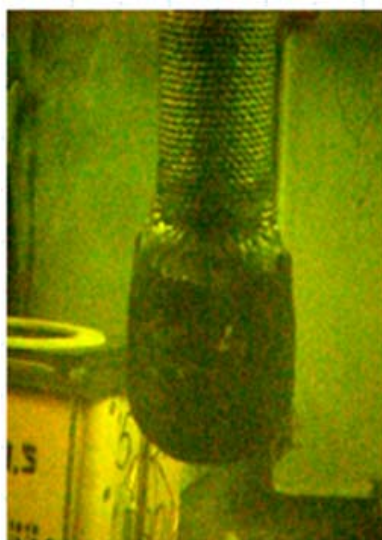


FIG. 13. Uranium-plutonium mixed oxide fuel manufacturing facilities at RIAR [71].



Metal content, %wt	87,75
Pyknometric density of granules, g/cm <sup>3</sup>	10,7
Bulk density of polydispersed granulate, g/cm <sup>3</sup>	6,0
O/M ratio (oxygen ratio)	2,00 <sup>+0,01</sup>
Mass fraction of process impurities, %:	
chlorine – ion	0,006
carbon	0,006

FIG. 14. Co-deposition of MOX on cathode and characteristics of the MOX granulates [71].

Regarding preparation of MA based oxide granulates by pyro-electrochemical reprocessing, the general conclusions are:

The whole of Np can be co- deposited in the cathode either as (U, Np)O<sub>2</sub> or as (U, Pu, Np)O<sub>2</sub> granulates;

- Am can be partially co-deposited in to an oxide matrix because of its weak propensity to formation of oxy-chloride ions in melt;
- Cm does not take part in the pyro electro chemical reprocessing of oxide fuel and it will collect in chloride melt together with rare earth element (REE) and residual Am;
- After extraction from melt the concentrate of Am and Cm can be used as the additive to pins with MOX-fuel or as a target for irradiation in SFRs.

### 2.3. INDUSTRIAL METHODS FOR FABRICATION OF UO<sub>2</sub> AND (U,Pu)O<sub>2</sub> FUEL PELLETS

The conventional ‘powder-pellet’ route, involving cold pelletization of powder and high temperature ( $\geq 1650^{\circ}\text{C}$ ) sintering, is currently followed all over the world for preparation of high density UO<sub>2</sub> and MOX fuel pellets [76–77]. For MOX fuel, co-milling of UO<sub>2</sub> and PuO<sub>2</sub> powders is needed prior to pelletization. Alternatively, the MOX powder is co-precipitated from nitrate solutions of uranium and plutonium by adapting AUPuC process, oxalate co-precipitation and direct de-nitration by microwave heating (MH).

Only few industrial MOX fabrication plants are devoted, presently to LWR or SFR fuels since the MOX fuel for water cooled thermal reactors differ a lot from the MOX fuel for SFRs. First, the Pu content of SFR fuel is significantly higher than that of LWR fuel. Secondly, since the burnup and operating temperature of SFR fuel are higher than that of LWRs, the smear density of SFR fuel has to be lower. The higher plasticity of SFR fuel, resulting from the higher irradiation temperature, justifies less restrictive specification tolerances and quality requirements than for LWR fuel. The uniformity of Pu isotopic composition within a batch of fuel assemblies is a key performance related quality for LWR fuel ( $^{239}\text{Pu}$  and  $^{241}\text{Pu}$  being fissile, both with quite different reactivity values, and  $^{240}\text{Pu}$  and  $^{241}\text{Am}$  being neutron absorbers), while it is rather unimportant for SFR fuel (all the Pu and Am isotopes being fissile to some degree). The oxidation potential of MOX fuel for SFR is higher than that of LWR fuel because of the higher plutonium content in the former. The sintered MOX fuel pellets for SFRs and LWRs should have a microstructure with homogenous distribution of Pu. There should not be any free  $\text{PuO}_2$  or mixed oxide with higher Pu content ( $>40\%$ ) phase because this could lead to problem of dissolution of spent MOX fuel in nitric acid during reprocessing. The  $\text{UO}_2$  and  $\text{PuO}_2$  should form a solid solution without any local Pu/HM content more than 40% in order to ensure easy dissolution of spent MOX fuel in nitric acid during the reprocessing step. The  $\text{UO}_2$  and  $\text{PuO}_2$  solid solution formation is confirmed by analysis of X ray diffraction line profile [78] and by dissolution test in nitric acid. Other important specifications of sintered MOX pellets are density and oxygen to metal ratio. The MOX pellets for SFR should be hypo-stoichiometric.

The operating MOX fuel manufacturing plants worldwide are listed in Table 4. Presently, there are only two industrial scale plants in the world. The first one is the MELOX plant at Marcoule, France with an annual capacity of 195 tons heavy metal and the second one is the Sellafield MOX plant (SMP) at UK. The Sellafield MOX plant in UK was down rated from 120 t/y to 40 t/y. In 2006, 40 t/y MOX plant in Belgium was closed. Two pilot scale MOX plants in Japan, namely the plutonium fuel fabrication facility (PFFF) and the plutonium fuel production facility (PFPF) were utilized for manufacturing MOX fuel for FUGEN, JOYO and MONJU reactors [79–80]. Construction activities in Japan are underway to start the J-MOX (with a capacity of 130 t/y) at Rokkasho-mura. Semi-industrial scale MOX fuel fabrication plants are in operation at Mayak, Russian Federation and at Tarapur, India.

The MELOX plant is being extensively used for MOX fuel fabrication for the reload fuel of more than 30 LWRs in Belgium, France, Germany and Switzerland. micronized master blend (MIMAS) process is followed at MELOX and the short binder-less route (SBR) is being utilized in SMP.

The J-MOX plant in Japan would manufacture MOX fuel for both BWR and PWR in Japan, adapting the well proven MIMAS process of MELOX plant, using  $\text{PuO}_2$  and  $\text{UO}_2$  powder as feed materials. The J-MOX would use MOX powder containing about 50%  $\text{PuO}_2$  as feed material instead of  $\text{PuO}_2$  powder used in MELOX plant. The MOX powder would be obtained by microwave heating (MH) de-nitration of mixed uranium plutonium nitrate solution at the Rokkasho reprocessing plant. The highest level of safety and security measures has been planned in J-MOX in terms of confinement of radioactive aerosol, radiation shielding, criticality accident, precaution against earthquakes, explosions and aircraft crash.

The MOX fuel pellet fabrication flow sheet followed at advanced fuel fabrication facility (AFFF) plant at Tarapur, India is shown in Figure 15. The process is similar to SBR. The facility uses an attritor for co-milling of  $\text{PuO}_2$  and  $\text{UO}_2$  powders and scrap, a rotary compaction press for pelletization, a batch furnace for sintering MOX pellets at  $1650^\circ\text{C}$  in

Ar + H<sub>2</sub> atmosphere and a dry centerless grinder for producing MOX pellets of as desired diameter. The MOX fuel pellets and assemblies from AFFF were successfully irradiated in the BWRs at Tarapur and in the PHWRs at Kakrapara. Later, a few plutonium rich MOX fuel assemblies were manufactured in this facility for the present core of the fast breeder test reactor. The facility is now being utilized for manufacturing MOX containing 20–25 % PuO<sub>2</sub> for the initial core of PFBR 500 which is under construction. Figure 16 shows the rotary compaction press and loading of MOX pellets in Molybdenum boat at AFFF.

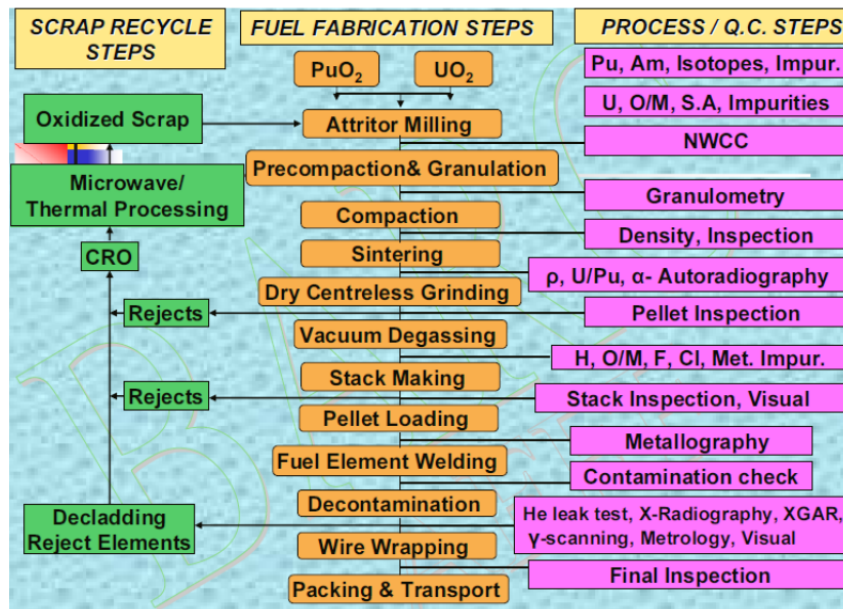


FIG. 15. Process flow sheet followed in AFFF, India for fabrication of MOX fuel [81].



(a) Rotary compaction press



(b) MOX pellets loaded in Mo boat

FIG. 16. Rotary compaction press and loading of MOX pellet at AFFF in India [81].



### 2.3.1. MIMAS process for production of MOX fuel pellets in France and Belgium

In the early 1970s, CEA, France developed the COCA process for manufacturing MOX fuel at their Cadarache plant. The acronym COCA stands for Cobroyage (co-milling) Cadarache [82]. In this process  $\text{UO}_2$  and  $\text{PuO}_2$  powders are simultaneously ball-milled and blended using a lubricant. The blended powder mixture consisting of micronized powder is forced through a sieve, resulting in free-flowing granules suitable as feed material for cold-compaction to obtain fuel pellets. The COCA process was extensively utilized for manufacturing MOX fuel pellets for the Phenix and Super Phenix SFRs in France. Later during 1989–1994, the COCA process was utilized for manufacturing MOX fuel pellets for LWRs.

During the same period, the ALKEM plant in Germany developed the optimized co-milling (OCOM) process [83]. In OCOM process, a primary blend is prepared by dry ball milling  $\text{UO}_2$ ,  $\text{PuO}_2$ , and dry recycle MOX powders. The plutonium content of this primary blend is maintained at the upper end of the range in which uranium and plutonium form a solid solution. This primary blend is then diluted with an eight to ten fold larger quantity of free-flowing ex-AUC  $\text{UO}_2$  powder. The primary blend is tumbled prior to its dilution to produce free-flowing granulate via self-agglomeration. The agglomerates are allowed to grow to a size that roughly corresponds to that of the diluent ex-AUC  $\text{UO}_2$  to enhance the dry blending. By restricting the primary blend to <15% of the secondary blend, the ceramic properties of the ex-AUC  $\text{UO}_2$  are retained. This allows direct pressing, with direct die lubrication, without prior granulation. The primary blend agglomerates form a solid solution during sintering so that the fuel mass itself has acceptable solubility in nitric acid. The OCOM process was initially used for manufacturing MOX fuel for SFR but was later used for LWR fuel fabrication.

The micronized master blend (MIMAS) process was developed by Belgo Nucléaire [84]. The MIMAS process is similar to OCOM in many respects and has been adapted in MELOX plant at France as advanced MIMAS (A-MIMAS) process. The MELOX plant with a capacity of 195 t HM per year is the largest MOX plant in the world.

Figure 17 shows the process flow sheet of the MIMAS process. In the MIMAS process, a mixture of  $\text{UO}_2$ ,  $\text{PuO}_2$  and scrap MOX powder is first subjected to micronization by co-milling in a ball mill to form a fine master mix of oxide powder containing ~ 30%  $\text{PuO}_2$ , which is not free-flowing. The master mix is then diluted to the desired plutonium concentration in a secondary blender, consisting of a conical screw mixer with a double envelope air cooling system by blending free-flowing  $\text{UO}_2$  powder prepared by AUC process. Scraps can be recycled at both stages in the process line after a specific treatment. The powders are fed into a large size blender (up to 640 kg), where the secondary batch is blended with lubricant and a suitable quantity of pore forming agent.

The micronization during ball milling causes intimate contact between  $\text{UO}_2$  and  $\text{PuO}_2$  particles and facilitates complete solid solution formation, during the short period (4–8 hours) of high temperature sintering at 1700°C in hydrogen, by diffusion of cations, leaving no un-dissolved  $\text{PuO}_2$  particles in sintered pellets. Thus, the problem of dissolution of spent MOX fuel in nitric acid is resolved. In addition, the larger contact area between the more abundant fine powder and the free flowing  $\text{UO}_2$  powder results in a less heterogeneous MOX structure. The blended powder obtained is pressed to form cylindrical pellets which are then passed through a high temperature furnace. The grinding operation is then performed to obtain MOX pellets of required diameter. The pellets are finally controlled and inserted into cladding tubes and encapsulated by welding of the end caps.

The A-MIMAS process [85] has incorporated a few minor modifications to the MIMAS process. First, instead of AUC powder,  $\text{UO}_2$  powder with high flowability, prepared by a modified ADU route, has been used. Secondly, forced sieving of the MOX blend is used to produce free-flowing and loosely held agglomerate that are soft and crush easily during the pelletizing step.  $\text{UO}_2$  powder produced by modified DC process has improved flowability and is also being used as feed material for industrial production of MOX fuel pellets by the A-MIMAS route.

The MELOX plant can receive any type of raw product and the ball mill has the possibility to use up to 50% pellet scraps as ingredient. The plant enables to meet several constraints, in particular those related to the inputs qualities. The use of aged plutonium coming from high burnup fuels, as well as high plutonium content is allowed. MELOX plant has been producing fuel assemblies for LWRs. Complete automation has been implemented in fuel assembly manufacture, quality control and materials handling. The plant enables use of aged plutonium coming from high burnup fuels, as well as high plutonium content.

### **2.3.2. The short binderless route (SBR) for fabrication of MOX fuel in the UK**

The short binderless route (SBR) [86] is an integrated process developed by British Nuclear Fuel Limited (BNFL) for manufacturing MOX fuel, mainly for LWRs, at the MOX fuel Demonstration Facility (MDF) and later at Sellafield MOX Plant (SMP). The annual capacity of MDF and SMP are 8 t HM and 40 t HM, respectively. The SBR derives its name from short processing time and lesser process steps. The SBR is based on co-milling of  $\text{UO}_2$ ,  $\text{PuO}_2$  and scrap powder in an attritor followed by granulation in a spheroidizer as shown in Fig. 18.

In the SBR route no binder is added and the processing equipment are stacked, so that the powder can be discharged by gravity from the feed dispensing and dosing glove-box through the processing equipment into the hopper of the pellet compaction press. It may be noted that in all modern fabrication processes, including MIMAS and OCOM, there is no addition of binder. As a result, separate de-waxing step and equipment is not needed. Prior to sintering, there is a preheating zone where the admixed lubricants and other additives (pore formers) are removed.

### **2.3.3. Industrial MOX technology under development for SFR fuel in Japan**

As part of development of MOX fuel technology for SFRs in Japan, efforts are underway to have an integrated facility, combining advanced aqueous reprocessing and simplified pelletizing routes, for manufacturing MOX fuel economically and safely incorporating features of easy maintenance and proliferation resistance (PR) [87]. Figure 19 shows the schematic diagram of the new extraction system for TRU recovery (NEXT) [88–89] under development.

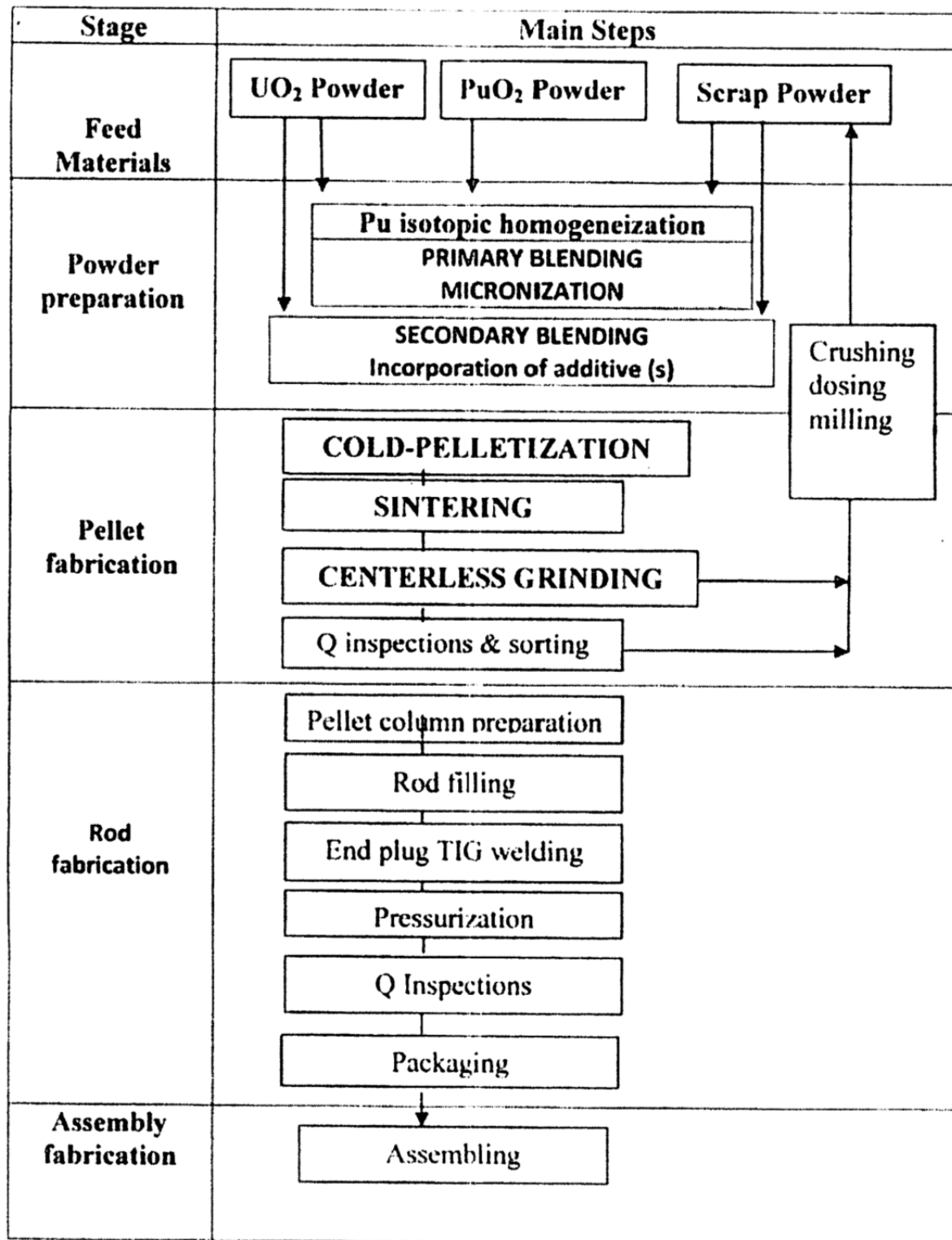


FIG. 17. MIMAS process for manufacturing mixed oxide fuel [85].

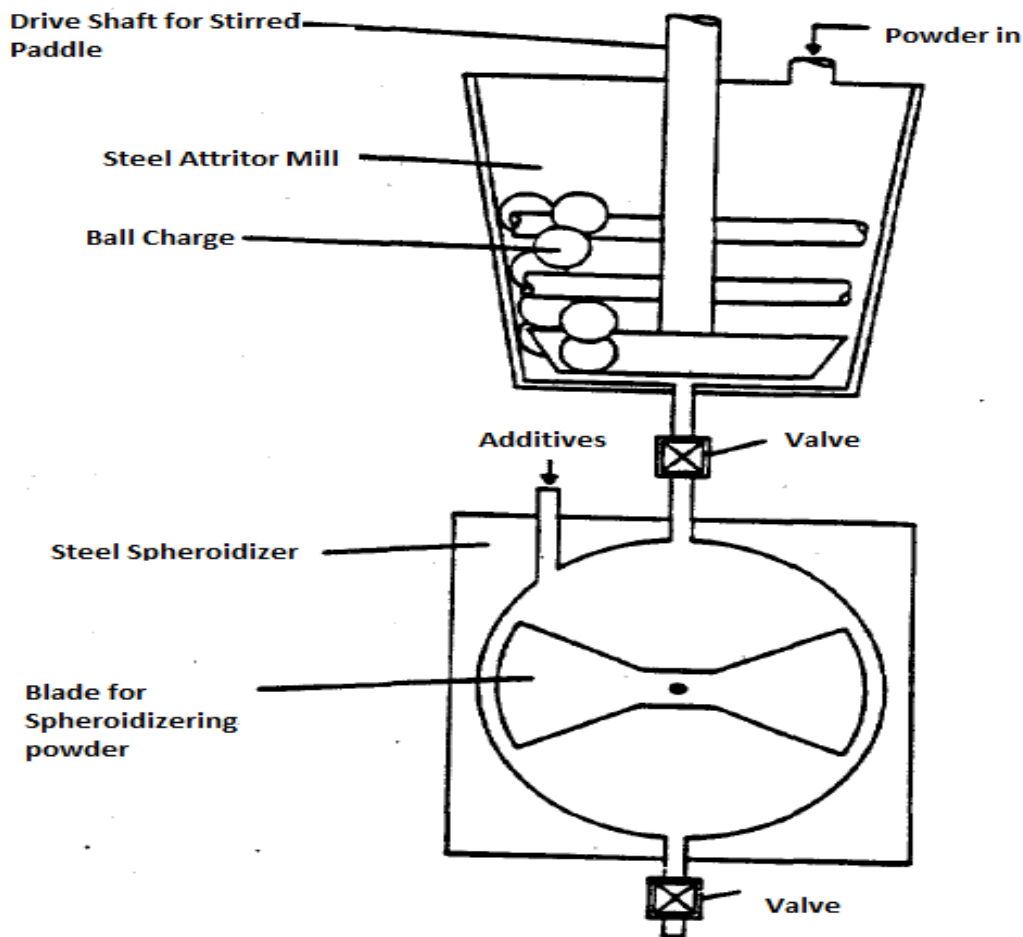


FIG. 18. Original SBR process as implemented in MDF [86].

The reprocessing plant will deliver:

- Uranyl nitrate hexahydrate (UNH) crystal;
- Co-extracted mixed nitrate solution of uranium, plutonium and neptunium containing the desired ratio of uranium and plutonium; and
- Am/Cm recovered from the raffinates of solvent extraction as feed materials for manufacturing MOX fuel, MA target and DU blanket for SFRs.

After U crystallization, Pu is recovered together with U and neptunium (Np) by a co-recovery (co-extraction and co-stripping) using centrifugal contactors, thus avoiding separate plutonium stream and enhancing proliferation resistance.

The capacity of the planned MOX fuel manufacturing plant is 200 t HM/year. The fabrication process for MOX fuel pellet is simple, dust-free and amenable to automation and remote operations inside alpha tight hot cells with heavy shielding against beta, gamma and neutron radiation. Adequate cooling system will take care of the high decay heat associated with  $^{238}\text{Pu}$ ,  $^{240}\text{Pu}$  and MA isotopes. The six R&D issues of simplified pelletizing process for MOX fuel fabrication are listed in Fig. 20.



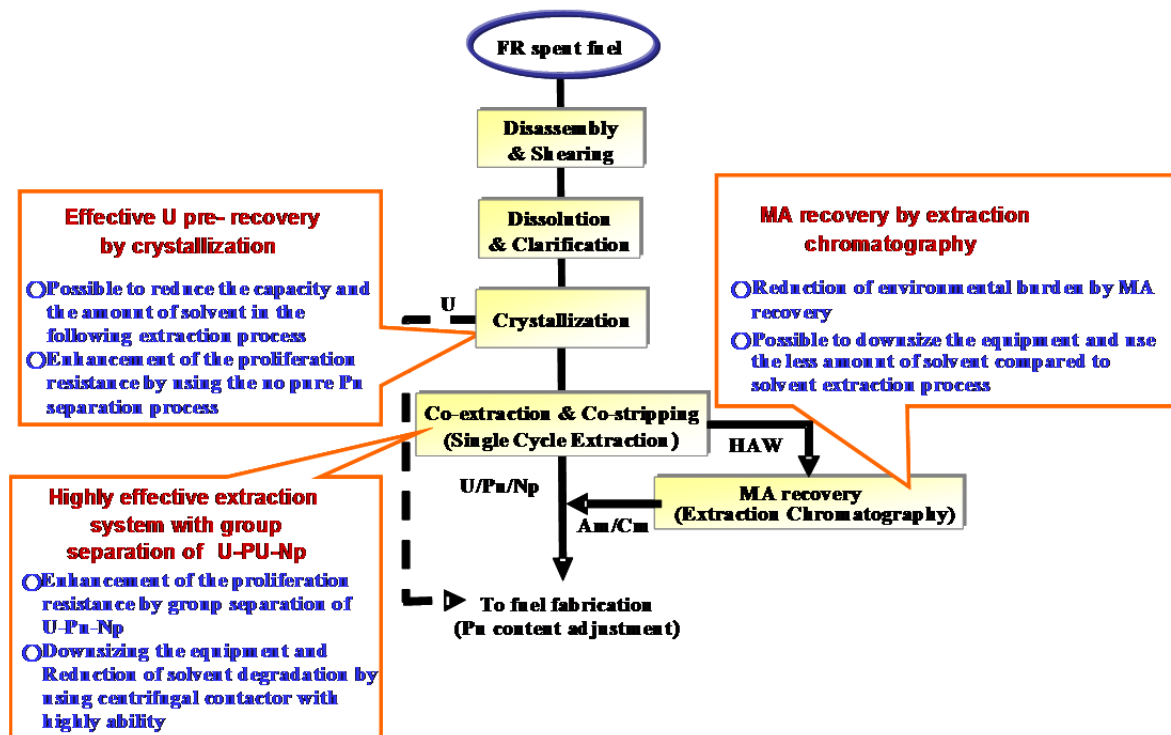


FIG. 19. Feature of the NEXT process technology [88–89].

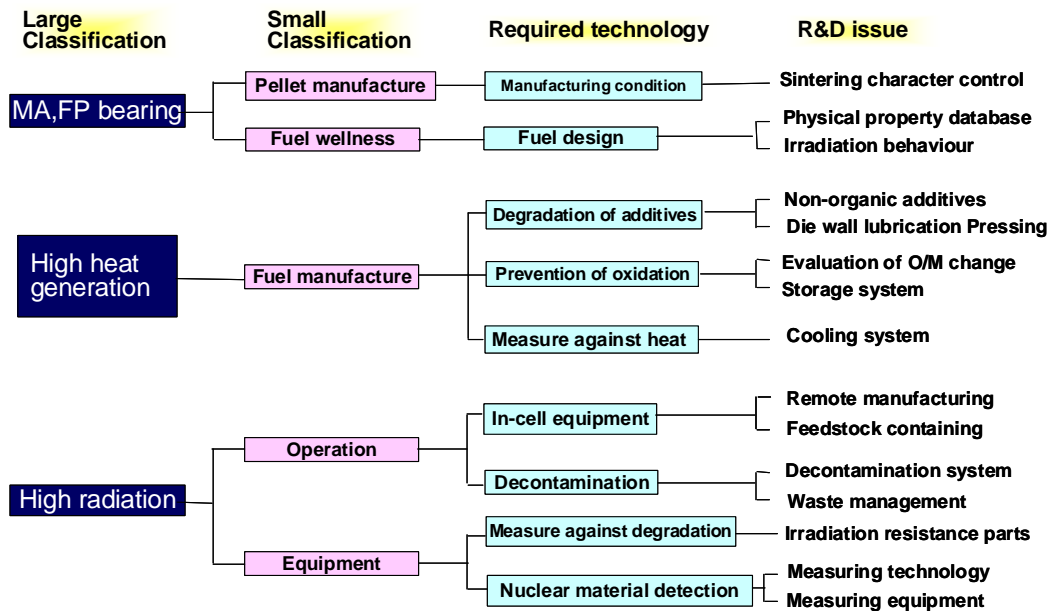


FIG. 20. Six research and development issues on the simplified pelletizing process.

The mixed nitrate solution containing U, Pu and Np is subjected to direct denitration by microwave heating (MH) for co-conversion and direct production of MOX powder. The technology of producing MOX containing up to 50% PuO<sub>2</sub> by MH is already established in Japan and more than 16 tons of MOX powder has been produced by this technique in the past for manufacturing MOX fuel pellets for FUGEN, JOYO and MONJU. The UNH will be converted to UOX powder by the ADU process after which the depleted UO<sub>2</sub> pellets would be manufactured by the powder route for use as axial and radial blanket materials.

The proposed flow sheet for the short process [90–91] using MH de-nitration followed by tumbling granulation is shown in Fig. 21. Preliminary trials using this process were carried out recently in batches of 300 g of microwave heated de-nitrated (MH)-MOX powder containing 20 or 30 wt% plutonium oxide were processed by a tumbling-granulator to obtain free-flowing coarse granules as shown in Fig. 22. The MH-MOX granules were compacted at 300 to 500 MPa into annular pellets using die-wall lubrication. De-bonding for removal of lubricant and sintering of green pellets were carried out in the same furnace. The pellets were sintered at 1700°C for 2 hours in Ar + 5% H<sub>2</sub> atmosphere. The sintered pellets, as shown in Fig. 23, had density in the range of 96–97% theoretical density with mean grain size of 14 μm.

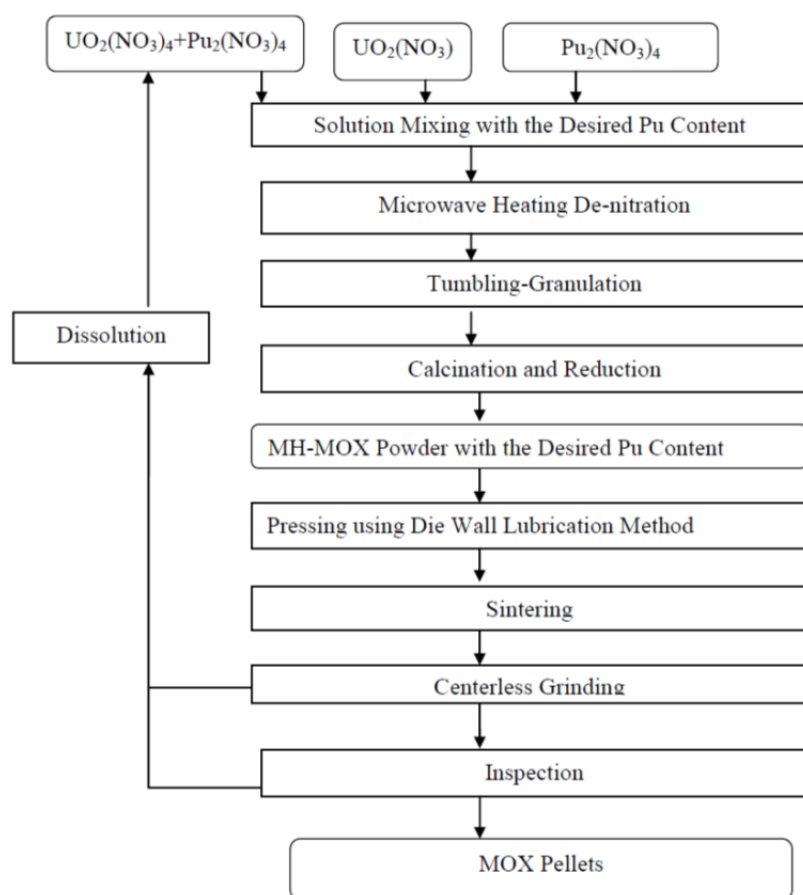


FIG. 21. The proposed flow sheet for mixed oxide fuel fabrication in Japan by the short process using powder from ex-MH de-nitration process as feed materials [90].

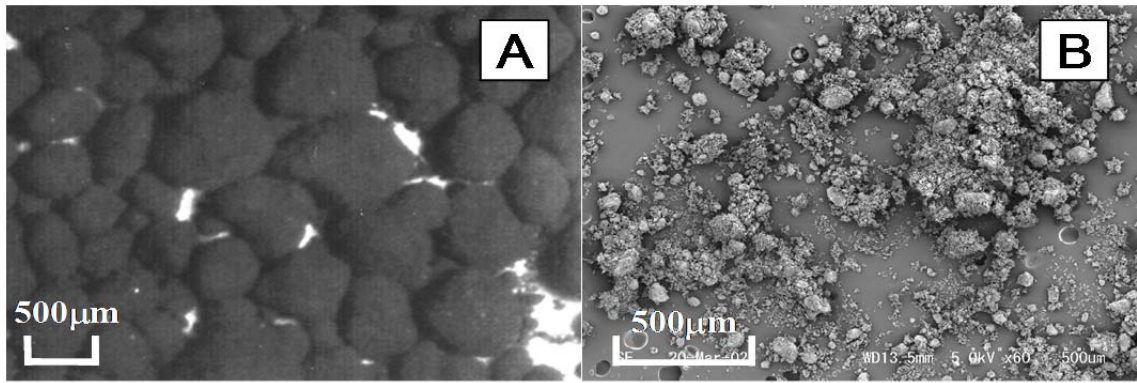


FIG. 22. Microstructure of coarse and easily crushable (during pelletization) MOX granules obtained by tumbling granulation [90].

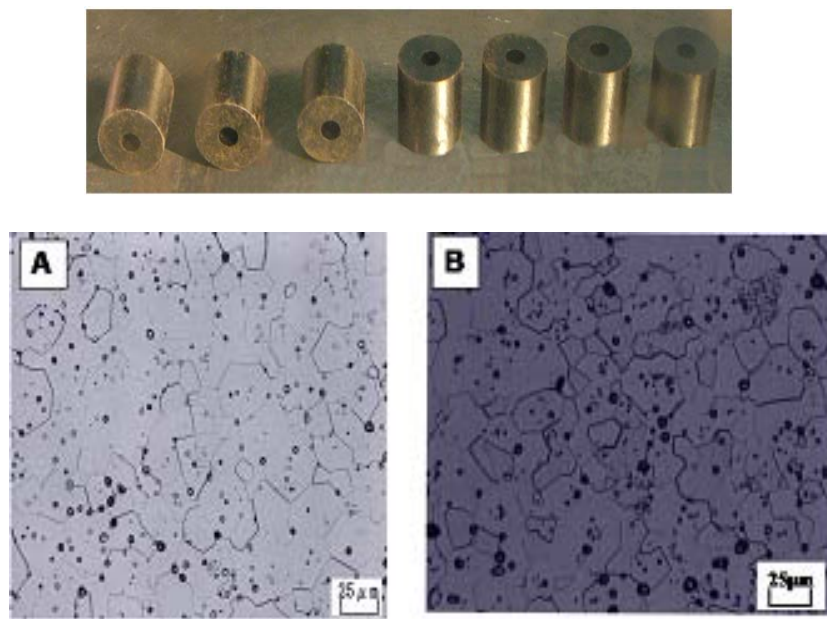


FIG. 23. Top: High density sintered annular MOX pellets. Bottom: Microstructure of sintered MOX pellets manufactured by: (A) short process; (B) conventional route followed in Japan [90].

#### 2.3.4. Fabrication of $\text{UO}_2\text{--Gd}_2\text{O}_3$ fuel as burnable absorber

The utilization of  $\text{UO}_2\text{--Gd}_2\text{O}_3$  pellets as a burnable absorber was initiated in the 1970s, initially in BWR and later in PWR. The natural isotopes of gadolinium namely,  $^{157}\text{Gd}$  and  $^{155}\text{Gd}$  have high neutron absorption cross-section of 254 000 and 61 000 barns respectively. These isotopes are converted as a result of neutron absorption to  $^{158}\text{Gd}$  and  $^{156}\text{Gd}$  isotopes respectively with low neutron absorption cross-section (1000 and 3.5 barn respectively). In high and ultrahigh burnup  $\text{UO}_2$  fuel for LWRs, the  $^{235}\text{U}$  enrichment level is increased to 5 % (5% is the upper limit in existing nuclear reactor licenses). To take care of the high reactivity at beginning of life, gadolinium is admixed homogenously as  $\text{Gd}_2\text{O}_3$  with  $\text{UO}_2$ . Thus, the depletion of  $^{235}\text{U}$  with burnup is made to match the burnup rate of gadolinium, and keep the net reactivity relatively constant in the fuel. The expected  $\text{Gd}_2\text{O}_3$  content in mixed uranium gadolinia fuel is in the range of 5–10 % in high and ultrahigh burnup UOX or MOX fuel [92–93]. Such high  $\text{Gd}_2\text{O}_3$  content will reduce the melting point of fuel and also its thermal conductivity.

The addition of  $\text{Gd}_2\text{O}_3$  to  $\text{UO}_2$  and MOX fuel imposes more requirements on the manufacturing process. Primarily, a homogeneous distribution of Gd in the oxide and mixed oxide fuel matrix is necessary for a good in-pile performance. Furthermore, the Gd addition decreases the thermal conductivity. Since the thermal conductivity in a mixed oxide strictly depends on degree of solid solution and number and size of Gd rich particles, the manufacturing must guarantee a safe and reliable control of the solid state structure. In addition, grain size and pore structure must also be adjusted in an appropriate manner in order to achieve a good in-pile behavior in terms of dimensional behavior, fission gas retention, etc.

For a good Gd homogeneity, in most cases a pre-mix or master-mix step is applied, i.e. an intensive mixing of the  $\text{Gd}_2\text{O}_3$  powder with part of the  $\text{UO}_2$  followed by a second blending step, the homogenization of the master mix in the bulk of  $\text{UO}_2$  powder. After that a usual granulation procedure is applied to prepare the press feed granulate. In one of the established processes, the homogenization step is done by very intense milling in a vibro-mill; this yields in an excellent Gd homogeneity and allows a direct pressing without pre-compaction/granulation, due to the good flowability of the vibro-milled powder agglomerates.

For manufacturing high density UOX pellets with high  $\text{Gd}_2\text{O}_3$  content, sintering aids like Al and Al + Si were found to be effective. The sintering aids are admixed as  $\text{Al}_2\text{O}_3 - \text{Al}(\text{OH})_3$  and mullite powders respectively, or by utilizing Al-Di-Stearate (ADS) as lubricant.

The following two adaptations in the conventional furnace are necessary to guarantee stable, well-defined mixed oxide phases and to avoid crack formation in Gd bearing oxide fuel pellets:

- Oxygen potential in the sintering furnace has to be higher and closely controlled as compared to that of  $\text{UO}_2$  sintering; and
- Cooling rate after sintering has to be lower than that of  $\text{UO}_2$  sintering.

Figure 24 shows the process steps in fabrication of  $\text{UO}_2\text{-Gd}_2\text{O}_3$  pellets, involving co-milling of  $\text{UO}_2$  and  $\text{Gd}_2\text{O}_3$  powders, followed by cold pelletization and high temperature sintering in reducing atmosphere.  $\text{UO}_2$  powder derived from DC, AUC and ADU processes have all led to  $\text{UO}_2\text{-Gd}_2\text{O}_3$  pellets of similar density and microstructure. More than 99% of  $\text{Gd}_2\text{O}_3$  was in solid solution with  $\text{UO}_2$  and the diameter of free  $\text{Gd}_2\text{O}_3$  particles were, 40  $\mu\text{m}$ .

A master blend approach and admixing of ~ 200 ppm  $\text{Al}(\text{OH})_3$  to have Al ‘sintering aid’ improved the homogeneity and sinterability of  $\text{UO}_2\text{-Gd}_2\text{O}_3$  powder mixture, enabling dry scrap recovery. A two-step sintering process consisting of oxidative sintering at ~1100°C followed by reductive sintering at ~ 1700°C also produced high quality  $\text{UO}_2\text{-Gd}_2\text{O}_3$  pellets [94].

## 2.4. R&D ON ADVANCED PROCESSES FOR FABRICATION OF $\text{UO}_2$ , MOX AND MA BEARING OXIDE FUELS

The focus on the R&D should be co-precipitation of MOX by microwave de-nitration, oxalate precipitation and co-immobilization on ion exchange resin. In addition, one has to address the challenges of ‘radiotoxic dust hazard’, particularly for fabrication of highly radiotoxic Pu, MA and  $^{233}\text{U}$  bearing fuel pellets. Table 5 summarizes the main objectives of advanced methods of manufacturing ceramic nuclear fuels

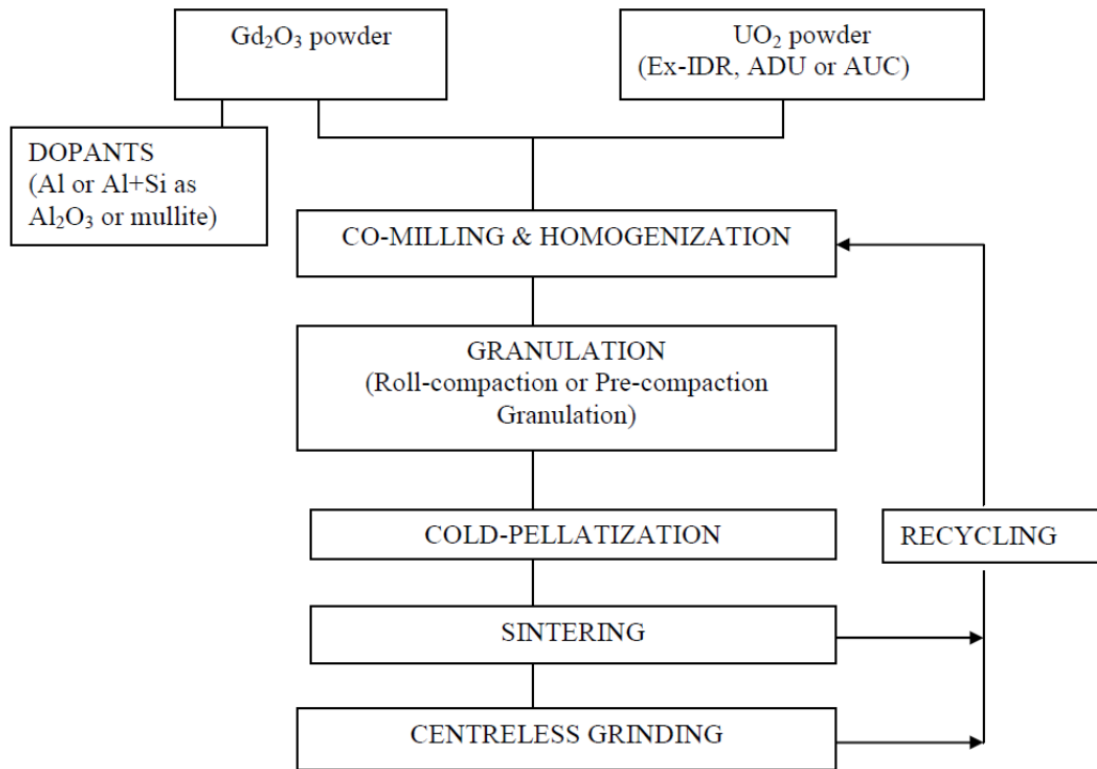


FIG. 24. Process flow sheet followed for fabrication of  $UO_2$ - $Gd_2O_3$  pellets.

TABLE 5. OBJECTIVES OF ADVANCED METHODS OF MANUFACTURING CERAMIC NUCLEAR FUELS

Safety and security	Economics	Performance
<ul style="list-style-type: none"> <li>- avoid fine powder for minimizing radiotoxic dust hazard</li> <li>- automation and remote fabrication for minimizing personnel exposure to radiation</li> <li>- ensure proliferation –resistance by avoiding separate streams of fissile materials like HEU, <math>^{239}Pu</math> and <math>^{233}U</math></li> </ul>	<ul style="list-style-type: none"> <li>- minimize process steps</li> <li>- reduce fuel synthesis &amp; sintering temperatures</li> <li>- reduce gas cost by recirculation &amp; purification and use of less expensive gas during sintering</li> <li>- reduce process losses and rejects</li> </ul>	<ul style="list-style-type: none"> <li>- tailor-made microstructure of fuel for high burnup</li> <li>- high density (<math>&gt; 94\%</math> TD) , large grain size, and uniformly distributed “closed” pores <math>\geq 1\ \mu m</math> in order to control in-pile densification ( for LWR &amp; PHWR fuel pellets)</li> <li>- micro-homogeneity of fissile and fertile materials in fuel</li> <li>- minimize surface flaws in fuel pellet like chips to avoid missing surface PCMI particularly for LWRs</li> </ul>

Advanced fabrication methods focus mainly on minimizing radioactive aerosol and reduction in operator dose by avoiding generation and handling of fine powder and by remote operations and automation. The other objectives are minimization of process steps and fabrication costs and improvement in microstructure of fuel for satisfactory operation without failure up to high burnup. In addition, it is essential to avoid separate streams of fissile materials like HEU,  $^{239}Pu$  and  $^{233}U$  in the reprocessing and fuel manufacturing plant to enhance proliferation resistance. The fabrication costs could be brought down significantly by:

- Modifying existing fabrication route such that rejects are minimized;
- Manufacturing high density  $\text{UO}_2$  and  $(\text{U}, \text{Pu})\text{O}_2$  pellets by low temperature oxidative sintering, using dopants for producing pellets with large grains and using relatively cheaper gas as sintering atmosphere for oxidative sintering.

#### 2.4.1. Low temperature oxidative sintering of UOX and MOX pellets

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

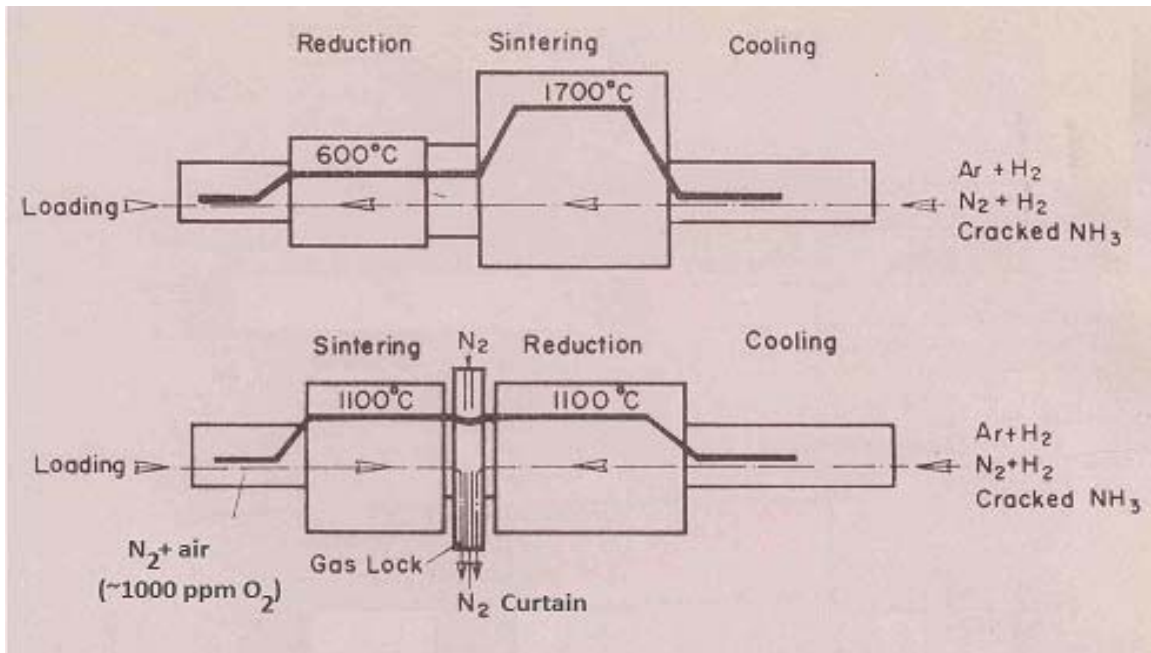


FIG. 25. Inter comparison of high temperature reductive sintering (top) and low temperature oxidative sintering (bottom) of  $\text{UO}_2$  and  $(\text{U}, \text{Pu})\text{O}_2$  [95].

The energy requirement and cost of sintering could be significantly reduced by “low temperature, short duration oxidative sintering” (LTS) technique developed in Germany, where the process is popularly known as NIKUSI [95]. In LTS or NIKUSI the high cation diffusion coefficient of uranium ( $D^{\text{U}}$ ) in hyper-stoichiometric  $\text{UO}_{2+x}$  [ $D^{\text{U}} \propto x^2$ ] is utilized for enhancing the sintering kinetics [96]. For this, ‘x’ in starting  $\text{UO}_{2+x}$  and oxygen partial pressures ‘ $p\text{O}_2$ ’ of sintering furnace in the densification region are closely controlled. Figure 25 shows the intercomparison of continuous furnaces for high temperature reductive sintering (HTS) and low temperature oxidative sintering. The NIKUSI continuous sintering furnace is essentially a three-zone furnace. The first zone is in controlled oxidative atmosphere of air plus nitrogen containing around 1000 ppm oxygen, where the sintering or densification of pellets takes place at a relatively low temperature of  $1100^\circ\text{C}$ . The second zone is an inert zone of nitrogen and the third is a reductive zone of nitrogen plus hydrogen, where the hyper-stoichiometric oxide is reduced to the desired oxygen to metal ratio. The pellets are also cooled in the reductive zone. As a result of reduction in sintering temperature (from  $1700^\circ\text{C}$  to  $1100^\circ\text{C}$ ) and shorter sintering cycle ( $< 9$  hours), the energy saving in LTS is up to 25%.



Further, cheaper heating elements (kanthal) could be used in place of tungsten or molybdenum. The  $H_2$  consumption is also lowered leading to 10% saving in gas cost. The NIKUSI process was also used to produce  $UO_2$  pellets of large grain size without using a dopant. The NIKUSI process has been demonstrated on a pilot plant scale in Germany for preparation of some 50 tons  $UO_2$  pellets, which were successfully irradiated in a commercial LWR in the 1990s, amongst them complete reloads with NIKUSI fuel in KWO reactor [97].

By combination of AUC/AUPuC process and LTS (NIKUSI) it would, therefore, be possible to fabricate high density  $UO_2$  and (U Pu) $O_2$  fuel pellets economically. The steps involving generation and handling of fine powder, namely hammer milling, pre-compaction and granulation could also be avoided, thus minimizing the radiotoxic dust hazard. The LTS process has not been used on an industrial scale so far.

#### **2.4.2. Sol gel microsphere pelletization (SGMP) process**

The sol gel microsphere pelletization (SGMP) is a concept of fabrication of ceramic nuclear fuels, in general, and oxide and mixed oxide fuel with uranium and plutonium and MA, in particular, starting from nitrate solutions of these heavy metals. The SGMP process utilizes internal or external gelation process for preparation of dust-free and free-flowing gel microspheres of oxide or oxide-carbon mixture which after controlled air calcination followed by hydrogen reduction and stabilization produce porous and soft oxide microspheres that are suitable for direct pelletization 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 0.2–1.0mm) facilitate remote processing;
- Excellent micro-homogeneity is ensured in fuel pellets;
- Fabrication of both low( $\leq 85\%$  T.D.) and high ( $\geq 96\%$  T.D.) density oxide fuel pellets of controlled 'open' and 'closed' porosity is possible;
- Unlike 'vi-pac' pin, SGMP derived 'pellet-pin' has lesser chance of fuel wash-out, in the event of an early in-pile breach in cladding.

In India, significant quantities of high density  $UO_2$  pellets were manufactured by the combined SGMP-LTS process in a pilot plant, utilizing ammonia internal gelation for preparation of hydrated gel microspheres of  $UO_3 + \text{carbon}$  [98]. The carbon particles were removed from microspheres by controlled air calcination at  $\sim 700^\circ\text{C}$  in order to obtain porous microspheres. The microspheres thus produced were subjected to hydrogen reduction followed by stabilization treatment in order to obtain dust-free and free-flowing coarse (size:  $\sim 600\ \mu\text{m}$ )  $UO_{2+x}$  particles, which could be directly pelletized and sintered to high density by the LTS process.  $UO_2$  fuel bundles, thus prepared were successfully irradiated in two operating PHWR units at Madras Atomic Power Station in India [100]. The LTS was also extended for manufacturing mixed uranium plutonium oxide pellets containing 5%  $PuO_2$  and 30%  $PuO_2$  as part of MOX fuel development programme for LWRs and SFRs respectively [99], [101].

### 2.4.3. DUPIC process

The DUPIC fuel cycle technology aims to directly fabricate CANDU – PHWR fuel from spent PWR fuel through a dry thermal/mechanical process without any separation of stable fission products and transuranic elements. Figure 26 shows the schematic of DUPIC process developed at Korea Atomic Energy Research Institute (KAERI) [102]. The spent PWR fuel containing U, Pu, fission products and MAs is first disassembled, and then the zirconium alloy cladding is removed mechanically to retrieve the irradiated fuel pellets. The retrieved material is treated by oxidation and reduction of oxide fuel (OREOX) process, to make the irradiated fuel material re-sinterable. Once the re-sinterable powder feedstock has been prepared, the remaining fabrication steps are similar to the conventional CANDU fuel fabrication process, i.e. powder treatment, compaction, sintering, end cap welding and bundle assembly. The existence of residual fission products in fresh DUPIC fuel is a distinctive feature of DUPIC fuel. Owing to the high radioactivity of the fuel material, all the manufacturing processes should be performed remotely in a highly shielded facility. Since all the fabrication processes should be performed in a shielded facility throughout the whole process, a designated remote fabrication laboratory, called the DUPIC Fuel Development Facility (DFDF), was established in 2000 by refurbishment of an existing hot cell at KAERI [103].

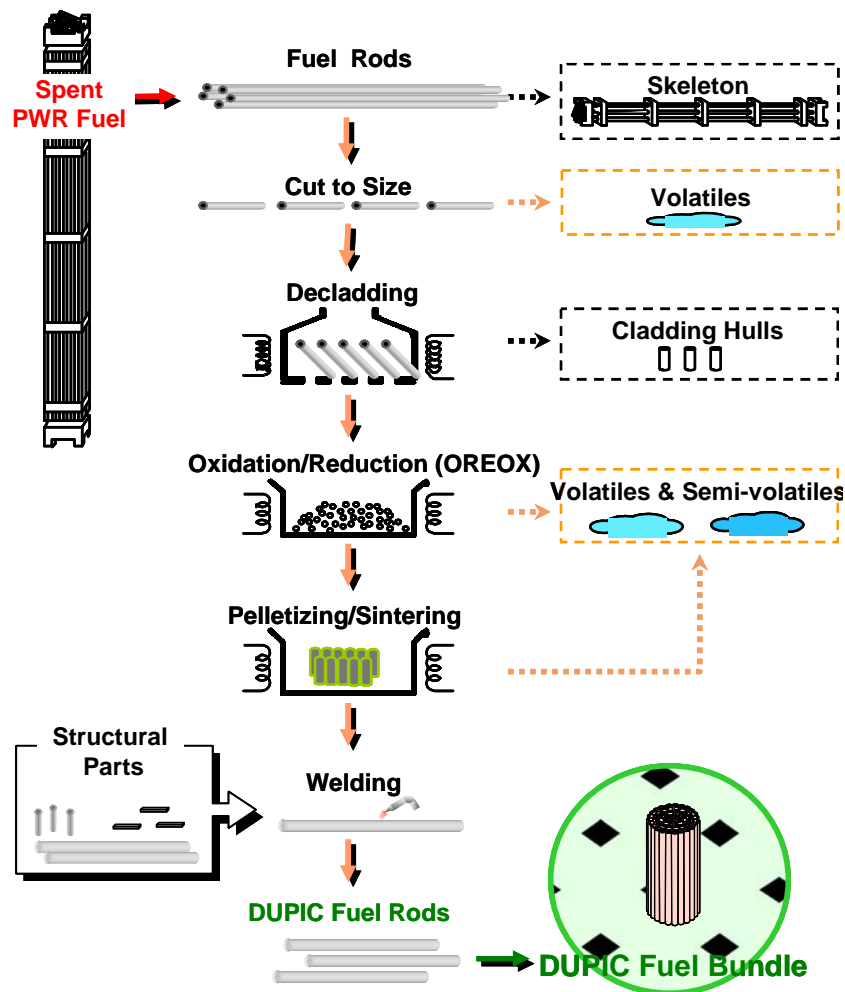


FIG. 26. Schematic of DUPIC process developed at KAERI [103].



A major DUPIC fuel fabrication campaign was started for fabrication of DUPIC fuel pellets and elements for the performance evaluation through irradiation tests at the HANARO research reactor. KAERI has successfully fabricated several DUPIC fuel elements in a remote manner at DFDF, and the performance evaluation through the irradiation tests at HANARO and the post-irradiation examination (PIE) at the Irradiated Material Examination Facility (IMEF) and at the Post-Irradiation Examination Facility (PIEF) is completed. The DUPIC technology is internationally acknowledged as a typical proliferation resistant fuel cycle technology.

#### **2.4.4. Vibro-sol process for fuel pins of low smeared density**

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

- Preparation of gel microspheres (0.1mm to 2mm) of oxide from uranium and plutonium nitrate feed solutions;
- Calcinations, reduction & sintering of these gel microspheres for production of high density ( $\geq 96\%$  T.D.) oxide microspheres (0.01 to 0.8 mm);
- Vibro-packing (vi-pac) of microspheres of one, two or three sizes in fuel tubes.

The vibro-sol process avoids generation and handling of fine powders. The dust free and free flowing microspheres minimize radiotoxic dust hazard and are suitable for remote and automated fuel fabrication. Further, since the heavy metal nitrates are mixed in the liquid state, vibro-sol fuels have a high degree of micro-homogeneity. Apart from this, vibro-sol route has the maximum flexibility of operation because fuel cladding tubes of any internal dimensions can be easily vibro-filled to a wide range of smear density (60–90% T.D.) by packing microspheres of one, two or three sizes.

For vibratory compaction of fuel microspheres various types of pneumatic and electro-dynamic vibrators have been developed to achieve high compaction efficiencies. For smear densities typical of SFR fuels (75–80% T.D.) two size fraction particles, typically 750  $\mu\text{m}$  and 70  $\mu\text{m}$  are used in the ratio of 3:1 in vi-pac pins. The highest achievable smear density of 90% T.D. is obtained by mixing the coarse, medium and fine (size  $\sim 8 \mu\text{m}$ ) fractions in the ratio of 7:2:1. The rates of infiltration of vibration 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 [104–106].

The vibro filling of different size fraction of microspheres or particles could be carried out either by infiltration or parallel filling as shown in Fig. 27.

Vi-pac  $\text{UO}_2$  and  $(\text{UPu})\text{O}_2$  test fuel pins have demonstrated satisfactory performance in both thermal and fast reactors to burnups comparable to pellet pins. However, the irradiation experience is very limited compared to the pellet-pins and vi-pac fuel pins have, in general, the following limitations:

- The maximum achievable smear density of fuel pin is 90% T.D. which is not suitable for fabrication of PHWR fuel pins;

- The studies on defect behavior of vi-pac pins have shown that in the event of an accidental breach of the cladding, 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.

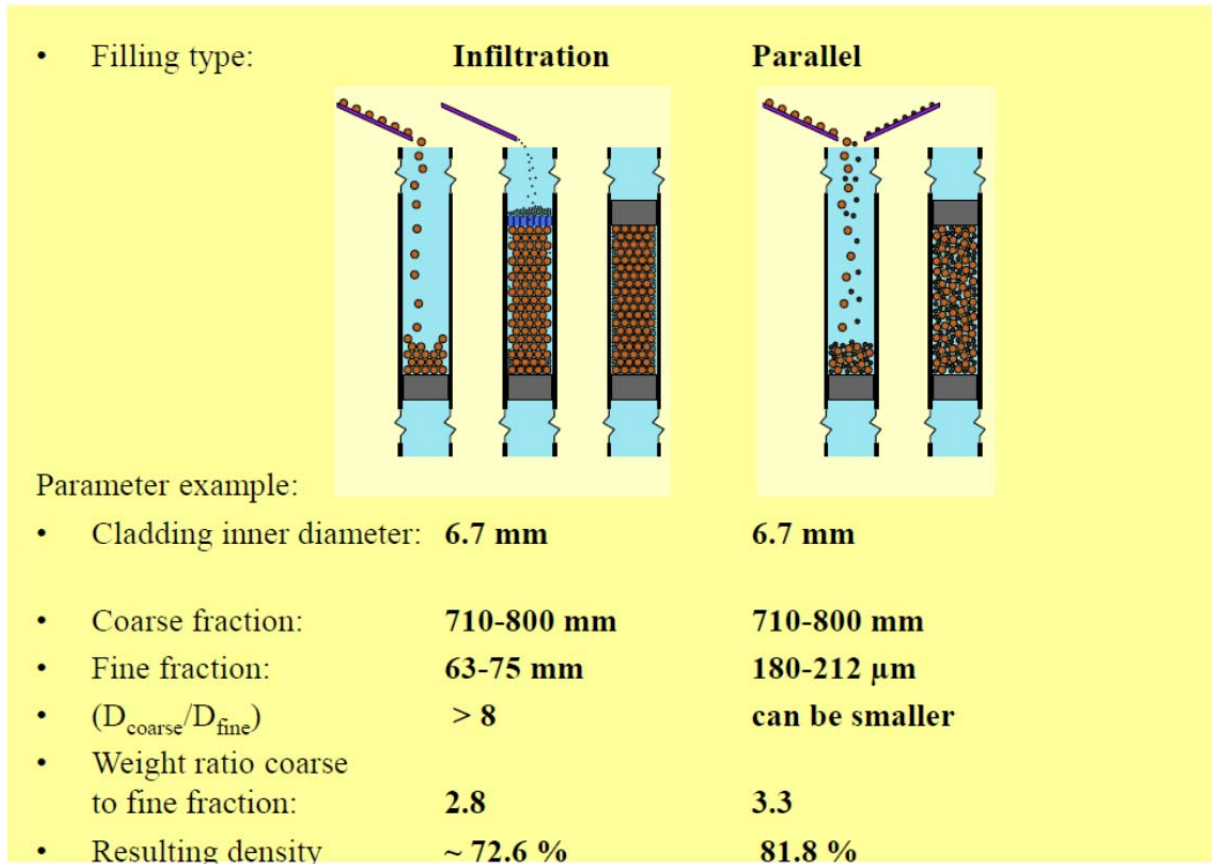


FIG. 27. Infiltration and parallel filling of Sphere-pac.

#### 2.4.5. DOVITA process for MOX and MA bearing MOX fuel fabrication

The acronym DOVITA stands for [107]:

- Dry technologies for fuel reprocessing;
- Oxide fuel application as the most widely studied one;
- Vibro-packing for production of fuel pin;
- Integrated location of spent fuel reprocessing and fuel assembly fabrication facilities in the same site with the reactor;
- TA: Transmutation of actinides

Figure 28 shows the DOVITA scheme of RIAR, Russian Federation for manufacturing vibro compacted MOX fuel pins with and without MA oxides. Vibropacked MOX fuel manufactured by this route has been used in BOR 60 and successfully tested in BN 600. A semi-industrial vibro-packed MOX fuel plant with an annual capacity of manufacturing some fifty BN 600 fuel assemblies is in operation at RIAR [108].

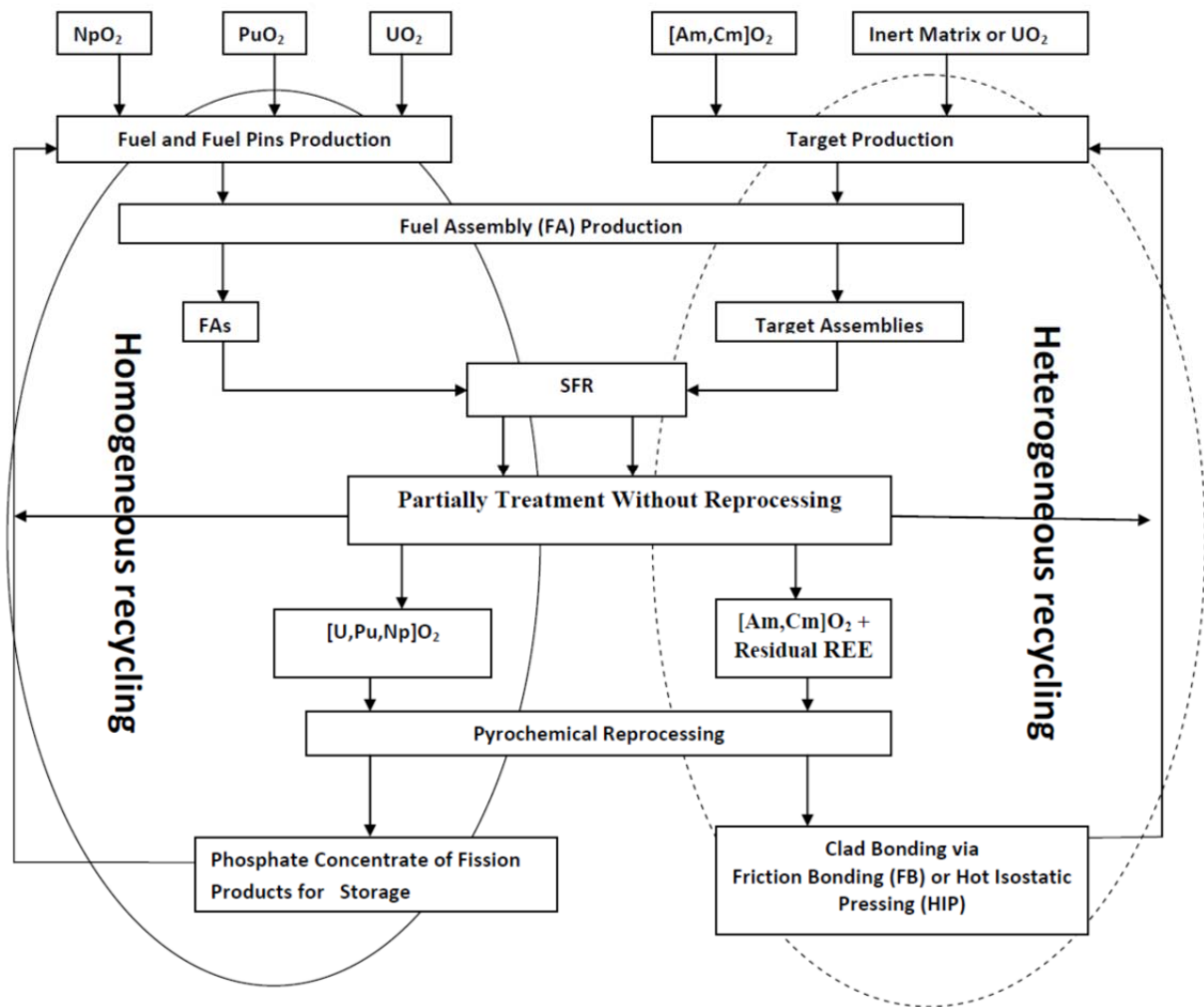


FIG. 28. DOVITA schemes for homogeneous and heterogeneous recycling of U, Pu and MAs in SFR [107].

#### 2.4.6. Infiltration technique for fabrication of MA bearing oxide in inert matrix

The infiltration process, shown schematically in Fig. 29, has been recently developed for manufacturing MA based oxide and mixed oxide fuel pellets on a laboratory scale [109–112]. The key step in this process is the infiltration of a porous material with the MA nitrate solution in a controlled manner. Subsequently, a thermal treatment step is applied to convert the MA nitrate in the porous material to the corresponding oxide. At this stage of the process, a composite is obtained, which is then compacted into pellets for sintering. Due to the very small size of the MA oxide in the porous host, the final product is again a solid solution.

The porous media can be generated by simple granulation of powders, e.g. by compaction and sieving steps, whereby dust is avoided through the use of relatively large sieves ( $>50\ \mu\text{m}$ ). Though this simple process functions, it is limited in application due to the relatively low porosity of the granules. The production of the porous media by sol gel methods is much more favorable, and the porosity can be augmented, through the addition of porogens to the feed solution in the sol gel step.

The infiltration process has been used successfully to produce (Zr, Y, Am)O<sub>2</sub> from (Zr, Y)O<sub>2</sub> precursors, for irradiation tests in both Phénix and HFR Petten. More recently, the production of (U, Am)O<sub>2</sub> by this method has been demonstrated .

A particular advantage of this process lies in the absence of MA bearing liquid wastes, as the MA conversion step is in fact the thermal decomposition of the nitrate salt, releasing NO<sub>x</sub>, which can be easily removed, filtered and sent to the off gas. The quantity of MA that can be infiltrated can be increased by multiple infiltration — calcination cycles, but it is limited to about 25%, which is sufficient for most fast reactor applications.

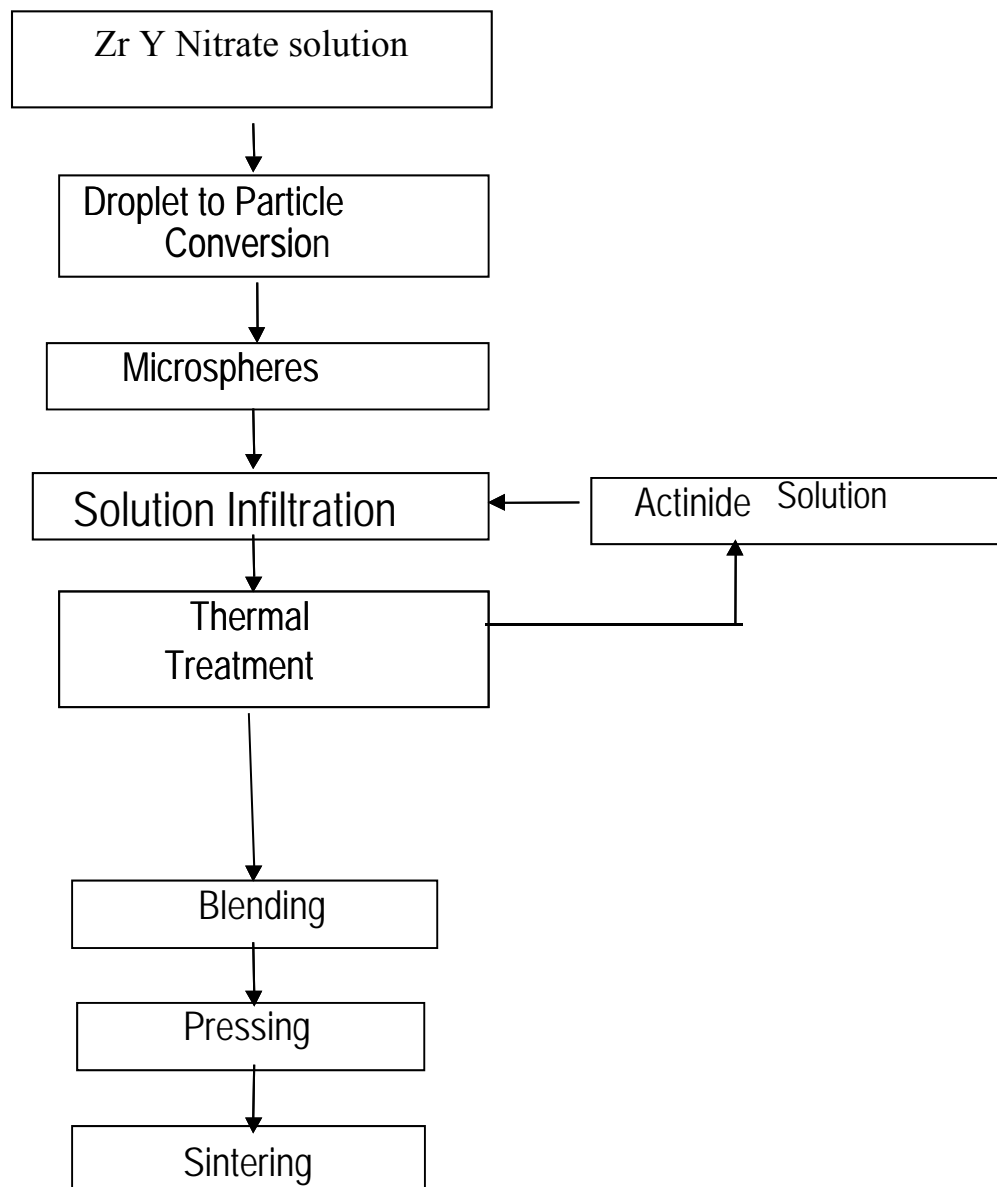


FIG. 29. Infiltration process for manufacturing of MA based oxide fuels.

The infiltration process has also been used to produce mixed plutonium americium oxide where porous  $\text{PuO}_2$  beads (50–150  $\mu\text{m}$ ), prepared by the external gelation route, were infiltrated with Am nitrate and subsequently treated to produce  $(\text{Pu}_{0.8}\text{Am}_{0.2})\text{O}_{2-x}$ . These beads were then blended with Mo powder and compacted and sintered to produce Mo- $(\text{Pu}_{0.8}\text{Am}_{0.2})\text{O}_{2-x}$  metallic matrix composite pellets. This fuel has been subjected to irradiation testing in Phénix and the HFR, Petten.

One of the major challenges of the process, before it could be considered for industrial utilization, is ensuring micro-homogeneity of the fissile materials in the matrix of the fuel pellets.

## 2.5. SUMMARY

The manufacturing technology of  $\text{UO}_2$  and MOX fuel pellets, based on ‘powder–pellet’ route has attained a high level of industrial maturity during the last four decades. The DC is being followed in most countries for production of LEU oxides for manufacturing  $\text{UO}_2$  fuel pellets for LWRs, RBMK and AGR. Although in recent years, the DC process has been modified to improve the flowability of  $\text{UO}_2$  powder, still the granulation step is needed for press-feed material. For preparation of natural uranium oxide powder for manufacturing PHWR fuels the ADU process is most commonly used. The AUC process is used in very few countries for preparing both natural and LEU oxide using uranium nitrate solution and  $\text{UF}_6$  as feed materials. The ex-ADU powders are extremely fine and not free flowing. A granulation step is needed if these powders are used as feed material. The ex-AUC  $\text{UO}_2$  powder is free-flowing and suitable for direct pelletization without the granulation step. Further, the AUC process could be extended for co-precipitation of MOX by the AUPuC process.

For MOX fuel fabrication, the MIMAS process has emerged as the most established route for large scale manufacturing of LWR fuel. The challenge associated with ‘radiotoxic dust hazard’ has to be resolved.

The modified PUREX process aims at avoiding separate plutonium stream for enhancing proliferation resistance. The mixed oxide could be co-precipitated from the solution mixture of uranyl nitrate and plutonium nitrate by: (i) microwave heating (MH) denitration, (ii) co-extraction followed by oxalate precipitation, (iii) AUPuC process and (iv) ammonia external/internal gelation process. These processes would also ensure complete solid solution formation between  $\text{UO}_2$  and  $\text{PuO}_2$  in MOX pellets, thereby facilitating dissolution of spent MOX fuel pellets in nitric acid during subsequent reprocessing. Another alternative is co-immobilization on ion exchange resin. The alternative SGMP process reduces radiotoxic dust hazard and facilitates remote and automated fuel production because of free flowing and dust-free sol-gel derived microspheres. Co-location of fuel reprocessing and SGMP plant will significantly minimize the high active liquid effluents.

Finally, secured automated fabrication (SAF), with proper physical protection and real time accounting of nuclear material is essential for industrial scale manufacturing of MOX fuel.

## 3. MANUFACTURING OF THORIA AND THORIA BASED FUELS

### 3.1. INTRODUCTION

Thorium fuels and thorium fuel cycle options have been widely investigated in the past in Canada, Germany, India, the Russian Federation, UK and the USA and documented in several

international conference proceedings and IAEA publications [113–137]. These studies, as listed in Tables 6 and 7, show that virtually every type of operating power reactor can accommodate thorium-based fuels and it is possible to have breeding with  $^{232}\text{Th}$ - $^{233}\text{U}$  in both thermal and fast reactors. Unfortunately most of these activities have been discontinued. In recent years, there has been renewed interest in thorium fuel cycle mainly from the point of view of proliferation resistance and utilization of natural resources [138–139].

TABLE 6. THORIUM FUEL UTILIZED IN EXPERIMENTAL AND POWER REACTORS WORLDWIDE [137]

Name and Country	Type	Power	Fuel	Operation period
AVR, Germany	HTGR Experimental (Pebble bed reactor)	15 MW(e)	Th+ $^{235}\text{U}$ Driver Fuel, Coated fuel particles Oxide & dicarbides	1967 – 1988
THTR, Germany	HTGR Power (Pebble Type)	300 MW(e)	Th+ $^{235}\text{U}$ , Driver Fuel, Coated fuel particles Oxide & dicarbides	1985 - 1989
Lingen, Germany	BWR Irradiation-testing	60 MW(e)	Test Fuel (Th,Pu)O <sub>2</sub> pellets	Terminated in 1973
Dragon, UK OECD-Euratom also Sweden, Norway & Switzerland	HTGR Experimental (Pin-in-Block Design)	20 MWt	Th+ $^{235}\text{U}$ Driver Fuel, Coated fuel particles Dicarbides	1966 - 1973
Peach Bottom, USA	HTGR Experimental (Prismatic Block)	40 MW(e)	Th+ $^{235}\text{U}$ Driver Fuel, Coated fuel particles Oxide & Dicarbides	1966 – 1972
Fort St Vrain, USA	HTGR Power (Prismatic Block)	330 MW(e)	Th+ $^{235}\text{U}$ Driver Fuel, Coated fuel particles Dicarbide	1976 - 1989
Borax IV & Elk River Reactors, USA	BWRs (Pin Assemblies)	2.4 MW(e) 24 MW(e)	Th+ $^{235}\text{U}$ Driver Fuel Oxide Pellets	1963 - 1968
Shippingport & Indian Point, USA	LWBR PWR (Pin Assemblies)	100 MW(e) 285	Th+ $^{233}\text{U}$ Driver Fuel, Oxide Pellets	1977 – 1982 1962 - 1980

Pioneering work on thorium and thorium fuel cycle was carried out in the USA, where the Shippingport PWR, 60 MW (e) demonstrated breeding in  $^{232}\text{Th}$ - $^{233}\text{U}$ . ThO<sub>2</sub> based fuel was also used in Elk River 22 MW (e) BWR in the USA. Thorium fuel was extensively used as coated fuel particles in prismatic graphite blocks in two HTGRs in the USA, namely 40 MW (e) Peach Bottom and 330 MW (e), Fort St. Vrain in the 1970s. The Dragon reactor in UK, a HTGR, also utilized thorium fuel. In Germany, coated fuel particles of thorium uranium dicarbide in the form of pebbles were routinely manufactured for several years for the two HTGRs, namely, 15 MW (e) AVR and 300 MW (e) THTR. In addition, the feasibility of zirconium alloy clad thoria-plutonia and thoria-urania fuel pins was studied in Germany in collaboration with Brazil. ITU in Karlsruhe prepared ThO<sub>2</sub>-PuO<sub>2</sub> pellets for irradiation in KWO and carried out post-irradiation examination.

In India, thoria is being used as blanket material in the 40 MW(t) FBTR and ThO<sub>2</sub> bundles were used for neutron flux flattening of the initial cores of PHWR after startup.

TABLE 7. THORIUM BASED FUELS: THEIR TYPES AND FUEL GEOMETRY [137]

REACTOR TYPE	COMPOSITION	FUEL SHAPE	FUEL ELEMENT
High temperature Gas cooled reactors	$\text{ThO}_2$ , $(\text{Th,U})\text{O}_2$ , $\text{ThC}_2$ , $(\text{Th,U})\text{C}_2$ ( $^{235}\text{U}$ or $^{233}\text{U}$ )	Microspheres 200-800 $\mu$ coated with multiple layers of buffer & pyrolytic carbon and SiC	Mixed with graphite and pressed into large spheres (~60 mm) for Pebble-Bed Reactor or fuel rods for HTGRs with prismatic fuel elements
Light water reactors	$\text{ThO}_2$ , $(\text{Th,U})\text{O}_2$ , $(\text{Th,Pu})\text{O}_2$ ( $<5\%$ Pu, $^{235}\text{U}$ or $^{233}\text{U}$ )	<ul style="list-style-type: none"> <li>• High-density Sintered Pellets</li> <li>• High-density Microspheres</li> </ul>	<ul style="list-style-type: none"> <li>• Zircaloy clad Pin Cluster encapsulating Pellet-Stack</li> <li>• Zircaloy clad 'vi-pac' Pin Cluster encapsulating fuel microspheres</li> </ul>
PHWR	$\text{ThO}_2$ for neutron flux flattening of initial core		
AHWR	$(\text{Th,U})\text{O}_2$ , $(\text{Th,Pu})\text{O}_2$ ( $<5\%$ Pu, $^{235}\text{U}$ or $^{233}\text{U}$ )	High-density Sintered Pellets	Zircaloy clad Pin Cluster encapsulating Pellet-Stack
Fast reactors	<ul style="list-style-type: none"> <li>• <math>\text{ThO}_2</math> blanket</li> <li>• <math>(\text{Th,U})\text{O}_2</math> &amp; <math>(\text{Th,Pu})\text{O}_2</math> (~25% Pu, <math>^{235}\text{U}</math> or <math>^{233}\text{U}</math>) fuels</li> </ul>	High-density Sintered Pellets & Injection-cast Fuel Rods	Stainless steel (SS) clad Pin Cluster encapsulating Pellet- Stack  SS clad Pin Cluster encapsulating Fuel Rods

India is planning to use  $(\text{Th, Pu})\text{O}_2$  and  $(\text{Th, }^{233}\text{U})\text{O}_2$  as driver fuel in the advanced heavy water reactor (AHWR), but construction of the reactor has not yet started.

Thorium cycle is really attractive only if bred  $^{233}\text{U}$  is recycled which implies the reprocessing of the spent fuel. The THOREX process of reprocessing was carried out in US and India on a laboratory scale. Dissolution of spent thorium based fuel in nitric acid is challenging and requires addition of hydrofluoric acid which is highly corrosive. Significant R&D programmes would be needed to develop a competitive industrial process for reprocessing and recycling spent  $(\text{Th, }^{233}\text{U}/^{235}\text{U})\text{O}_2$  and  $(\text{Th, Pu})\text{O}_2$  in thermal and fast reactors. Likewise, re-fabrication of  $^{233}\text{U}$  based fuels is a major technical hurdle requiring remote handling because of high radiation level of unavoidable  $^{232}\text{U}$  daughter products. This is feasible but would be very costly and would need significant technological developments.

The manufacturing processes of  $\text{ThO}_2$ ,  $(\text{Th, U})\text{O}_2$ ,  $(\text{Th, Pu})\text{O}_2$  and  $(\text{Th, U})\text{C}_2$  have been summarized in several IAEA documents and by Hart et al and Belle and Berman [140–141]. Pilot plants were in operation for small scale fabrication of  $\text{ThO}_2$  and Thorium based mixed oxide and mixed carbide fuels containing  $^{235}\text{U}$ ,  $^{239}\text{Pu}$  and  $^{233}\text{U}$  fuels by powder - pellet route and sol-gel processes in USA, Germany and India [142–150]. New techniques based on impregnation and sol-gel microsphere pelletization (SGMP) processes have been reported [151–152]. However, currently thorium bearing fuel is not being used in any power or non – power reactors.

### 3.2. FABRICATION OF $\text{ThO}_2$ BASED FUELS

The following methods have been developed for manufacturing (Th, U) $\text{O}_2$  and (Th, Pu) $\text{O}_2$  fuels:

- Powder-pellet route;
- Vibro-sol route;
- Sol-gel microsphere pelletization;
- Impregnation technique.

#### 3.2.1. Powder–pellet route

In this process the usual starting materials are  $\text{ThO}_2$ ,  $\text{UO}_2$  and  $\text{PuO}_2$  powders. The essential steps are co-milling of oxide powders, granulation, cold pelletization and sintering. Thoria powder derived from the ‘oxalate’ process has a flat, square platelet morphology, which requires pre-milling for making it ‘sinter active’. Since  $\text{ThO}_2$  has a very high melting point ( $\sim 3350^\circ\text{C}$ ), the sintering has to be carried out at temperatures higher than  $2000^\circ\text{C}$  to obtain high-density pellets. However, with small addition of ‘sintering aids’ like  $\text{Nb}_2\text{O}_5$ , high-density  $\text{ThO}_2$  pellets could be obtained by sintering in air at temperature as low as  $1150^\circ\text{C}$ . Alternatively, small addition of divalent metal oxide, like  $\text{CaO}$  and  $\text{MgO}$ , enhances the diffusion of  $\text{Th}^{+4}$  by creating anion vacancies. Addition of around 2%  $\text{U}_3\text{O}_8$  was also found to enhance the densification of  $\text{ThO}_2$  and high density (96% T.D.) pellets could be obtained by sintering in air at  $1100^\circ\text{C}$ .

The powder route has the usual problem of radio toxic dust hazard and is not ideally suited for manufacturing radiotoxic Pu and  $^{233}\text{U}$  bearing fuels.

#### 3.2.2. Sol gel route for microspheres suitable for Vi-pack pin & coated fuel particles

Sol-gel derived  $\text{ThO}_2$ , (Th, U) $\text{O}_2$  and (Th, Pu) $\text{O}_2$  microspheres have been prepared in the past for manufacturing:

(i) ‘vi-pac’ fuel pins of controlled density discussed in details in chapter II by loading one, two or three size fractions (typically  $1000\ \mu\text{m}$ ,  $100\ \mu\text{m}$  and  $10\ \mu\text{m}$ ) of microspheres in one end closed cladding tube followed by vibratory compaction

(ii) coated fuel particles for HTGR, where high density fuel microspheres are subjected to multilayer coating of pyrolytic carbon and silicon carbide, popularly known as TRISO and BISO particles,

In the early-mid 1960s, sol gel microspheres of (Th,  $^{233}\text{U}$ ) $\text{O}_2$  were prepared in USA in Babcock and Wilcox unshielded pilot plant at Virginia and at semi-shielded Kilorod facility at Oak Ridge National Laboratory (ORNL), Tennessee for manufacturing vi-pac fuel pins [153–154]. The ORNL sol gel process based on dehydration reaction was replaced by the more efficient ‘ammonia gelation’ processes, which cause rapid gelation of droplets of sols or solutions of the nitrates of U, Th or Pu either ‘externally’ by ammonia gas and ammonium hydroxide or ‘internally’ by an added ammonia generator such as hexa methylene tetra amine (HMTA).



Figure 30 shows the pilot plant at research centre (formerly KfA) , Juelich, Germany for preparation of hydrated gel microspheres of thorium and uranium oxide based on ammonia external gelation, using the nitrate solutions of thorium and uranium as starting materials [155]. Similar facility could be installed inside glove box or hot cell for manufacturing  $^{233}\text{U}$ , Pu or MA bearing mixed oxide microspheres using the heavy metal nitrates as feed solution. The belt drier for drying mono-layer of the hydrated gel microspheres is shown on the right.

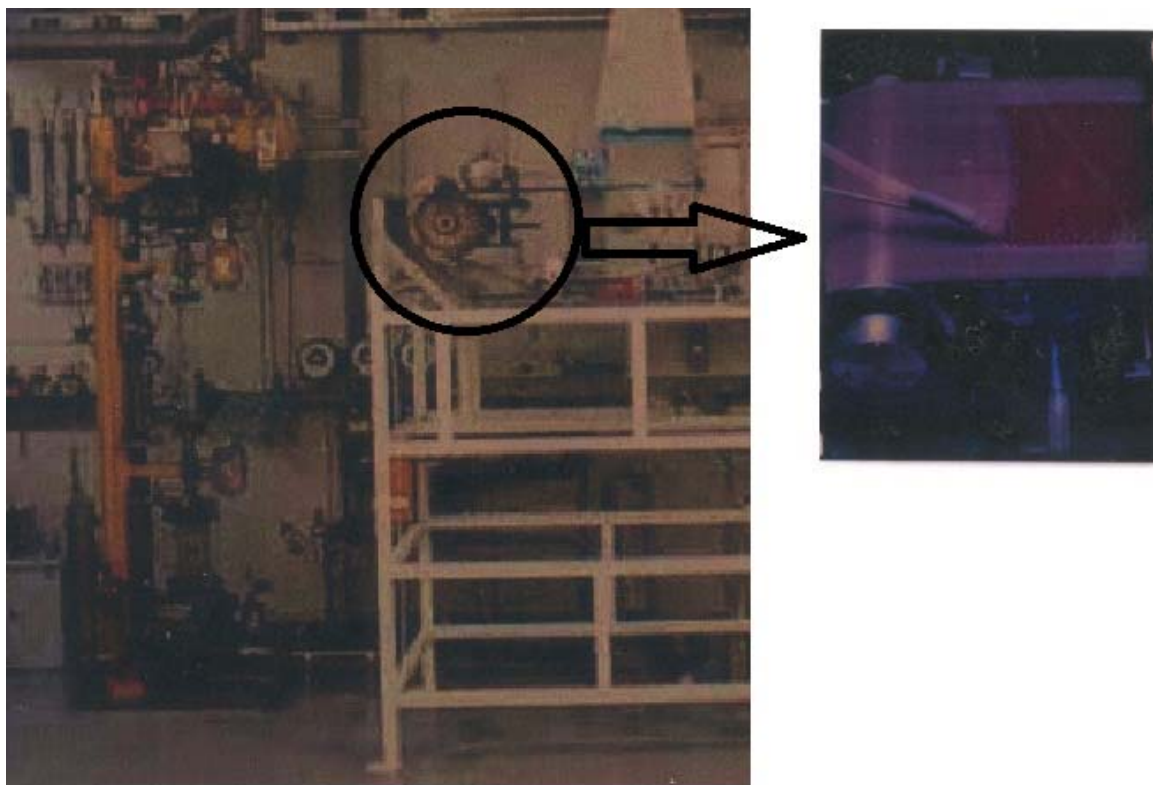
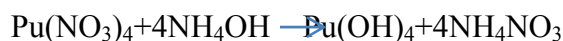


FIG. 30. Ammonia external gelation of uranium (EGU) and thorium (EGT) pilot plant in Juelich, Germany [155].

In the EGT process, the sols are prepared by passing controlled amount of ammonia gas in the nitrate solutions of thorium, thorium uranium mixture or thorium plutonium mixture of molarity 1–1.2 at 350–370 K for pre-neutralization as per the following reactions:



A small amount (5–15 g) of poly vinyl alcohol (PVA) is added to the nitrate solution prior to the pre-neutralization step. The precipitation reactions are controlled by continuous monitoring of the pH and viscosity. A pH in the range of 3.2–3.5 and viscosity  $\sim 0.02 \text{ Pa}\cdot\text{s}^{-1}$  at a shear speed of  $160 \text{ s}^{-1}$  are the ideal values for completion of the pre-neutralization step. Next, droplets of the sol are introduced through an electromechanical vibrator with a horizontal jetting nozzle inside a containment box that houses two horizontal ammonia gas pipes and the gelation bath as shown in Fig. 30. Thus, the droplets pass through a curtain of  $\text{NH}_3$  gas and quickly coat itself with a gel skin before falling into the gelation bath in a parabolic path. In the gelation bath the droplets gel and settle to the bottom of the containment box. The bath

composition is water with 1%  $\text{NH}_4\text{OH}$  and 4 molar  $\text{NH}_4\text{NO}_3$  / L with pH value close to 8. The  $\text{NH}_4^+/\text{NH}_3$  buffer system establishes the conditions essential to achieve the suitable gelation rate. The nozzle bore diameter used was between 0.6 and 0.8 mm. With a sol flow rate of 30 mL/min at the nozzle and a nozzle frequency of 500 to 600cps, droplet diameters between 1.2 and 1.4 mm are achieved. The gelled microspheres containing  $\text{NH}_4\text{NO}_3$  are next transferred to a glass column containing water with  $\sim 1\%$   $\text{NH}_3$  to wash out the ammonium nitrate.

The washed microspheres were next dried in a humid air atmosphere at  $\sim 100^\circ\text{C}$ , on a continuous belt drier and subjected to controlled calcinations followed by sintering at  $1200\text{--}1300^\circ\text{C}$  to obtain high density microspheres. The steps in EGT process are summarized in Fig. 31.

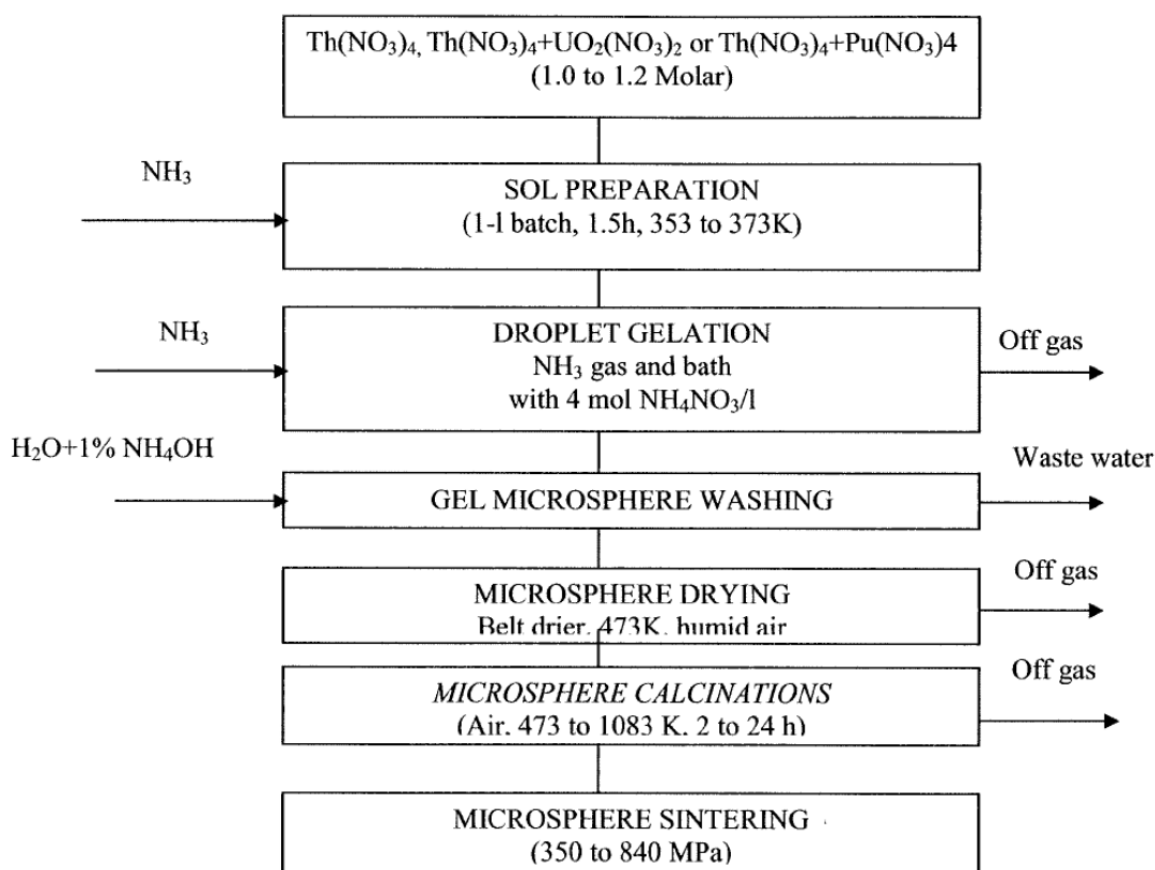


FIG.31. EGT processes for manufacturing  $\text{ThO}_2$  based high density microspheres.

### 3.2.3. Sol gel microsphere pelletization

The flow sheet of SGMP process has been developed on laboratory scale for manufacturing high density  $\text{ThO}_2$  and (Th, U) $\text{O}_2$  pellets. The EGT process of Germany was modified for obtaining dust free and free flowing 'porous'  $\text{ThO}_2$  based oxide and mixed oxide microspheres, which could be easily pelletized by cold compaction and sintered to high density pellets. For this, the following three major modifications were made:

- (i) Using Th-nitrate and (Th, U)- nitrate feed solutions of relatively low molarity (1–1.2M);

- (ii) Addition of 'carbon black' pore former to the 'sol' prior to gelation and later removing carbon by controlled air calcinations at 700°C to obtain 'porous microspheres' of very low crushing strength; and
- (iii) Addition of around 1wt%  $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  to thorium and mixed thorium uranium nitrate feed solution to obtain 0.4% CaO as 'sintering aid' in the calcined fuel microspheres (magnesium nitrate could also be used as sintering end)

Without the use of carbon black pore former, the EGT process leads to 'non-porous' microspheres on calcination, which retain their individual identity during pelletization and sintering and lead to low-density oxide pellets with open porosity and a 'black-berry' microstructure because of densification within the microspheres and not between them during the sintering process.

#### 3.2.4. Impregnation technique

In the impregnation process shown in figure 32, the inert and relatively less radioactive natural  $\text{ThO}_2$  is first prepared in an unshielded area in the form of 'low density pellets' ( $\leq 80\%$  T.D.) with 'open porosity' or sol gel derived 'porous microspheres'. Next, the pellets or microspheres are impregnated in uranyl nitrate ( $^{235}\text{U}$ ) or plutonium nitrate solution of molarity in the range of 1 to 3, in a shielded facility, followed by sintering in case of the pellets or cold pelletization followed by sintering in case of the microspheres to obtain  $\text{ThO}_2$  based mixed oxide pellets of high density and excellent micro-homogeneity [156–157]. The solid solution between  $\text{ThO}_2$  and  $\text{UO}_2$  or  $\text{PuO}_2$  is formed during the sintering step. Thus, fine  $^{235}\text{U}$  or Pu bearing powders are avoided and handling of these materials is restricted only in certain parts of the fuel fabrication plants. Process steps like precipitation of ammonium diuranate or plutonium oxalate, calcination, mixing, grinding, granulation, etc. which are associated with 'radiotoxic dust hazard' are eliminated.

The impregnation technique has not been used so far even on a laboratory scale for manufacturing  $^{235}\text{U}$  bearing (Th, U) $\text{O}_2$  pellets. The process has been demonstrated on a laboratory scale using natural uranium.

### 3.3. SUMMARY

Thorium is estimated to be about three to four times more abundant than uranium in the earth's crust. However, unlike uranium, systematic exploration and documentation of thorium resources have still not been made. In the initial years of nuclear energy it was envisioned that thorium would supplement uranium as a fertile material as uranium reserves gets depleted. However, since uranium resources are still abundant research in thorium fuels and fuel cycles waned. Recently, there has been renewed interest in thorium based fuels for improving proliferation - resistance and waste characteristics of used nuclear fuel. Thorium fuels have been used in several power and research reactors.

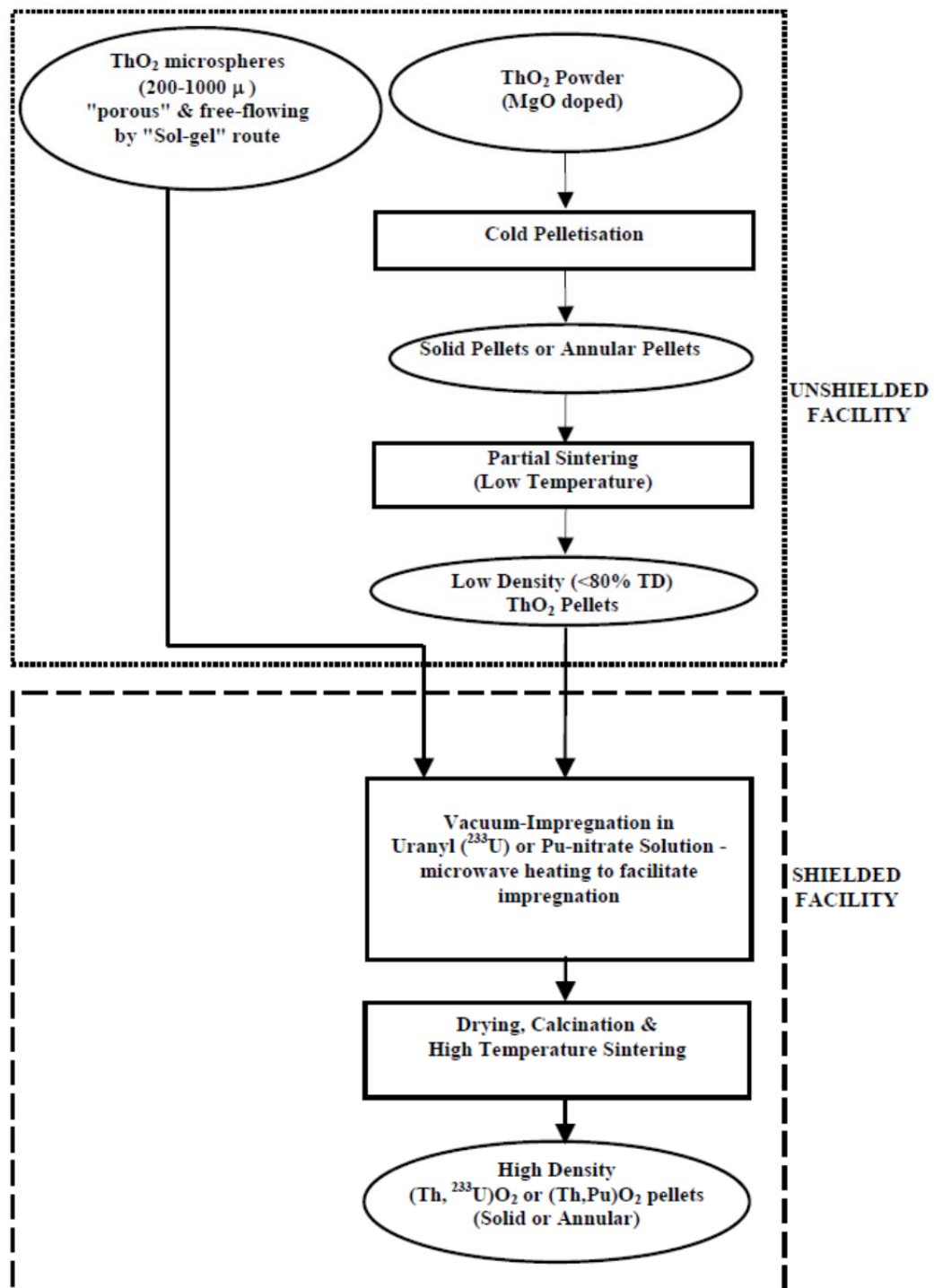


FIG. 32. Impregnation technique for preparation of ThO<sub>2</sub> based mixed oxide fuel pellets.

## 4. MANUFACTURING OF MIXED CARBIDE AND MIXED NITRIDE FUELS

### 4.1. INTRODUCTION

Mixed uranium plutonium monocarbide (MC) and mononitride (MN) have been identified as advanced SFR fuels in the early 1960s, on the basis of their high heavy metal density, high breeding ratio (and in turn short doubling time), high thermal conductivity and excellent chemical compatibility with sodium coolant. In the mid-1960s, Russian Federation used UC and UN as driver fuels in BR5 experimental fast reactor and India has been operating the 40 MW (t) fast breeder test reactor (FBTR) with plutonium rich mixed carbide core since 1985. The mixed carbide core has successfully operated to a burnup exceeding 150 GW d/t without any failure. However, compared to mixed oxide fuel, the experience on mono-carbide and mononitride fuels, although significant, remains very limited. The R and D activities on fabrication, out-of-pile properties and irradiation behavior of mixed carbide and mixed nitride fuels for SFRs peaked during the period from the mid-1970s to the mid-1980s in the USA, Russian Federation, UK, France, Germany, Switzerland, Japan and India and the results have been very well documented [157–163]. Since the 1990s these activities have progressively slowed down mainly because of slowing down of fast reactor programme worldwide and partly due to the challenges in manufacturing and reprocessing of these fuels. In recent years there has been renewed interest in fast reactors and related fuel cycle. As part of this activity, the IAEA has updated information on fast reactor fuel and fuel cycle [164–165].

The fabrication of UC, (U, Pu)C, UN and (U, Pu)N fuels have, so far, been carried out in a very limited number of countries either on a small laboratory scale or in a pilot plant for manufacturing driver fuel for small experimental SFRs or for preparing samples for out-of-pile property evaluation and in-pile testing.

MC and MN belong to the same family on the basis of their crystal structure (fcc, NaCl type) and similar physical and chemical properties. The monocarbides and mononitrides of uranium and plutonium are completely solid soluble. Hence, the different techniques of synthesis and consolidation of MC and MN fuels are similar.

Figure 33 summarizes the different processes for manufacturing UC, PuC, (U, Pu)C, UN, PuN & (U, Pu)N fuel pellets, using uranium and plutonium metal, oxide powders or nitrate solutions as feed materials. The preparations of mixed uranium plutonium monocarbide and mononitride fuels are difficult and more expensive as compared to oxide fuel because of the following reasons:

- (i) The number of process steps is higher compared to that of oxide fuel;
- (ii) These compounds are highly susceptible to oxidation and hydrolysis and are pyrophoric in powder form. The entire fabrication is, therefore, required to be carried out inside leak tight glove boxes maintained in an inert cover gas ( $N_2$ , Ar, He etc.) atmosphere containing minimal amounts of oxygen and moisture (<20 ppm each);
- (iii) Stringent control of carbon contents is needed during the different stages of fabrication in order to avoid the formation of the unwanted metallic phase and for keeping higher carbides ( $M_2C_3$  and  $MC_2$ ) within acceptable limits. Higher nitrides ( $M_2N_3$  and  $MN_2$ ) dissociate to MN at elevated temperature ( $\geq 1400^\circ C$ ) in inert atmosphere and pose no problem.

Table 8 summarizes the differences in manufacturing of oxide and non-oxide ceramic fuels.

TABLE 8. COMPARISON OF MIXED URANIUM PLUTONIUM OXIDE, CARBIDE & NITRIDE FUEL FABRICATION USING  $\text{UO}_2$  &  $\text{PuO}_2$  POWDERS AS FEED MATERIALS

Basis of comparison			Oxide fuel	Mono-carbide /mono-nitride fuels
1.	Principal steps in fabrication		(i) Co-milling of $\text{UO}_2$ & $\text{PuO}_2$ (ii) Compaction (iii) Sintering	(i) Mixing of $\text{UO}_2$ , $\text{PuO}_2$ & Carbon (ii) Tableting (iii) Carbothermic reduction (iv) Crushing (v) Milling (vi) Compaction (vii) Sintering
2.	Glove box atmosphere		Air	Inert gas: Ar or $\text{N}_2$ containing < 20 ppm each of $\text{O}_2$ & moisture
3.	Process controls		(i) O/M (ii) Pellet density (iii) $\text{UO}_2$ and $\text{PuO}_2$ complete solid solution formation	(i)C/M or N/M (ii)O, C & N contents of powder and pellet (iii) $\text{MO}_2$ , $\text{M}_2\text{C}_3$ & $\text{MC}_2$ or $\text{MO}_2$ , $\text{MN}_2$ & $\text{M}_2\text{N}_3$ contents of powder and pellets (iv)Pellet density
4.	Additional equipment for (U,Pu)C fabrication			(i) High temperature furnaces for carbothermic synthesis (ii) O, N and C analysers (iii) Trace oxygen & moisture monitors (iv) Personnel safety oxygen monitors (v) Inert gas system – once through or recirculation–purification

M = U + Pu

The two main steps for fabrication are:

- (i) Synthesis of monocarbide or mononitride in the form of buttons, powders, clinkers, or sol gel microspheres;
- (ii) Fabrication of fuel pellets, followed by loading of the fuel pellet stack in cladding tube and encapsulation or vibro-packing of granules or microspheres in fuel cladding tube followed by encapsulation.

#### 4.2. SYNTHESIS OF MC AND MN

The principal methods of synthesis of MC and MN as summarized earlier [166] are as follows:

- (i) Direct synthesis by arc-melting;
- (ii) Hydriding–dehydriding of bulk metal to form fine metal powder followed by carburization and nitridation with methane/propane and nitrogen for obtaining fine powders of MC and MN respectively;
- (iii) Carbothermic reduction of oxide-carbon mixture in vacuum/argon and flowing nitrogen for preparation of MC and MN respectively.

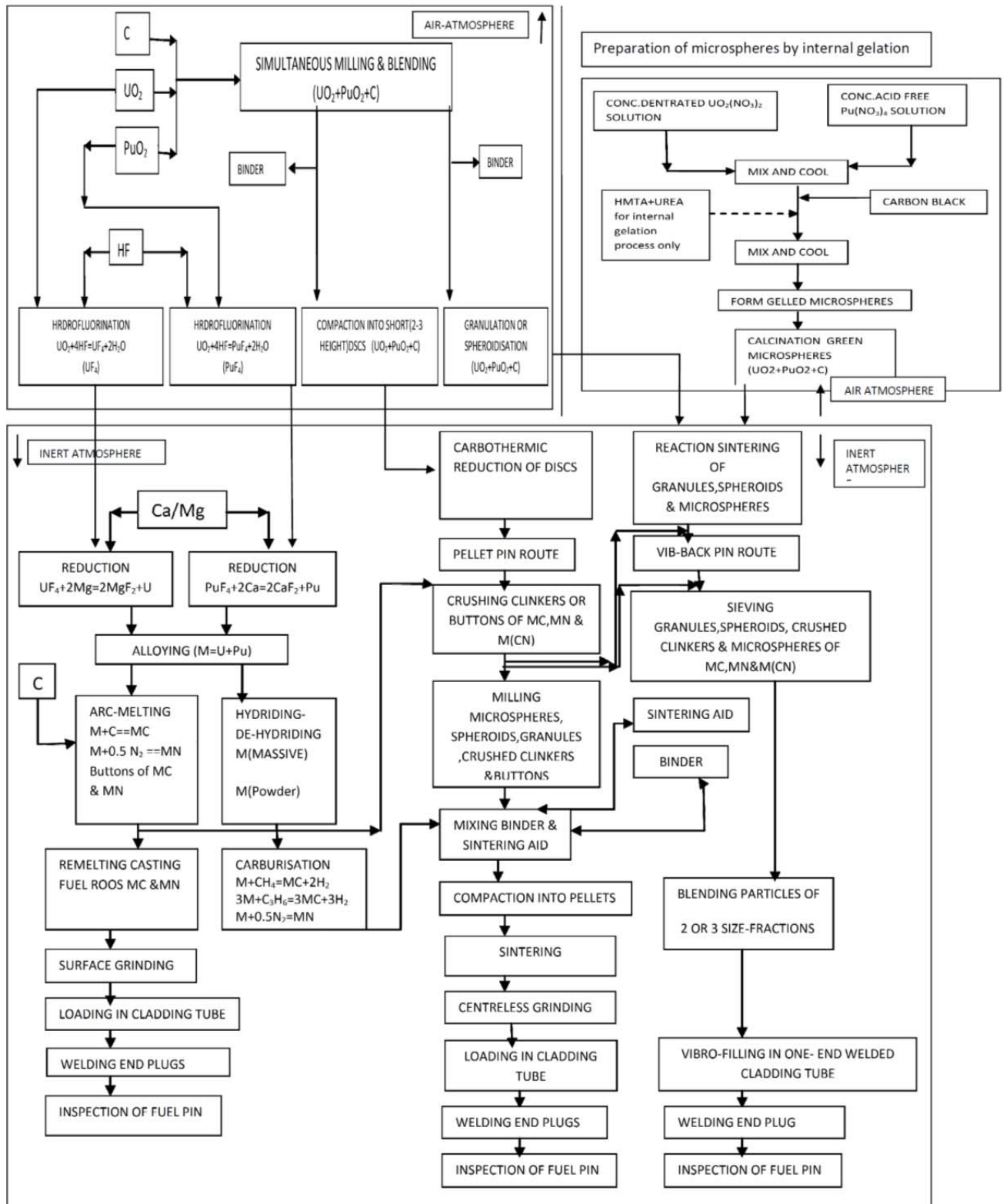
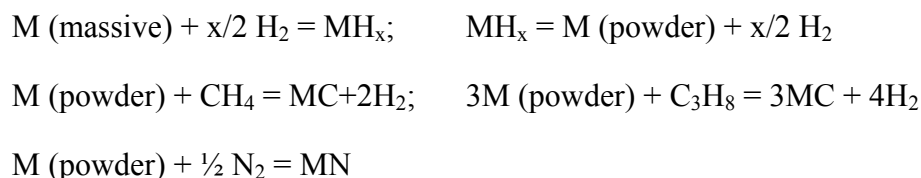


FIG. 33. Summary of the methods developed so far for fabricating monocarbide and mononitride fuels of uranium and plutonium using metal, oxide powder and nitrate solutions as starting materials.

The direct synthesis involves non-consumable electrode arc melting of stoichiometric powder mixture of uranium, plutonium and carbon in vacuum or flowing organ for synthesis of MC and in high nitrogen over pressure (>2 MPa) for MN [167–168]. Tungsten is the commonly used non-consumable electrode. However, tungsten has a tendency to erode and contaminate the melt. For the synthesis of MC, the graphite has also been used in place of tungsten. However, in such case there is carbon pick-up from the electrode leading to the formation of higher carbide second phase. Multiple re-melting is required for obtaining a homogeneous end product. The main advantage of the melting process is that the MC and MN thus produced have very low oxygen impurity (<0.02 wt%). The method has not been pursued on an industrial scale because of economic reasons and for the problem of criticality hazard.

Hydriding and de-hydriding of uranium and plutonium method followed by carburization for carbide and nitridation for nitride has been utilized by several laboratories for synthesis of mono-carbide and mono-nitride respectively [169–171]. Since the diffusivity of carbon in massive uranium or plutonium is very low even at 1300 K, the massive metal is first converted into fine powders of high specific surface area by hydriding and de-hydriding at 450–525 K and 800–1000 K. The freshly produced metal powder can easily be carburized to MC by methane or propane at 1000–1100 K or nitrided to MN by flowing nitrogen. The chemical reactions involved are:



This method of synthesis of MC and MN has two main attractions. First, the reaction temperatures are low thereby avoiding plutonium losses by volatilization. Secondly, the end products are fine and highly reactive MC and MN powders which can be directly compacted for sintering. The only disadvantage of this method is that the starting materials, namely uranium and plutonium metals, are required to be prepared from oxide by hydro-fluorination followed by calico-thermic or magnesio-thermic reduction. This technique has been used only on a laboratory scale, particularly in US and Japan.

#### 4.2.1. Carbothermic reduction of oxide for synthesis of MC

The carbothermic reduction of oxides is the most attractive route for large-scale production and has, therefore, been studied extensively [172–175].

The overall simplified chemical equation for the production of mono-carbide by carbothermic reduction of oxide can be represented by the reaction  $\text{MO}_2 + 3 \text{C} = \text{MC} + 2 \text{CO}$ , where  $\text{MO}_2$  is either mechanical mixture or solid solution of  $\text{UO}_2$  and  $\text{PuO}_2$ . Figure 34 summarizes the various techniques developed for the synthesis of MC [176].

“Single-step solid state synthesis in a static bed” is the simplest technique for preparation of MC. In this method, the MC end product will always contain  $\text{M}_2\text{C}_3$  second phase and residual oxygen and nitrogen impurities. This is because oxygen and nitrogen act as carbon equivalents and replace 'C' in the MC lattice to form the compound  $(\text{U,Pu})(\text{O}_x\text{N}_z\text{C}_{1-x-z})$  where x, z and their summation is less than 1.0.



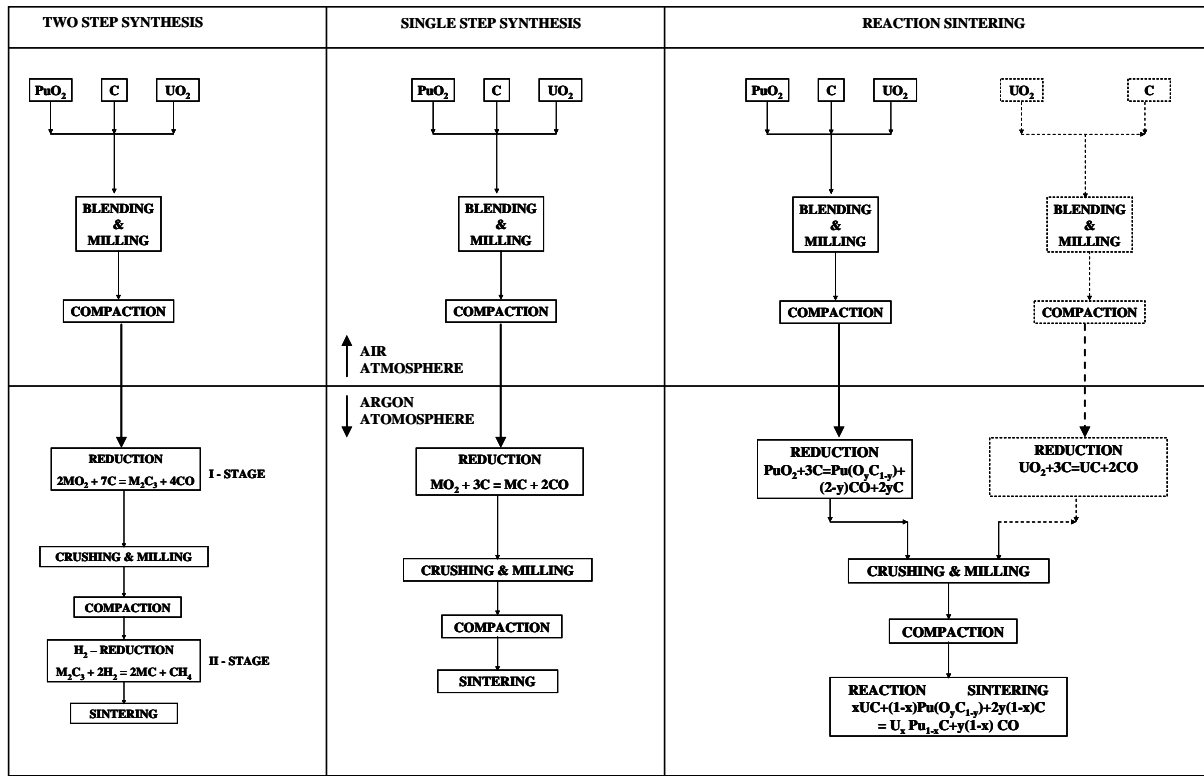


FIG. 34. Different carbothermic reduction processes for synthesis of (U,Pu)C starting from  $UO_2$  &  $PuO_2$  powders.

“Two-step solid-state synthesis in a static bed” is an improvement over the single-step synthesis and aims at the preparation of single-phase MC with very low oxygen and nitrogen contents and with practically no losses of plutonium by volatilization.  $M_2C_3$ , unlike MC, has very little oxygen and nitrogen solid-solubility and can be easily formed at a lower carbothermic temperature, thereby, minimizing plutonium volatilization loss. In the first step, carbo-thermic reduction at a relatively low temperature with excess carbon ensures that only  $M_2C_3$  is formed. In the second step, the  $M_2C_3$  is crushed, milled and treated with hydrogen at  $\sim 1123$  K in order to reduce it to MC and remove free carbon as methane. The three-step “reaction-sintering” process involves separate preparation of UC and plutonium oxy-carbide by carbothermic synthesis of the respective oxides. The low temperature of plutonium oxy-carbide formation minimizes the plutonium volatilization loss. In the third step, the uranium carbide and plutonium oxy-carbide powders are blended, compacted and subjected to reaction sintering.

During carbothermic reduction, the control of the partial pressure of carbon monoxide is very important since the evolution of this gas not only constitutes the primary reduction mechanism but also controls kinetics of this reaction. The empirical relationships are:

$$k = k_0 [1 - (P/P_{CO})^{1/2}] \quad \text{Pickles [177]}$$

$$k = k_0 [1 - (P/P_{CO})^{1/4}] \quad \text{Ainsley [178]}$$

$k$  is a reaction rate to the ambient CO over pressure  $P$  in terms of the rate constant at zero over pressure  $k_0$  and equilibrium CO pressure  $P_{CO}$ .

In the carbothermic reduction of oxide, a high degree of micro-homogeneity of the starting oxide-carbon mixture is necessary. Otherwise, localized deficiencies and excesses of carbon will lead to the formation of unwanted phases. The requisite homogenization is achieved either by a 'dry method' involving prolonged milling and blending of the oxide-carbon powder-mixture followed by pelletizing or alternatively by a 'wet chemical route', popularly known as the 'sol-gel' process. In the 'sol-gel' route, gelled microspheres (100–200  $\mu\text{m}$ ) of oxide plus carbon are prepared from the nitrate solution of uranium and plutonium by ammonia external or internal gelation processes.

Figure 35 shows the sol-gel process adapted by the Paul Scherrer Institute (PSI), Switzerland, for fabrication of high density (U, Pu)C and (U, Pu)N microspheres for manufacturing 'vibro-sol' fuel pins [179–181]. The ammonia 'internal gelation' was followed for preparation of the hydrated gel-microspheres.

Figure 36 shows the process flow sheet with the process control steps developed in India for synthesis of plutonium rich (U, Pu)C with controlled amounts of residual oxygen and (U, Pu)<sub>2</sub>C<sub>3</sub>, by single step carbothermic synthesis in a static bed [182–183].

#### 4.2.2. Carbothermic reduction of oxide for synthesis of MN

The carbothermic synthesis of MN is represented by the overall simplified reaction:



Nitrogen plays the dual role of the reactant and the carrier for the removal of CO. The reaction product will have the general formula (MN<sub>1-x-y</sub>C<sub>x</sub>O<sub>y</sub>). The oxygen and carbon retained in MN will depend on the partial pressures of nitrogen and carbon monoxide, flow rate of reacting gas (N<sub>2</sub>, N<sub>2</sub> + H<sub>2</sub>), the oxide to carbon mole-ratio of the starting MO<sub>2</sub>-C mixture and whether hydrogen is used for removing the excess carbon. The ideal way to obtain nearly single phase MN with very low oxygen, carbon and higher nitride is to use around 10% excess carbon in the oxide-carbon mixture, a synthesis temperature of 1500–1600°C in flowing N<sub>2</sub>, followed by N<sub>2</sub> + H<sub>2</sub> and Ar. The CO in the exhaust gas should be closely monitored. The kinetics of the carbothermic synthesis of MN is a first order reaction where the rate constant 'k' at a given nitrogen flow rate 'F' (cm<sup>3</sup>/min) and temperature 'T' can be expressed by the following equation [184]:

$$\ln k = (-86000/RT) + 18.1 + 0.02F$$

The removal of CO is the primary kinetic effect of the flowing nitrogen and the above equation is valid for both fixed and fluidized bed reductions. In the powder route, which is most common, the UO<sub>2</sub>, PuO<sub>2</sub> and carbon powders are co-milled in a ball mill/attritor and compacted into tablets at 75–150 MPa. The tablets are loaded in a furnace and heated in the temperature range 1823–1923 K in flowing N<sub>2</sub>, followed by nitrogen-hydrogen mixture for removal of excess carbon and finally in argon for decomposition of sesqui-nitride, if any, to mono-nitride. The clinkers are crushed and ball milled to obtain mono-nitride powder. Sol-gel derived UO<sub>2</sub> + PuO<sub>2</sub> + C hydrated microspheres are ideal for carbothermic synthesis as the high specific surface area and homogenous powder mixtures facilitate the kinetics of the reaction. In addition, the number of process steps is less and fine powders are avoided. The nitride microspheres thus produced are of high density because of reaction sintering and could be directly vibro-packed in to one end welded fuel cladding tubes.

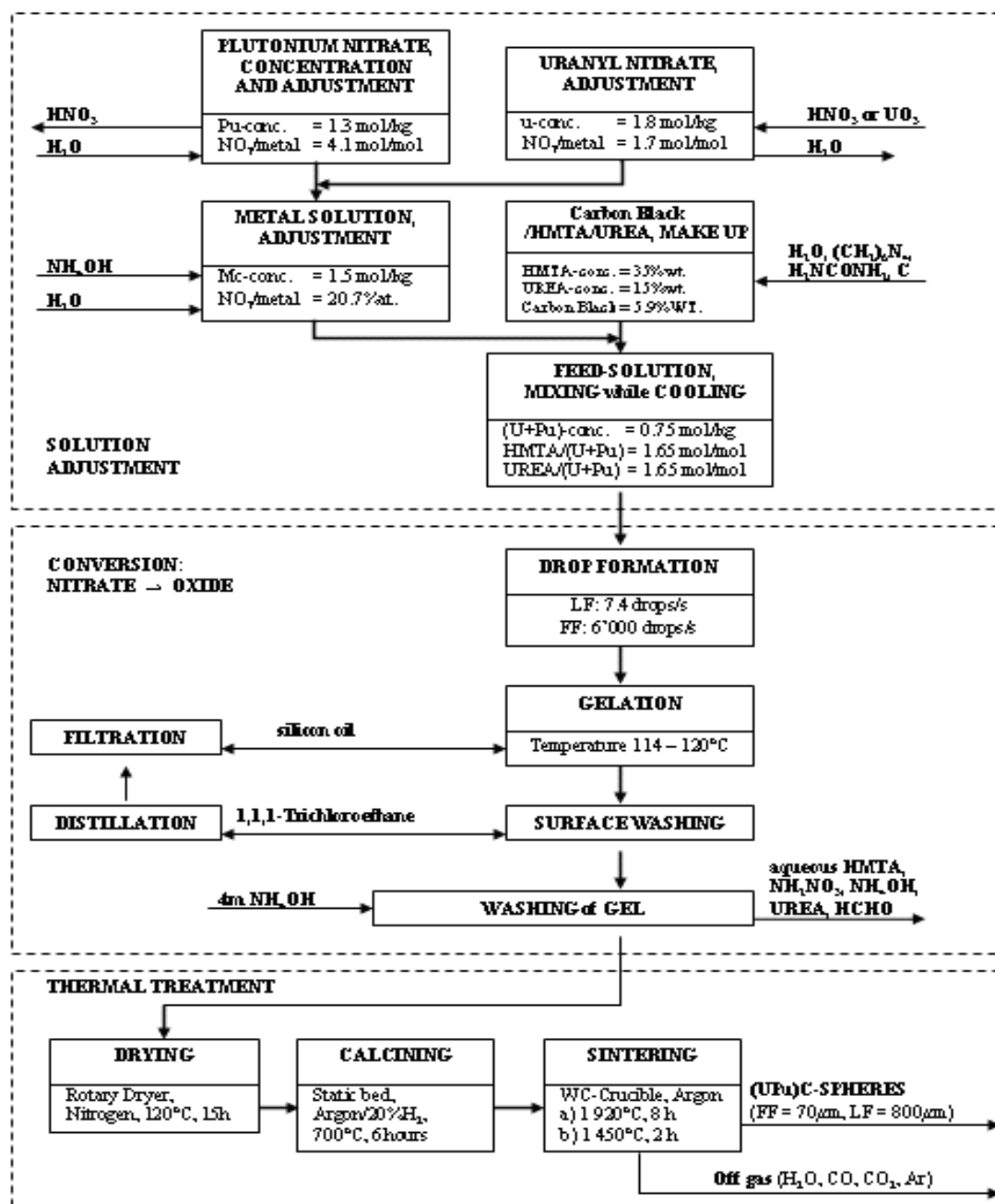


FIG. 35. Vibro-sol process, using ammonia internal gelation, for manufacturing (U, Pu)C and (U, Pu)N fuel pins in PSI, Switzerland.

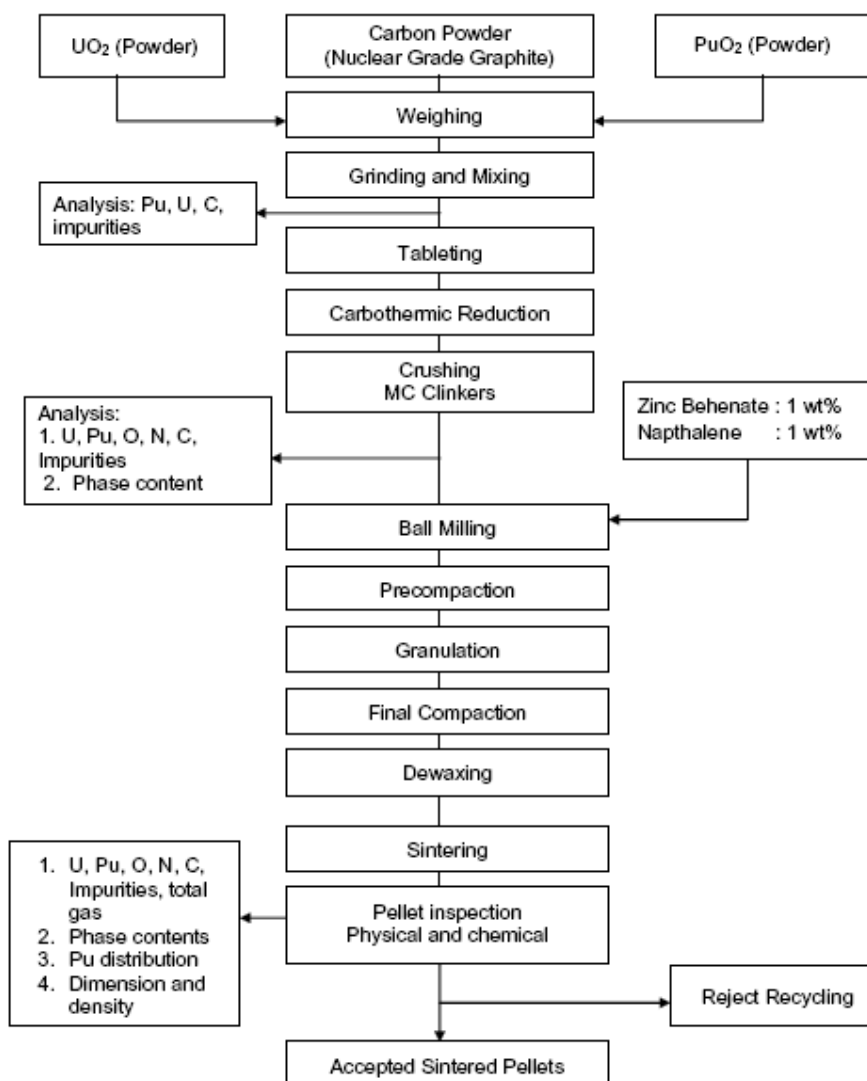


FIG.36. Process steps followed in India for preparation of plutonium rich (U, Pu) C pellets for FBTR. 'Single step' carbothermic synthesis in a static bed was followed for preparation of (U, Pu)C powder from  $\text{UO}_2$  and  $\text{PuO}_2$  feed powders.

The process flow sheets followed for synthesis and consolidation of (U, Pu)N fuel by 'powder-pellet', SGMP and vibro-sol processes are shown in Fig. 37 [185–186].

#### 4.3. CONSOLIDATION OF MC AND MN

The principal methods of consolidation of MC and MN buttons (ex-melting and casting process), clinkers, granules, spheroids, microspheres or powder in the form of small diameter fast reactor fuel pins are:

- Arc melting and skull casting;
- Cold pelletization of the powder into pellets followed by sintering;
- Direct pressing;
- Vibratory compaction of the granules, microspheres or crushed clinkers in cladding tubes;
- Sol gel microsphere pelletization.

The melting and casting route was not found to be attractive because of the need for the multiple re-meltings and high nitrogen over pressure ( $> 2$  MPa) during melting. Carbide and nitride rods made by this technique usually has very low oxygen impurity ( $< 0.04$  wt%) and large grains ( $> 100$   $\mu\text{m}$ ).

In the fabrication process involving cold pelletization followed by sintering, suitable binders and sintering aids (if any) are added to the milled powder and the milling is continued for several hours for proper homogenization. However, the use of attritor instead of ball mill reduces the milling time for powder homogenization significantly. The powder is then compacted into pellets (length to diameter ratio  $\sim 1.6$ ), preferably in a double action press at 60–200 MPa, followed by sintering in argon – hydrogen gas or vacuum in the temperature range 1400–1900°C. Pellets of MN with density 88–95% of theoretical are produced by pressing at 100–300 MPa and sintering in vacuum or in an atmosphere in argon and hydrogen mixture at  $\sim 1600^\circ\text{C}$ .

In the “direct pressing” route, the MC or MN clinkers after carbothermic synthesis are directly compacted and sintered thus avoiding the crushing and milling steps [187]. This process generates fuel pellets with densities in the range of 80–88% TD, reduces oxygen contamination, risk of self-ignition, dust generation, radiation exposure to personnel, concentration of metallic impurities, etc.

The vibratory compaction or vibro-sol route has several advantages over the “powder-pellet” route. First, the number of fabrication steps is lesser and there is maximum flexibility of operation. Given two or three different sizes of particles, fuel cladding tubes of any internal dimensions can be vibro-filled to a wide range of smear densities (60–90% TD). Unlike the other methods, the questions of surface grinding of rods, centerless grinding of pellets and die or mold sizing for particular pins do not arise at all. The vi-pack route is amenable to automation and remotization and avoids handling and generation of fine MC and MN powders, which are highly radiotoxic and pyrophoric.

The SGMP process is a hybrid of the Vibro-sol and the powder-pellet routes, where the fabrication advantages of sol-gel process is combined with the in-pile performance advantages of pellet-pin design.

The advantages of SGMP process are as follows:

- Radiotoxic dust hazard and pyrophoricity hazard are minimized;
- Dust free and free-flowing microspheres facilitate automation and remotization;
- Fabrication steps for monocarbide and mononitride fuel pellets are significantly reduced;
- Excellent micro-homogeneity is ensured in fuel pellets because U and Pu are mixed as nitrate solutions;
- Fabrication of relatively low-density pellets ( $\sim 85\%$  T.D.) with ‘open’ pore structure specified for He-bonded SFR fuel pins is possible without addition of pore former.

The process flow sheet developed in India consists of the following major steps:

- Preparation of hydrated gel-microspheres of  $\text{UO}_3 + \text{PuO}_2$  and  $\text{UO}_3 + \text{PuO}_2 + \text{C}$  by "ammonia internal gelation" process, using hexa methylene tetra amine (HMTA) as ammonia generator, urea as a buffer and silicone oil at  $90^\circ\text{C}$  as gelation bath;
- Carbothermic synthesis in vacuum and flowing  $\text{N}_2/\text{N}_2 + \text{H}_2$  for preparation of press-feed microspheres of (U, Pu)C and (U, Pu)N respectively;
- Cold-pelletization and sintering.

The dust-free and free-flowing MC and MN microspheres are directly cold-pelletized at around 1200 MPa and sintered at  $1700^\circ\text{C}$  in  $\text{Ar} + 8\%\text{H}_2$  atmosphere. The sintered pellets thus prepared have relatively low density ( $\sim 85\%$  TD) with lot of open porosity [188]. The blackberry microstructure is due to sintering within microspheres and not between them. Such a microstructure is desirable for He-bonded MC or MN fuel as the fission gas release is facilitated, thereby minimizing fuel swelling.

#### 4.4. MANUFACTURING OF CARBIDE AND NITRIDE FUELS WITH MA FOR IRRADIATION TESTING

Minor actinide bearing material have alpha specific activity two to three orders of magnitude higher than mixed uranium plutonium fuels and are associated with penetrating gamma and very high neutron radiation, requiring their fabrication to be done remotely in an alpha tight containment tight glove box or hot cell lined with heavy gamma and neutron shielding. The classical powder-pellet route is not suitable since the large number of powder handling steps increase radiotoxic dust hazard and requires frequent decontamination of the inner surface of the glove box/hot cell and the equipment inside. There is no industrial scale experience in fabricating high minor actinide bearing fuels. Presently, the preparation of this fuel is being carried out on a laboratory scale by avoiding the powder route.

As part of recent international collaboration between DOE, USA, ITU, Germany, JAERI, Japan and CEA, France on R&D on 'Fuels for Transmutation of Trans Uranic elements in Phenix (FUTURIX)' [189–192], a few mixed carbide and nitride fuel pins containing MAs have been prepared in the above laboratories. Figure 38 describes the process flow sheet developed in ITU, Germany for fabrication of mixed uranium, plutonium americium mono-nitride pellets by judicious combination of sol gel, impregnation (or infiltration) and pelletization process.

First, hydrated gel- microspheres of  $\text{UO}_3 + \text{PuO}_2 + \text{C}$  was prepared by the classical external gelation of ammonia process. Next, the microspheres were subjected to controlled calcination to form porous microspheres of  $\text{UO}_2 + \text{PuO}_2 + \text{C}$ . These microspheres were impregnated in Am nitrate solution such that the solution infiltrates into the microspheres. Thereafter, the microspheres containing Am is subjected to controlled carbothermic synthesis in flowing nitrogen atmosphere to obtain (U, Pu, Am)N microspheres, which were directly pelletized and sintered to (U, Pu, Am)N pellets. The same technique could be extended to (U, Pu, Np, Am)N. For burning Pu and MA, (Am, Np, Zr)N and (Pu, Am, Zr)N pellets could be prepared by first preparing  $\text{PuO}_2 + \text{ZrO}_2 + \text{C}$  microspheres by external gelation and infiltrating Am/Np nitrate solution followed by carbothermic nitridation, pelletization and sintering [193–197].

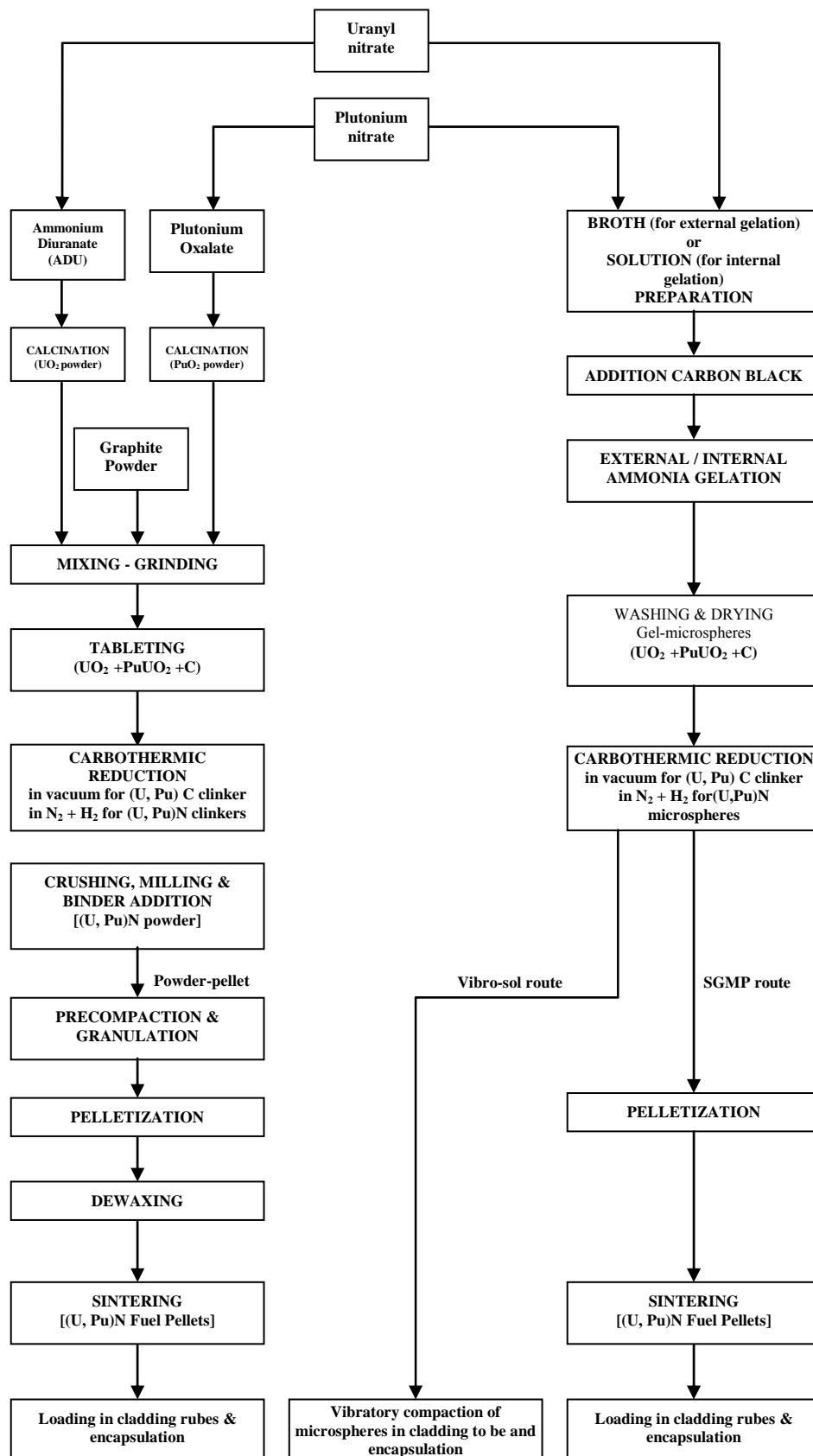


FIG. 37. Process flow sheet generally followed for synthesis of (U,Pu)N from  $UO_2$  and  $PuO_2$  powders.

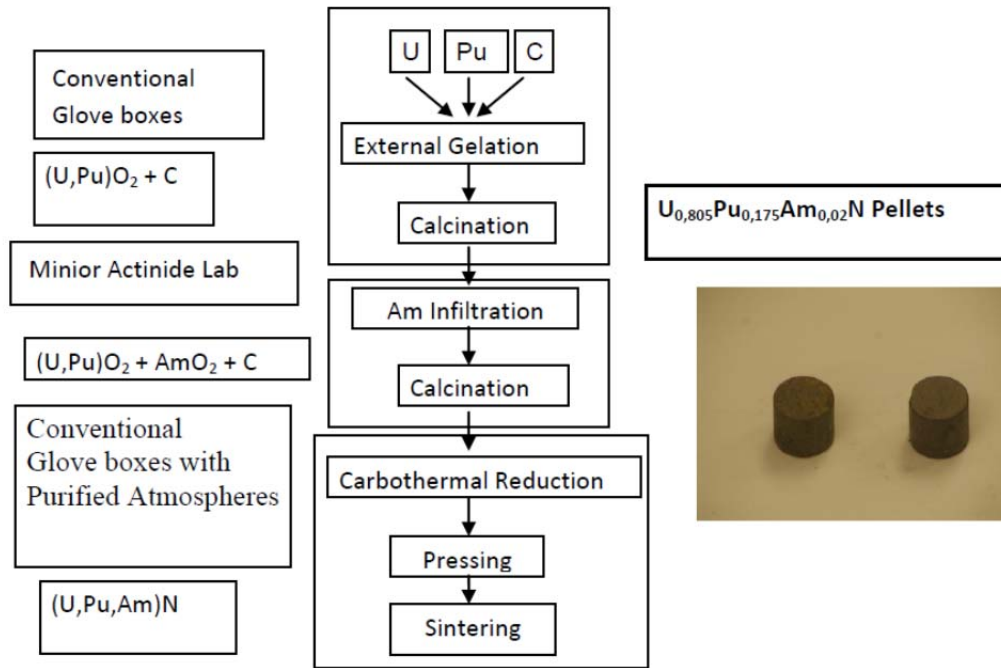


FIG. 38. Process flow sheet developed in ITU, Germany for fabrication of mixed uranium, plutonium americium mononitride pellets [196].

#### 4.5. SUMMARY

Mixed uranium plutonium mono-carbide and mono-nitride are advanced fuels for SFRs on the basis of their higher breeding ratio and better thermal conductivity compared to the mixed oxide fuel. The chemical compatibility of these fuels with sodium coolant and stainless steel cladding is excellent. However, so far, the manufacturing experiences of mono-carbide and mono-nitride fuels have been restricted to pilot plant and laboratory scale preparation mainly for irradiation testing experiments. These fuels are pyrophoric in powder form, involve more number of process steps, as compared to oxide fuel and are difficult to manufacture as single phase materials. The manufacturing processes require stringent control of oxygen, carbon and nitrogen content. The sol gel processes, including the vibro-sol (sphere-pac) and SGMP are ideally suitable for manufacturing these fuels as these processes are dust-free and amenable to remote processing and automation. In recent years, MA bearing MC and MN fuel pins have been prepared on a laboratory scale by adapting the sol gel processes and infiltration technique.

### 5. FABRICATION TECHNOLOGY OF METALLIC FUELS

#### 5.1. INTRODUCTION

Metallic fuel was first manufactured for the experimental fast reactors in the USA and UK, in the 1950s. The EBR-I in US used unalloyed uranium, U-Zr and Pu-Al and the Enrico Fermi reactor was fuelled with U-Mo alloy. The DFR in UK utilized the U-Mo alloy fuel and also tried the U-Cr alloy. The major drawbacks of metallic uranium and plutonium and some of their alloys are unusual irradiation growth and swelling attributed to anisotropic crystal structure and formation of low melting eutectic with stainless steel cladding material. With addition of proper alloying elements and following proper heat treatment the isotropic phases



are made predominant which enhanced the dimensional stability. The EBR-II initially operated with U-5%Fs (Fs is fission, a simulated mixture of noble metal fission products of composition (wt%): 2.4% Mo, 1.9% Ru, 0.3% Rh, 0.2% Pd, 0.1% Zr and 0.01% Nb) cores and later used U-Zr as driver fuel. Later, an integral fast reactor (IFR) concept was developed in the USA, for which the choice of fuel was U-19 wt% Pu-10 wt% Zr. Zirconium was added to increase the solidus temperature of the fuel and to enhance the chemical compatibility between fuel and stainless steel cladding. A number of U-Pu-Zr fuel pins were irradiated in EBR-II and FFTF to high burnup (20 at.%) [198–201].

## 5.2. METALLIC AND THE INTEGRAL FAST REACTOR (IFR)

The integral fast reactor (IFR) concept [202–203] and its fuel cycle were developed in USA with the objective of co-locating the fast reactor with the spent fuel reprocessing and fuel fabrication plant in order to minimize transportation cost of special nuclear material, improve nuclear security and reduce fuel cycle cost. In addition, short cooled spent fuel could be reprocessed and the U, Pu and MA recycled thereby minimizing the volume, radio-toxicity and decay heat of high level waste for permanent disposal in repository. The IFR fuel cycle, shown in Fig. 39, is based on pyro-processing of its spent U-Pu-Zr alloy fuel using electro refining process with molten salt electrolyte. The process avoids separate plutonium stream thereby enhancing proliferation resistance in fuel cycle. The molten salt electro refining operation involves the following steps:

- Chopping of fuel pin containing spent fuel into pieces and loading into the electro refining cell in a basket;
- Addition of  $\text{CdCl}_2$  to the electro refining cell at a temperature of 773 K to transfer most of the actinides, sodium and fission products as chlorides to the electrolyte (eutectic mixture of KCl and LiCl);
- Deposition of U on a solid cathode (dendritic deposit);
- Introduction of cadmium cathode in the cell as the pre-determined concentration of Pu is reached in the electrolyte to deposit Pu and the remaining actinides, including an approximately equal amount of uranium on the cadmium cathode.

A cylindrical rod of low carbon steel (zirconium, molybdenum or uranium also may be used) is used as the cathode for selective deposition of uranium. The higher thermodynamic stability of  $\text{PuCl}_3$  compared to  $\text{UCl}_3$  renders the deposition of plutonium on solid cathode impossible, unless the  $\text{PuCl}_3$  to  $\text{UCl}_3$  ratio is  $>2$  which is not realizable under normal process conditions. However, co-deposition of uranium and plutonium on liquid cadmium cathode is enabled by the lower activity coefficient of Pu in cadmium compared to that of uranium. Liquid cadmium cathode (liquid cadmium in a beryllia crucible) is used in the IFR reactor fuel cycle pyro-processing. The deposit of uranium and plutonium on the cadmium cathode tends to grow and short the electrodes and hence a rotating cathode is used to compress the salt/cadmium surface to produce a deposit without dendrites. Cathode deposits are removed from the electro-refining cell after the process is completed. Uranium is separated from the salt (in case of solid cathode) and U-Transuranium elements (TRU) from cadmium (in case of molten cadmium) through distillation in a retort and then melted. Ingots of materials are used for fabrication of fuel elements by injection casting process.

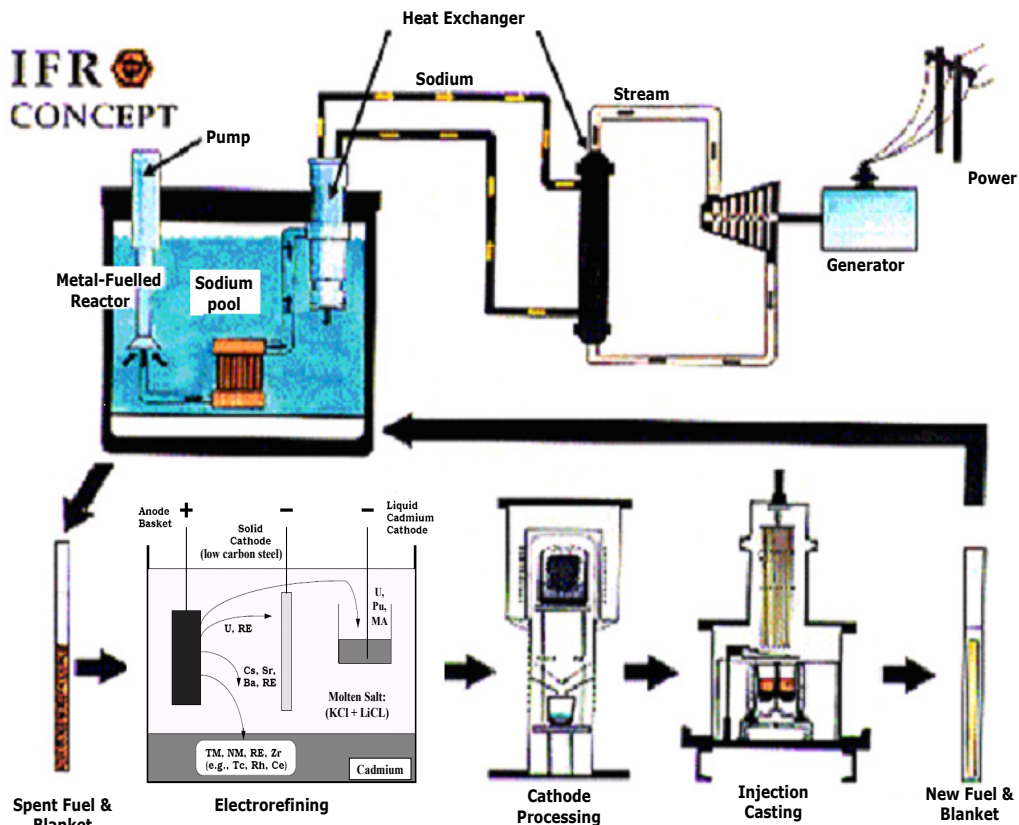


FIG. 39. Schematic of Integral Fast Reactor (IFR) with metallic fuel showing co-location of reactor spent fuel electro refining and fuel Re-fabrication plants[202].

The closed fuel cycle, with the reprocessed product always remaining highly radioactive, was the key to proliferation resistance of IFR. This fuel cycle made use of the minor actinides and as well the bred plutonium by multiple recycling.

### 5.3. MELTING AND CASTING OF U-Zr AND U-Pu-Zr FUEL PINS

#### 5.3.1. Activities in the USA

The U-Zr and U-Pu-Zr alloys were developed by Argonne National Laboratory (ANL) and Idaho National Laboratory (INL) in USA along with EBR-II programme and the integral fast reactor (IFR) concept [204–208].

Figure 40 shows the principal components of a metal fuel pin. The fuel slug is cast such that a gap exists initially between fuel and cladding. The gap is sized to allow enough fuel swelling for interconnected porosity and gas release to occur. The gap is filled with sodium for adequate heat transfer during early stages of irradiation, before the fuel has swelled to contact the cladding. The sodium partially fills the porosity when interconnection occurs. The free plenum above the fuel is sized to keep the hoop stress on the cladding, due to gas pressure from fission gas release, within tolerable limits, to accommodate displaced sodium and also to accommodate axial expansion of fuel rod. The plenum above the fuel is initially filled with helium and a xenon isotope tag gas. The wire wrap around the cladding ensures pin to pin separation and uniform flow of the liquid sodium coolant.

Injection casting technique has proved to be the best method for remote and automated fabrication of highly radiotoxic sodium-bonded U-Zr and U-Pu-Zr fuel. Around 10wt% of

zirconium increases the solidus temperature of U-Pu binary alloy and provides adequate safety margin during in-pile operation. The technique has been utilized for remote fabrication of some 35 000 fuel pins of U-Zr and U-Pu-Zr. A few fuel pins of U-Pu-Zr-Np-Am were also fabricated for irradiation testing in EBR-II.

Figure 41 shows the flow sheet for preparation of these fuels using uranium, plutonium and zirconium metals as feed materials. First, the feed materials are loaded in yttria coated graphite crucible and subjected to melting in an induction furnace with dual frequency. At high frequency the field couples with the graphite crucible for heating of the melt while at low frequency the field couples with the melt for a stirring effect, which facilitates homogeneous distribution of U, Pu and Zr in the melt. The yttria coating prevents the melt from reacting with the graphite crucible. The crucibles are capable of repeated use. The melt is heated to about 1600°C under an argon atmosphere. The furnace is then evacuated and a pallet containing some 100 one-end closed quartz molds is immersed with the open end of the molds in the melt. The furnace is immediately pressurized with argon to fill the quartz molds. The pallet that contains the molds is lifted from the melt where the cast fuel immediately solidifies. Figure 42 shows a photograph of the injection casting facility at the Argonne National Laboratory.

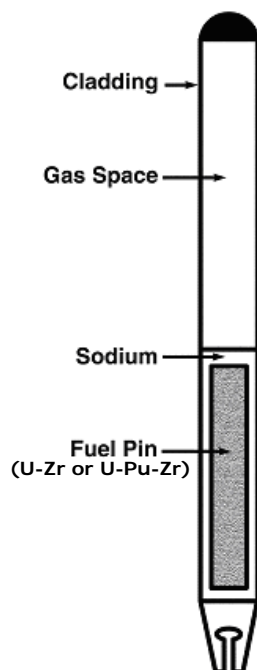


FIG. 40. Principal components of sodium-bonded metallic (U-Zr & U-Pu-Zr) fuel pin.

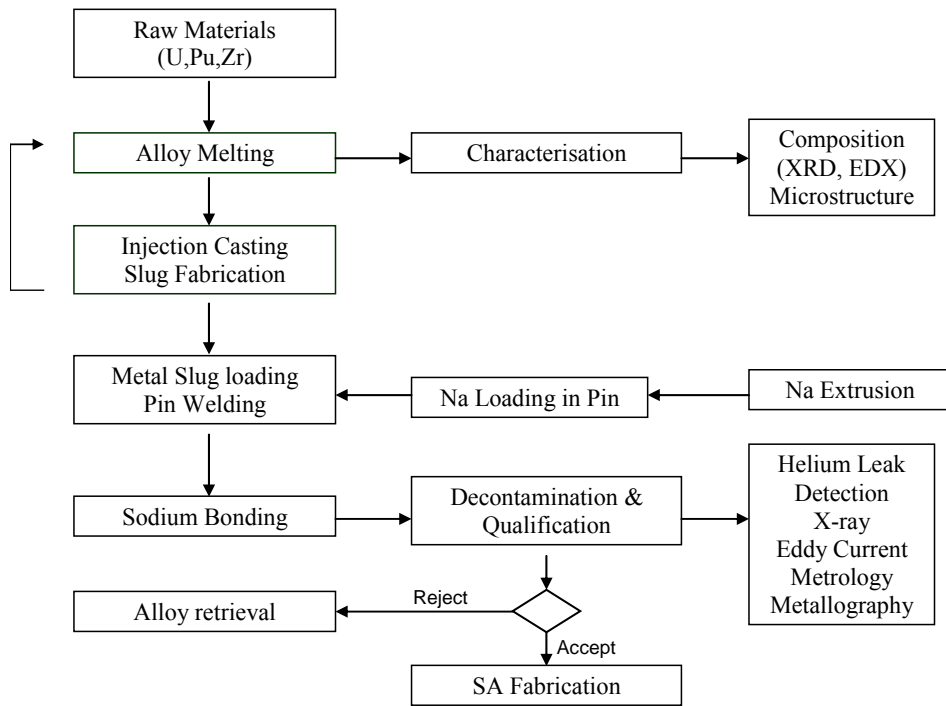


FIG. 41. Flow sheet for fabrication of sodium-bonded U-Zr and U-Pu-Zr fuel pins.

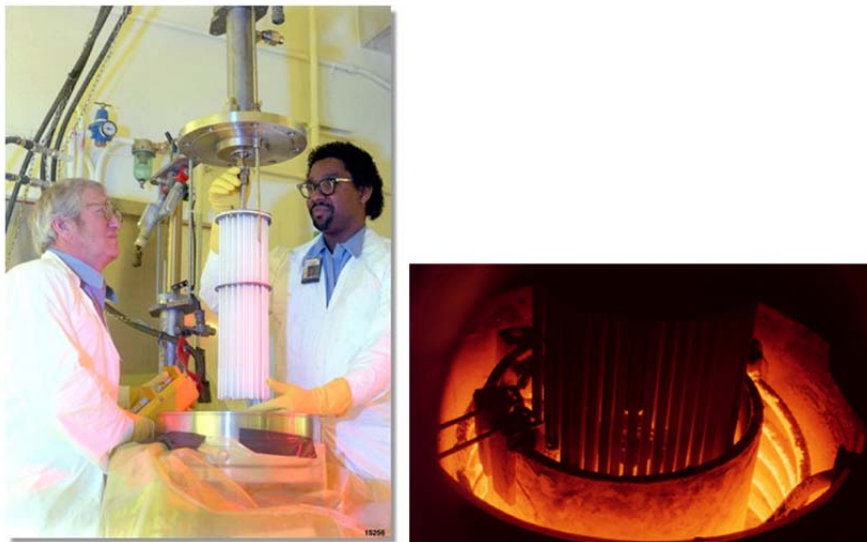


FIG. 42. Facilities for injection casting of U-Zr and U-Pu-Zr metallic fuel in ANL, USA [208].

The quartz molds are coated with zirconia to prevent the fuel slugs from sticking to the molds. Upon cooling, the fuel slugs are removed from the quartz molds and sheared to length. No grinding of the surface of the slugs is necessary because the diameter of the fuel slugs reflect the precision of the quartz molds. The temperature of the melt should not exceed 1600°C because the quartz will soften to an unacceptable extent. Thus, the amount of zirconium added to uranium was limited to 10 wt%.

Once injection is cast, the fuel slugs are inserted directly into the cladding that contains the sodium bond. Any excess material after cutting the metal fuel slugs is simply put in the next casting rather than directed to the initial steps of a complicated ceramic powder preparation line. Subsequent steps for the loading of the fuel pin are first to put the fuel slug in the cladding jacket and then add the appropriate amount of solid sodium. This is done in a helium glove box for cold fuel. The pins are then heated to liquefy the sodium and xenon tag gas, if desired, is added. An end cap is then welded on the cladding jacket. Bond quality is deduced by measuring the sodium level in the plenum above the fuel with x-ray radiography and eddy current testing. All of the above steps lend themselves readily to remote fabrication in a hot cell environment.

The casting of the fuel pins is sensitive to a few parameters. The type of defects that would occur in the fuel slugs are porosity, hot tears, and short slugs. The parameters that need to be optimized to avoid these defects are the melt temperature, temperature of the molds prior to injection of the fuel, rate of pressurization, and the quality of the zirconia mold wash.

Improvements in the injection casting process involved the search for better molds to replace the quartz molds and reusable crucibles that would last longer than the graphite crucibles. One method that was successfully used was to cast directly into thin zirconium tubes. The idea was that since the zirconium migrated to the surface of the fuel during irradiation that the performance would not be altered. Both the fuel and the zirconium tube were put in the stainless steel cladding. Beryllia crucibles were successfully used on a limited basis to replace the graphite crucibles used for melting the fuel charge.

### **5.3.2. Activities in Japan**

Based on the successful developmental activities in USA, the Central Research Institute of Electric Power Industry (CRIEPI), Japan, has set up an engineering scale injection casting furnace (Fig. 43) with support from MEXT (Ministry of Education, Culture, Sports, Science and Technology) [209–211]. The maximum metal charge of the furnace is approximately 20 kg of the U-Zr alloy per batch. Uranium and zirconium metals are melted in a graphite crucible which is inductively heated in a 30 kW furnace at 3 kHz. The graphite crucible is internally coated with yttria for avoiding any chemical interaction between the molten metal and graphite. The mold bundle had 38–72 one end closed silica molds coated internally with zirconia. After melting, the crucible is evacuated and the open-ends of the silica molds are lowered into the molten metal alloy. The vessel is then refilled with argon in order to inject molten fuel alloy into the silica molds. After cooling, the fuel alloy castings are sheared off at both ends. The cast slugs met the following specifications:

Diameter:  $5 \pm 0.05$  mm, Length: ~400 mm, Density: 15.3–16.1 g/cm<sup>3</sup>, Zr:  $10 \pm 1$  wt%, Total impurity (C, N, O, Si): <2000 ppm.

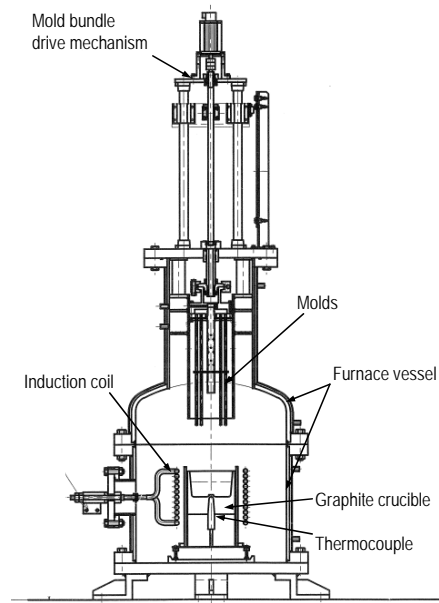


FIG. 43. Outline of metal fuel fabrication process by injection casting.

Small scale U-Pu-Zr injection casting tests were performed by CRIEPI in collaboration with JAEA [212–215]. Before casting of U-Pu-Zr fuel slug, U-Pu alloy ingots were prepared from MOX by electro-chemical reduction technique, as shown in Fig. 44 because of its high production efficiency. The apparatus was installed in high-purity Ar glove box with the salt distillation furnace. LiCl-1wt%  $\text{Li}_2\text{O}$  molten salt was loaded in MgO crucible and kept at 650°C. The anode was Pt, and the cathode was the sintered MOX pellets charged in the tungsten basket. The Pu content,  $\text{Pu}/(\text{U} + \text{Pu})$  in the MOX pellets was 60 wt%. The completion of the electrochemical reduction was determined from the change in the cathode potential. Because the cathode product is porous and includes the LiCl salt, it needs to be heated up for consolidation of the metal and distillation of the salt. The cathode product was loaded in the yttria crucible placed at the bottom of the graphite main vessel, which was heated up by the resistance heater.

Preliminary tests revealed the optimized heating sequence: heating up to 850°C under atmospheric pressure, keeping at 850°C under atmospheric pressure for 1 hour for the metal consolidation, then keeping at 850°C under reduced pressure ( $\sim 30$  Pa) for 1 hour for the salt distillation.

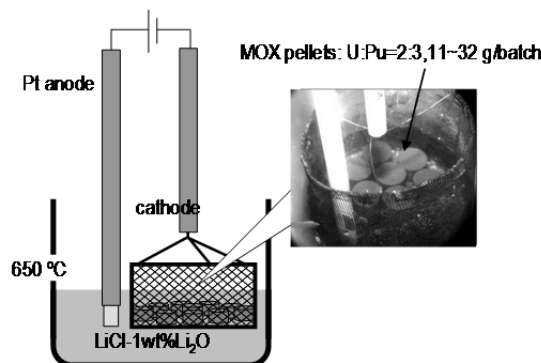


FIG. 44. Processes for the electro-chemical reductions of MOX.

The U-Pu ingot obtained after the salt distillation showed surface oxidation to some extent, but its cross-section shows metallic luster. The recovery ratio of U-Pu throughout the process was > 99%. The oxygen content in the ingot was less than 1000 ppm, which is allowable since the U-Pu ingot is diluted with high-purity U and Zr metal during the injection casting of fuel slug.

For the fabrication of the U-Pu-Zr fuel slug, a miniature-scale injection casting furnace was installed in high purity Ar glove box in JAEA, Oarai-site. The graphite crucible of 20 mm in inner diameter and 45 mm in height is coated with yttria and induction-heated by the water-cooled copper coil at the maximum power of 10 kW. The alumina thermal insulator is placed between the induction coil and the crucible. The silica mold has an inner diameter of 5mm and an inner height of 280 mm, and its inner surface is coated with zirconia. One mold is used for one casting batch.

The starting materials were the heel and scraps produced in the preceding casting batch, the U-Pu alloy ingots, U metal and Zr metal. The weights of these materials were adjusted so that the total amount and averaged composition was about 120g and U-20 wt% Pu-10 wt% Zr respectively. As in the case of the engineering-scale injection casting, the electro-magnetic force applied to the molten alloy was maximized by intermittently providing 100% induction heating power in order to enhance homogeneity of the molten alloy. The processes parameters for injection casting are as follows:

Melt temperature prior to injection casting: 1480°C,

Pressurizing rate: 0.13 MPa/s,

Terminal pressure: 0.18 MPa

The cast alloy rod was taken from the bottom end of the mold and the zirconia on the surface of the rod was removed. The top and bottom ends of the rod were cut off to obtain sufficiently homogeneous fuel slugs with good surface finish, as shown in Table 9 and Fig. 45. Six of these slugs were encapsulated into test pins for irradiation in JOYO.

CRIEPI, CEA and JRC-ITU have jointly conducted the METAPHIX (metal fuel irradiation in Phenix reactor) experiment for transmutation of MA. Nine sodium bonded metal fuel pins of compositions U-19 Pu-10 Zr (3 pins), U-19 Pu-10 Zr-2 MA-2 RE (3 pins), U-19 Pu-10 Zr-5 MA (2pins) and U-19 Pu-10 Zr-5 MA-5 RE were prepared by CRIEPI and subjected to irradiation testing in Phenix reactor successfully to burnup levels of 7–11 at.% [216].

TABLE 9. COMPOSITIONS (wt%) AT DIFFERENT AXIAL POSITIONS OF THE U-Pu-Zr FUEL SLUG

Position	U	Pu	Zr	Am
Upper	69.0	20.5	10.2	0.31
Middle	69.2	20.5	10.0	0.31
Lower	68.2	20.5	11.0	0.32

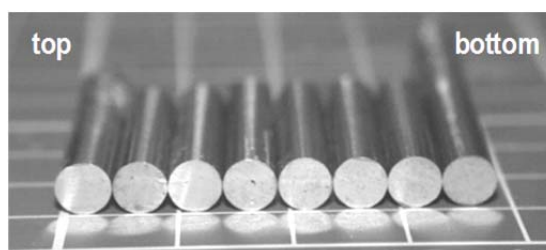


FIG. 45. Cross-sections at different axial positions of the U-Pu-Zr fuel slug.

### 5.3.3. Activities in the Republic of Korea

R&D activities related to manufacturing technology of metallic fuel for SFR are being developed at Korean Atomic Energy Research Institute (KAERI) since 2007. Various casting technologies are being explored on a laboratory scale. Rod-type samples of U-Zr and U-Zr-Ce (Cerium as Am surrogate) were fabricated by vacuum injection casting and vacuum-assisted gravity casting. Alternate fabrication techniques such as continuous casting which was used for fabrication of U rods and centrifugal atomization for the preparation of spherical powder of U-Zr are being developed.

U-(5, 10 & 15) wt% Zr binary-alloys and U-10 wt% Zr-(2, 4 & 6) wt% Ce ternary alloys were cast by vacuum injection casting using an assembly of quartz tube molds. The diameters of U-Zr and U-Zr-Ce rods were in the range of 4–7 mm and the lengths were around 200 mm. Although vacuum injection casting was a proven technology for mass production of metallic fuel pins, further improvements are needed in order to fabricate metallic fuel with minor actinides. High level vacuum on the melt may facilitate evaporation of Am with a high vapor pressure and use of the quartz mold may produce huge volumes of long-lived radioactive wastes. A vacuum-assisted gravity casting system was designed and installed recently as shown in Figure 46 in order to reduce the vaporization of Am during the casting process [217]. The upper chamber for a crucible and the lower chamber for a mold were separated to provide a pressure difference between the two chambers. During the casting of U-Zr rod, the crucible chamber was pressurized and the mold chamber was evacuated in order to facilitate an inflow of the melt into the mold assembly. High pressure of the crucible chamber and a crucible cover in this system can reduce the vaporization of Am under an inert atmosphere.

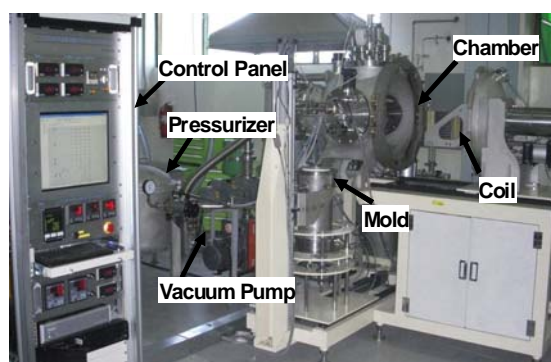


FIG. 46. Vacuum-assisted gravity casting system for metallic fuel installed in the KAERI [217].



Good quality U-(5, 10 & 15) wt.% Zr and U-10 wt% Zr-(2, 4 & 6) wt.% Ce rods with 6–10 mm in diameter and 300 mm in length were fabricated by the vacuum-assisted gravity casting.

Spherical U-10 wt% Zr powder was fabricated by the centrifugal atomization method [218]. Figure 47 shows the SEM micrograph of U-10% Zr powder. The spherical alloy powder of different size fractions could be subjected to vibro-packing into a stainless steel cladding or a Zr sheath tube. The atomized U-Zr powder has finer grains and lamellar structure which would enhance fission gas release rate during irradiation and in turn minimize fuel swelling as compared to conventional cast U-Zr alloy pin.

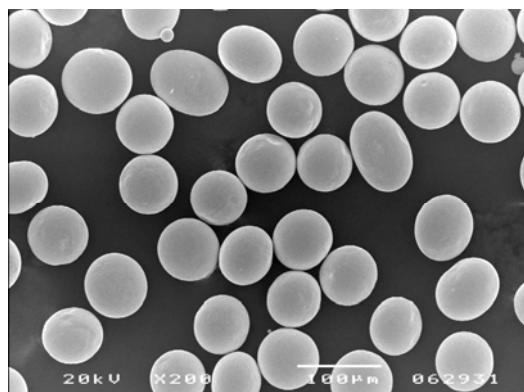


FIG. 47. Morphology of U-10wt% Zr powder fabricated by a centrifugal atomization.

An R&D activity is underway to explore the possibility of ‘continuous casting’ as an alternative route for manufacturing U-Zr and U-Pu-Zr metallic fuels [219]. This technique would avoid waste mould and the entire charge in the crucible transferred, leaving no residue. Preliminary trials with uranium metal yielded high quality uranium rods without any residue in the crucible (Figure 48). Continuous casting of U-Zr alloy with a smaller diameter is under development. It is difficult to optimize the continuous casting conditions for binary, ternary and multi-component (containing MA) uranium alloys because of the large temperature range for solidification as compared to pure uranium metal.

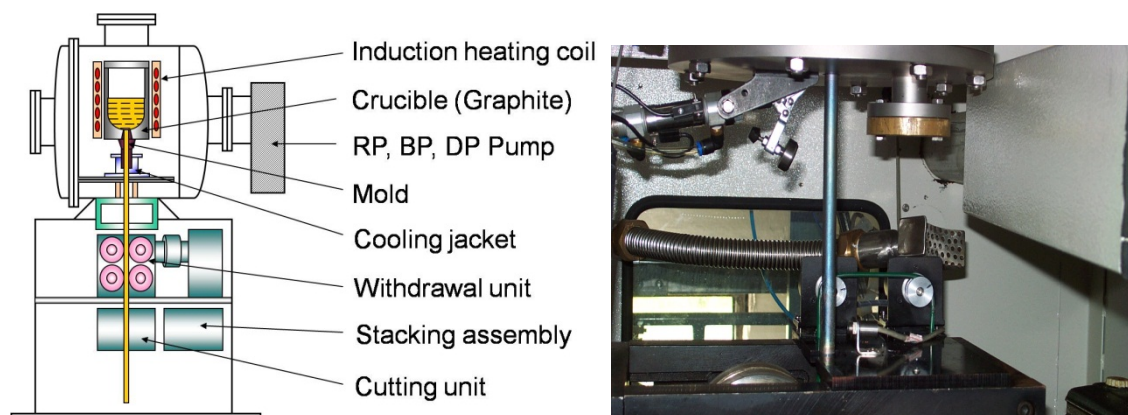


FIG. 48. Conceptual diagram of continuous casting system showing uranium rod extracted [219].

#### 5.4. FABRICATION OF MA BEARING METALLIC FUELS

In recent years there has been renewed interest in metallic fuel in USA with focus on developing process flow sheet for fabrication of MA bearing ternary and multi-component transmutation fuels for SFR. Transmutation fuels usually consist of a blend of five heavy metal elements (U, Pu, Am, Np, Cm) rather than just one or two (U and/or Pu) typical of conventional SFR fuels. The heavy metal elements used in transmutation fuels have thermodynamic properties considerably different from uranium and plutonium and their effect on fuel properties must be factored into the fabrication process. The final TRU fuel form must accommodate a variable composition in terms of the ratio and content of the heavy metal elements and associated fission product impurities. Considering the differences mentioned above, it is clear that the transmutation fuels of interest are not a simple extension of previously deployed fuels. It is important to note that the compositional and isotopic variability required of the fast reactor transmutation fuel is much wider than the narrow technical specifications used in a conventional fast reactor fuel that is obtained from a uniform feedstock. An international programme is underway on fabrication, irradiation, and post-irradiation examination of these fuels. The injection casting technique, used in the 1970s for fabricating binary U-Zr and ternary U-Pu-Zr alloys, was followed for preparing small slugs (~4cm) of the following MA bearing metallic fuel at Idaho National Laboratory and JRC-ITU and irradiated in the Advanced Test Reactor- (ATR) in USA and in Phenix reactor (the FUTURIX-FTA test):

- (i) U-29 Pu-4 Am-2 Np-30 Zr for FUTURIX-FTA (Phenix);
- (ii) U-19 Pu-10 Zr-(2,5) MA-(2,5) RE for METAPHIX (Phenix);
- (iii) U-20 Pu-10 Zr-2.1 Am-1.3 Np for EBR-II X501(ATR);
- (iv) U-Pu-Zr-MA-RE for AFC-1, 2 (ATR);
- (v) U-20 Pu-3 Am-2 Np-15 Zr;
- (vi) U-20 Pu-3 Am-2 Np-1 RE-15 Zr;
- (vii) U-20 Pu-3 Am-2 Np-1.5 RE-15 Zr;
- (viii) U-30 Pu-5 Am-3 Np-20 Zr;
- (ix) U-30 Pu-5 Am-3 Np-1 RE-20 Zr;
- (x) U-30 Pu-5 Am-3 Np-1.5 RE-20 Zr .

The study of transmutation of MA-bearing metallic fuel in SFR was also started in Japan by CRIEPI in 1986 in collaboration with Joint Research Center - Institute for Transuranium Elements (JRC-ITU). In order to determine the compositions of the MA bearing metallic fuel slugs to be irradiated, the miscibilities among the constituents of U-Pu-Zr-MA-RE alloys (RE stands for the mixture of rare earth elements) were examined as these may be entrained in MA during pyro-processing. Arc-melting tests of various U-Pu-Zr-MA-RE alloys have indicated that the homogeneous dispersion of RE rich precipitates cannot be attained when the RE content is higher than 5 wt%, but MA (Np and Am) dissolves uniformly in the U-Pu-Zr alloys containing no RE but <25 wt% MA. In U-19 Pu-10 Zr-5 MA-5 RE alloy, RE and Am rich precipitates disperse uniformly even after annealing at 500–850°C, as shown in Fig. 49.

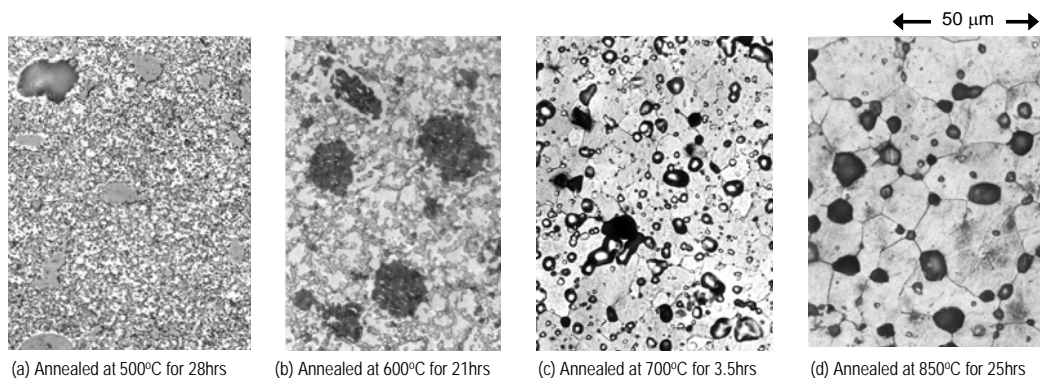


FIG. 49. Metallography of annealed U-19 Pu-10 Zr-3 Np-2 Am-0.2 Y-1.2 Ce-3.6 Nd alloy (wt %) etched.

The preparations of Am and Cm metals were needed to fabricate the MA-bearing fuel slugs. Am and Cm were procured in the form of dioxides.  $\text{AmO}_2$  and  $\text{CmO}_2$  then reduced to sesqui-oxides,  $\text{Am}_2\text{O}_3$  and  $\text{Cm}_2\text{O}_3$ . The Am and Cm sesqui-oxide powders were mixed with La and Th metal powders respectively, ball-milled and pelletized by pressing.  $\text{Am}_2\text{O}_3$ -La pellets were heated up to about 1600 K in a closed furnace in a vacuum atmosphere. Reduced Am metal was vaporized, condensed at the colder end of the furnace, and collected by scraping.  $\text{Cm}_2\text{O}_3$ -Th pellets were heated up to about 2100 K and condensed in the same manner. The Am and Cm metals thus produced were used for preparing MA bearing metal fuel in shielded hot cells in JRC-ITU.

Four types of metal fuel alloys, U-19 Pu-10 Zr, U-19 Pu-10 Zr-2 MA-2 RE, U-19 Pu-10 Zr-5 MA and U-19 Pu-10 Zr-5 MA-5 RE were cast into 20–50 mm long rods in yttria molds and used for irradiation testing in Phenix. The U-Pu-Zr and U-Pu-Zr-MA alloys without RE were easily prepared by arc-melting of the constituent metal mixture in an argon atmosphere. On the other hand, some difficulty was encountered in preparing homogeneous RE containing alloys by simple arc-melting because of the low miscibility of RE in U-Pu-Zr-MA alloys. To improve the homogeneity, powders of U-Pu-Zr-MA and RE were first prepared and then blended mechanically before melting, as shown in Figure 50. The metallography of the alloy obtained by arc-melting the powder of U-Pu-Zr containing 7 wt% RE confirmed that the RE rich precipitates were dispersed homogeneously in the actinide matrix. The four types of fuel alloys prepared by the above methods were compatible with the molten alloys. The cast fuel slugs are shown in Fig. 51.

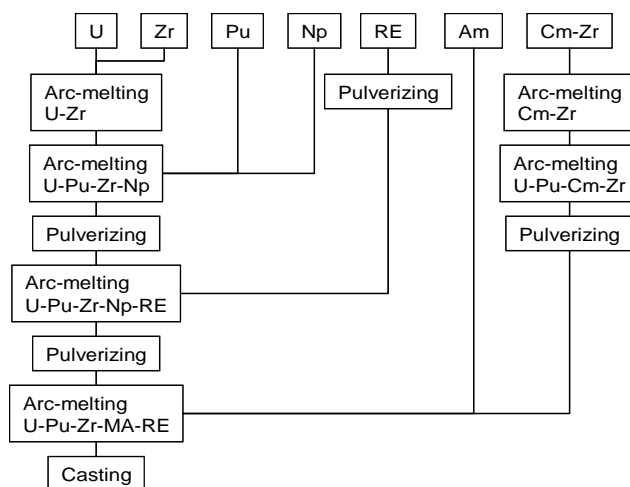


FIG. 50. Fabrication schedules of U-Pu-Zr, U-Pu-Zr-M and U-Pu-Zr-MA-RE alloy slugs.

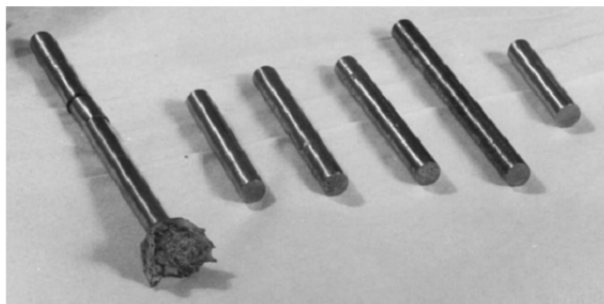


FIG. 51. Cast MA bearing fuel slugs.

Four types of metal fuel alloys with low MA + RE content has been fabricated by JRC-ITU for irradiation testing in PHENIX, namely, U-19 Pu-10 Zr, U-19 Pu-10 Zr-2 MA-2 RE, U-19 Pu-10 Zr-5 MA and U-19 Pu-10 Zr-5 MA-5 RE in CRIEPI/JRC-ITU joint programme.

## 5.5. SUMMARY

Most of the research on metallic fuel for SFRs was carried out in the 1970s and 1980s in ANL and INL, USA that led to the development of the U-Pu-Zr fuel and the IFR concept with several attractive features including ease of remote and automated fabrication, efficient utilization of uranium and plutonium resources, burning of MA and proliferation — resistance of fissile and fertile materials. Unfortunately, from 1985 onwards the activity on metallic fuel was progressively tapered off and finally terminated in 1992. In recent years, there has been renewed interest in USA in developing MA bearing metallic fuel for transmutation in SFR. International collaboration with CEA, ITU, JAEA, and CRIEPI for irradiation testing in fast reactors is underway. Metallic fuel is the preferred host for minor actinides because of the possibility of co-depositing MA with U and Pu during pyro-processing. However, the multicomponent MA bearing transmutation fuel is not a simple extension of previously deployed U-Zr and U-Pu-Zr fuels. In-depth research and development programme is required to investigate solutions to the challenges of developing, manufacturing, irradiation testing, and ultimately qualifying transmutation fuels. There is also a need to develop engineering-scale remote fabrication capabilities with automation for TRU bearing metallic fuels with batch size of several kilograms. Mitigating Am loss during fabrication is a challenge. Vacuum assisted gravity casting could be explored. Based on these experiences, industrial-scale plant could be set up in the future.

## 6. FABRICATION TECHNOLOGY OF FUELS FOR RESEARCH REACTOR

### 6.1. INTRODUCTION

Non-power reactors are essentially fission neutron sources. These reactors generate neutrons for either beam line experiments outside the reactor or for irradiation of materials inside the core. Hence, the main objective of most research reactors is to produce as much neutrons as possible in a compact core. The best way to do this is to increase the fissile material ( $^{235}\text{U}$ ) enrichment in the fuel. For this reason, historically, a large number of research reactors ran with HEU containing  $> 90\%$   $^{235}\text{U}$  in the 1960 and 1970s. Very few non-power reactors have been constructed with large core. These reactors are usually moderated by heavy water and cooled with either light water or heavy water and use natural uranium monolithic metal rod or pin cluster, clad in aluminium, as fuel. The 42 MW (t) NRX reactor

in Canada (shut down) and the 40 MW (t) CIRUS (shut down) and 100 MW (t) DHRUVA in India are examples of non-power reactors with large cores [220–221].

In most cases, non-power reactors do not utilize fission heat energy for generation of electricity or for non-electric application. These reactors are mostly light water cooled and moderated thermal reactors with compact cores, with the coolant temperature seldom exceeding 1000°C. Materials test reactors (MTR), pool or tank type [222], and testing, research and isotope production reactors of General Atomics, USA (TRIGA) [223] are most common. These reactors use aluminium and its alloys as structural material for the reactor core and fuel element and assembly. However, there are some non-power reactors that use graphite as moderator and structural material and high temperature helium or CO<sub>2</sub> gas as coolant. In addition, there are a few sodium cooled, non-power fast reactors.

The fuel design of water-cooled research reactors differs from reactor to reactor but is mostly in the form of assemblies of plates or pins. The plate fuel assemblies consist of a number of flat or curved plates arranged inside a box or frame. The fuel plates are manufactured by ‘picture frame technique’, followed by hot roll-bonding. The pin or tube assemblies are fabricated by co-extrusion. Nearly all non-power reactors use <sup>235</sup>U as fuel. The 30 kW (t) KAMINI (Kalpakkam Mini) in India is perhaps the only non-power reactor in the world to use <sup>233</sup>U as fissile material in the form of aluminium clad, Al-20% <sup>233</sup>U plate fuel assembly [224].

Non-proliferation of fissile material has always been an important issue since the beginning of the atomic age. Hence, many of the first generation non-power research reactors exported by USA and Russian Federation (Former Soviet Union) were fuelled with LEU. However, to have more compact core, higher neutron flux and longer time between refueling, HEU fuel with <sup>235</sup>U enrichment as high as 90% and beyond were used in vast majority of these exported research reactors till the late 1970s. Aluminium matrix, dispersion type nuclear fuels were mostly used with HEU. The common fuels used particularly in the West were:

- (i) Al-UAl<sub>x</sub> with uranium densities up to 1.7 g/cm<sup>3</sup> developed at the Idaho National Laboratory in the 1960s;
- (ii) Al-U<sub>3</sub>O<sub>8</sub> with uranium densities up to 1.3 g/cm<sup>3</sup> for MTRs at the Oak Ridge National Laboratory in the 1960s;
- (iii) UZrH<sub>x</sub> alloy fuel with U density of 0.5 g/cm<sup>3</sup> (8.5 wt% U) developed by General Atomics and used in TRIGA reactors.

## 6.2. LEU BASED FUELS FOR NON-POWER REACTORS

To guard against weapons proliferation from exported HEU fuel worldwide, in 1978 the USA launched an international programme, titled, reduced enrichment for research and test reactors (RERTR) for restricting <sup>235</sup>U enrichment to less than 20%. The objective of RERTR was to convert progressively all HEU cores to LEU cores without affecting the performance of the reactor, mainly in terms of neutron flux. A number of national and international fuel development and qualification programmes were initiated to allow these reactors to fully achieve their missions while using LEU fuels [225]. A parallel Russian RERTR programme [226] funded by the Russian Ministry of Atomic Energy and the USA — RERTR programme was started for use of LEU based fuel in Russian-designed research and test reactors. In 2004, the global threat reduction initiative (GTRI) was launched by USA, congruent with RERTR

objectives, mainly for accelerated removal of Russian-origin fresh and used HEU fuel to the Russian Federation and of USA-origin fuel to the USA [227].

It is possible to convert HEU core to LEU core for most designs of non- power reactors as long as the total amount of  $^{235}\text{U}$  in the fuel element is kept approximately the same, despite the decreased enrichment. In fact, it is necessary to have additional increase in the  $^{235}\text{U}$  content of the fuel, to compensate for the loss of reactivity due to the increased absorption of neutrons by the excess  $^{238}\text{U}$  in LEU fuel. As uranium enrichment in fuel is decreased, uranium density in the fuel must increase to maintain the net fissile ( $^{235}\text{U}$ ) atom density of the fuel. To increase the amount of U in each fuel element one can increase the volume of the part of fuel element occupied by uranium and/or increase the amount of uranium packed into the available volume. Over the last two decades, fuels with increasing uranium density have been developed as listed in Table 10 [228].

TABLE 10. RESEARCH REACTOR FUELS WITH INCREASING FUEL DENSITY

Compound/Alloy	UAl <sub>4</sub>	UAl <sub>3</sub>	UAl <sub>2</sub>	USi	U <sub>3</sub> Si <sub>2</sub>	U <sub>3</sub> Si	U <sub>6</sub> Fe	U-10wt%Mo	U
Theoretical Density (g/cm <sup>3</sup> )	6.2	6.8	8.14	10.96	12.2	15.3	17.4	17.2	19.05

During the 1980s, uranium densities of aluminium matrix LEU dispersion fuels could be increased to 2.3 g/cm<sup>3</sup>, 3.2 g/cm<sup>3</sup> and 2.5 g/cm<sup>3</sup> respectively, for Al-UAl<sub>x</sub>, Al-U<sub>3</sub>O<sub>8</sub>, and Al-UO<sub>2</sub> fuels. Currently, the highest uranium density LEU fuel licensed by the U.S Nuclear Regulatory Commission is based on Al-matrix fuel with a dispersion of U<sub>3</sub>Si<sub>2</sub> particles with uranium density of 4.80 g/cm<sup>3</sup> [229]. The major challenge with the silicide fuel is reprocessing.

Since 1996, international efforts are underway, particularly in US, France, ROK and Argentina, to develop and qualify fuels that have even higher uranium densities and are easy to reprocess as compared to U<sub>3</sub>Si<sub>2</sub> dispersion fuel. This will enable the operation of a number of high performance reactors with LEU fuels. The U-Mo alloy, containing 7–12 wt% Mo, having a single phase body centred cubic phase emerged as a candidate for both dispersion and monolithic type fuels. For the Al matrix U-Mo dispersion fuel, the target uranium density is 8.0–9.0 g/cm<sup>3</sup> and for the monolithic U-Mo alloy the uranium density targeted is in the range of 15–16 g/cm<sup>3</sup> [230–231].

Dispersion type fuel elements are mainly fabricated by the powder metallurgy process and the monolithic fuel by the classical melting and casting route. The monolithic or dispersion fuels are encapsulated in a cladding material having low neutron absorption cross section, high irradiation stability, higher thermal conductivity, excellent compatibility with fuel and coolant and high corrosion resistance. Usually an aluminium alloy is used as the material for cladding and other structural components of non-power reactor fuel assembly. After encasing, the fuel element is subjected to further thermo-mechanical treatment, like hot-rolling of picture-frame, co-extrusion, friction-bonding or hot-isostatic pressing during which metallurgical bonding takes place between the mating surface of the fuel and cladding material, which improves heat transfer from fuel to coolant. Often, a diffusion barrier in the

form of a thin layer is put between monolithic fuel and cladding to minimize or avoid chemical interaction between fuel and cladding materials.

### 6.3. THEORETICAL CONSIDERATIONS OF DISPERSION FUEL

Dispersion fuels are essentially aluminium matrix composite fuels where, relatively coarse particles of a fissile material in the form of a chemical or intermetallic compound is uniformly dispersed in a neutronically inert aluminium matrix of high thermal conductivity. Thus, high-energy fission events are isolated from the matrix. Dispersion fuels have three main advantages over the homogenous fuel system. First, the operational life of the fuel is increased through localization of fission product damage in and immediately adjacent to the fissile phase leaving a maximum fraction of the undamaged non-fissile matrix phase to provide integrity and strength to the composite material. Secondly, the fission product damage is minimized by proper selection of the most damage resistant fissile phase compatible with the matrix material. Thirdly, more material combinations are available to obtain desirable physical, chemical and metallurgical properties for a specific reactor design.

Dispersion fuels with aluminium matrix, clad in aluminium and roll-bonded in plate shape or co-extruded in pin form, are being extensively used all over the world in small, research reactors. Aluminium is chosen because of its low parasitic thermal neutron absorption cross section, low cost, easy availability, easy fabricability, adequate mechanical, physical and chemical properties and excellent corrosion resistance to water up to 100°C.

In dispersion fuel, relatively coarse particles of a fissile phase, large compared to the recoil range of fission products, are dispersed uniformly in a non-fissile matrix (like aluminium) which predominates in volume and exists as a continuous network of fission product-free second phase surrounding the fissile phase [232–233]. The fissile isotopes,  $^{235}\text{U}$ ,  $^{239}\text{Pu}$  or  $^{233}\text{U}$ , are used alone or in combination with the fertile species in the form of an inter metallic or a compound. The fissile atom density should preferably be high in the dispersion phase. The matrix material should have a high volume fraction, low parasitic neutron absorption cross sections, excellent mechanical and heat transfer properties and should be chemically compatible with the dispersion phase.

During fission, more than 80% of the released fission energy is imparted to the two fission fragments as kinetic energy. The extremely energetic fission fragments travel only a few microns (recoil range:  $\sim 5\ \mu\text{m}$ ), but in doing so, seriously damage the crystal lattice while dissipating their energy as heat. If the fission fragment recoil ranges overlaps, then large portions of the matrix phase will be hardened, embrittled or otherwise damaged. Added to this, the matrix will also be damaged by the neutrons, though their contribution is far less severe. The average particle size and volume fraction of the fissile phase should be such that minimum amount of the matrix phase is damaged by the fission fragment recoil. Weber et al [232] has modeled the effect of fuel particle size in a dispersion fuel having a constant volume fraction of the dispersoid phase in the form of uniform spherical particles as shown in Figure 52. The core plate made of Al alloy, containing the Al matrix dispersion fuel, is sandwiched between top and bottom Al alloy cover plates and subjected to hot roll - bonding in order to have metallurgical bonding between the mating surfaces of the core and cover plates.

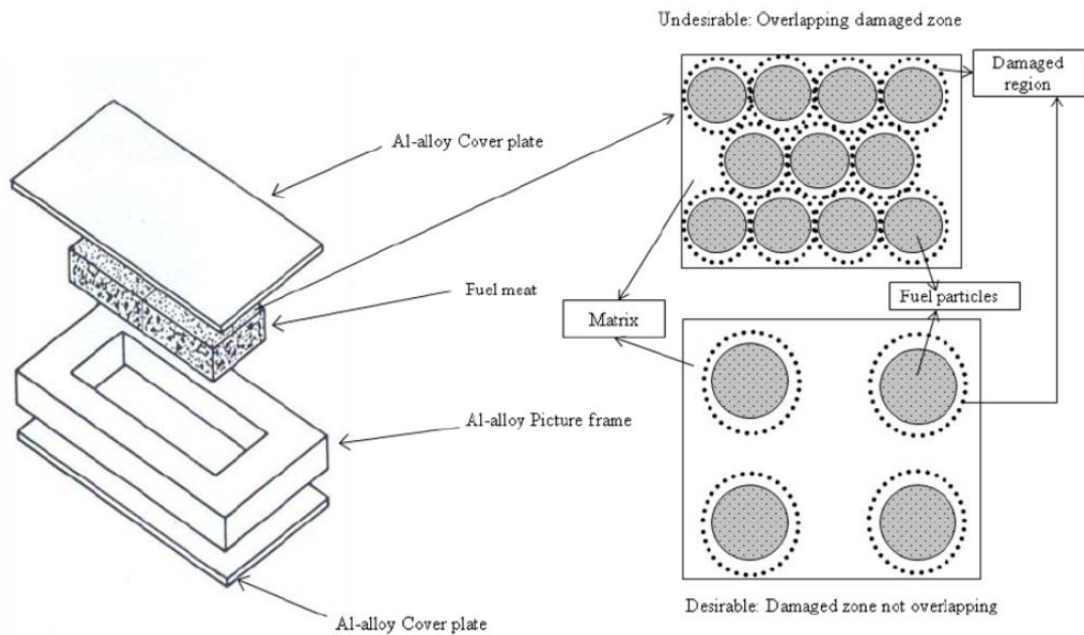


FIG. 52. The model of dispersion type plate fuel showing dispersoid phases in the metallic matrix (usually Al alloy).

Below a critical particle size no undamaged matrix region exists as shown in Figure 52. Similarly, it can be shown that increasing the volume fraction of dispersoid phase for any fixed fuel particle size would also increase the fraction of damaged matrix material. The volume fraction of matrix that remains undamaged by fission recoil increases with increasing fissile particle diameter, decreasing volume fraction of fissile phase and decreasing recoil range in the matrix. Most of the models and theoretical analysis of dispersion fuels are based assuming spherical fuel particles but in reality the dispersoids are often non-uniform and irregular shaped. However, the models, in general provide the guidelines for optimizing the particle size and spacing for all shapes of the dispersoid phase.

The dispersoid phase should have high uranium density and should be chemically compatible with Al matrix. The candidate dispersoid phase examined so far and their density as a function of the volume fraction the dispersoid phased is shown in Figure 53. Dispersion fuels are very robust, allowing high burnup (i.e. the amount of heavy atoms that are fissioned) at high power densities and enabling the production of the high neutron flux desirable for research and test reactor operation.

Though  $U_6Fe$  has the highest density, it was not found to be chemically compatible and had high swelling. The U-10%Mo alloy has emerged as a strong candidate for LEU based fuel, both in the form of Al matrix dispersion fuel and monolithic fuel.



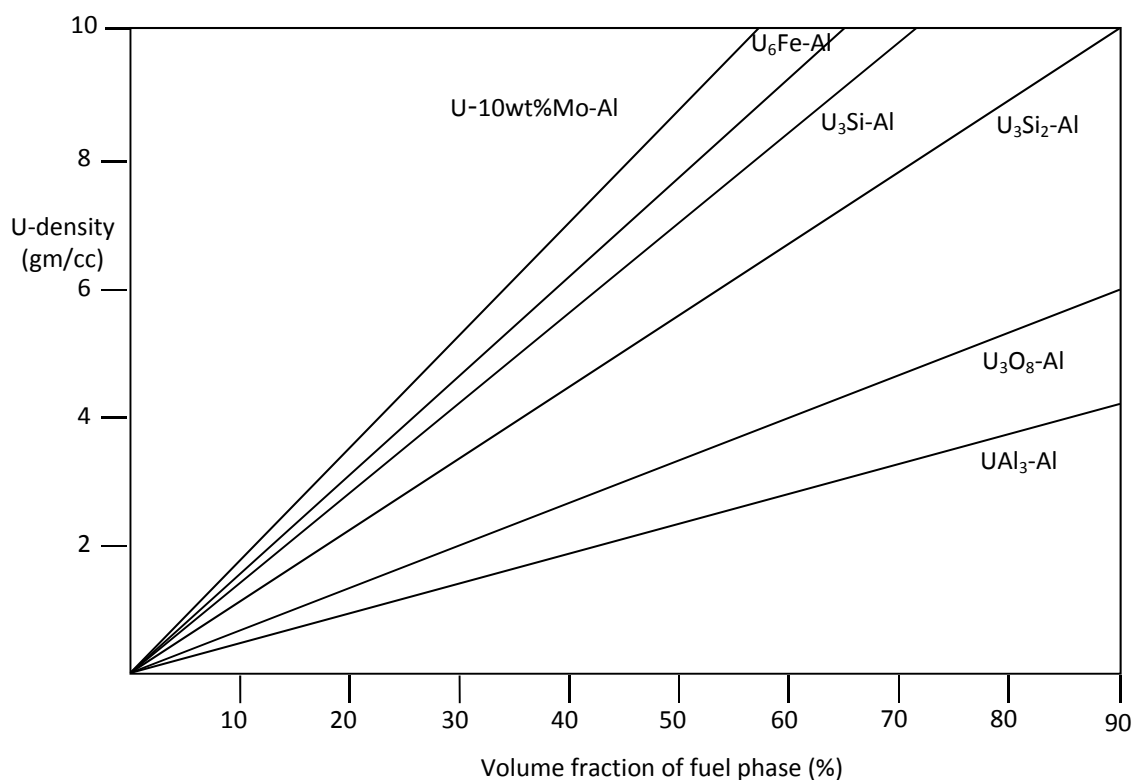


FIG. 53. Uranium density in different type of Al-matrix dispersion fuels

#### 6.4. MANUFACTURING EXPERIENCE OF Al MATRIX DISPERSION FUEL

##### 6.4.1. Al - <sup>233</sup>U alloy and dispersion fuel for KAMINI

The Al-U alloys containing 13–25 wt% U, prepared by the classical melting and casting route, can be tailored to satisfy the criteria for dispersion fuel because they essentially consist of the brittle UAl<sub>4</sub> phase surrounded by a continuous matrix of Al. Since the solid solubility of ‘U’ and Al is very low, by proper heat treatment or small addition of Si or Zr, the UAl<sub>4</sub> or UAl<sub>3</sub> particles could be distributed in the Al matrix, satisfying the requirement of dispersion fuel. These alloys do not have cold/hot rolling problems. However, alloys with more than 25 wt% U contain significant quantities of UAl<sub>4</sub> and is difficult to roll. Beyond 20 wt% U, the UAl<sub>3</sub> first forms from the melt and then reacts particularly to form UAl<sub>4</sub> + liquid, and finally UAl<sub>4</sub> + Al at the eutectic temperature. At the same U concentration, UAl<sub>3</sub> is desirable in place of UAl<sub>4</sub> because of two reasons. First, UAl<sub>3</sub> is less brittle than UAl<sub>4</sub>. Secondly, the compound UAl<sub>3</sub> required 20% less volume of material as a dispersed phase than UAl<sub>4</sub>. This decreased volume of the dispersoid phase leads to better ductility for fabrication and less damage to the matrix by fission products. The UAl<sub>3</sub> phase is retained by rapid cooling or adding small amount of Si as an alloying element, when U(Al, Si)<sub>3</sub> remains as a stable phase at room temperature. The UAl<sub>3</sub> can also be stabilized by small addition (1–2%) of Zr to the alloy during melting. Al-U alloys containing between 20 and 50% U are stronger and hence to match the fuel core strength with the cladding it is desirable to use harder aluminium alloys like grade 6061 in place of softer 1100 type. Otherwise the difference in strength can lead to problems like dog-boning during rolling. The process flow sheet followed for manufacturing Al clad Al-20% <sup>233</sup>U plate fuel for KAMINI reactor in India is shown in Figure 54 [234].

The main steps are as follows:

- Preparing Al-40%<sup>233</sup>U master alloy using Al and <sup>233</sup>U metals as starting materials;
- Remelting master alloy, dilution by adding aluminium and casting Al-20%<sup>233</sup>U alloy ingots;
- Hot-rolling at 800 K of ingots in a 2 high rolling mill, followed by cold-rolling to 3.2 mm thick fuel meat;
- Fuel alloy core preparation, picture framing, and sandwiching in aluminium plates;
- Roll-bonding by hot rolling at 700 K;
- Annealing at 673–773 K for 30 minutes and ‘blister-testing’ of roll-bonded fuel plates;
- Locating fuel alloy core by X ray radiography;
- Decontamination, trimming and straightening and machining the fuel elements to final dimensions;
- Roll-swaging of eight fuel plates in the grooved spacer strips;
- Encasing in aluminium cover box and riveting the coolant entry channel and gripping handle of the subassembly.

For Al-U alloys containing beyond 50 wt% U, the powder metallurgy route is preferred to melting-casting. The process consists of preparation of UAl<sub>3</sub> master alloy, crushing and milling to 150 µm size, blending with –325 mesh aluminium powder, cold compaction of powder-mixture at 700 MPa and sintering at 450–600°C for 4–8 hours.

#### **6.4.2. Al matrix, uranium silicide dispersion fuel**

The uranium-silicon phase diagram displayed in Fig. 55 shows many line compounds, out of which only U<sub>3</sub>Si<sub>2</sub> and U<sub>3</sub>Si have received maximum attention due to their higher heavy atom density. The U<sub>3</sub>Si<sub>2</sub> is a congruent melting compound while U<sub>3</sub>Si is formed from peritectoid reaction. Between U<sub>3</sub>Si and U<sub>3</sub>Si<sub>2</sub>, the latter has evolved as better fuel due to its ease of preparation, better friability and lower swelling rate. The major disadvantage with U<sub>3</sub>Si compound is its unacceptable breakaway swelling characteristics at medium burnup at higher fuel loading due to its thermal instability (i.e. U<sub>3</sub>Si goes under peritectoid reaction at 930°C under equilibrium condition). The performance of Al-U<sub>3</sub>Si<sub>2</sub> dispersion fuel was found to be very satisfactory and the U.S. Nuclear Regulatory Commission (NRC) issued a formal approval for use of this fuel with uranium densities upto 4.8gU/cm<sup>3</sup> in domestic research and test reactors. A whole-core demonstration using this fuel was successfully completed in the Oak Ridge Research Reactor (ORR) in 1987 [235].

Miniplates with U<sub>3</sub>Si-Al fuel and up to 6.1 gU/cm<sup>3</sup> were fabricated in the mid 1980s by Argonne National Laboratory and by the Comision Nacional Energia Atomica in Argentina. These miniplates were irradiated in the ORR reactor to a burnup of 84–96% of the initial <sup>235</sup>U content. Post-irradiation examination of these miniplates gave good results, but showed that burnup limits would need to be imposed for higher uranium densities.

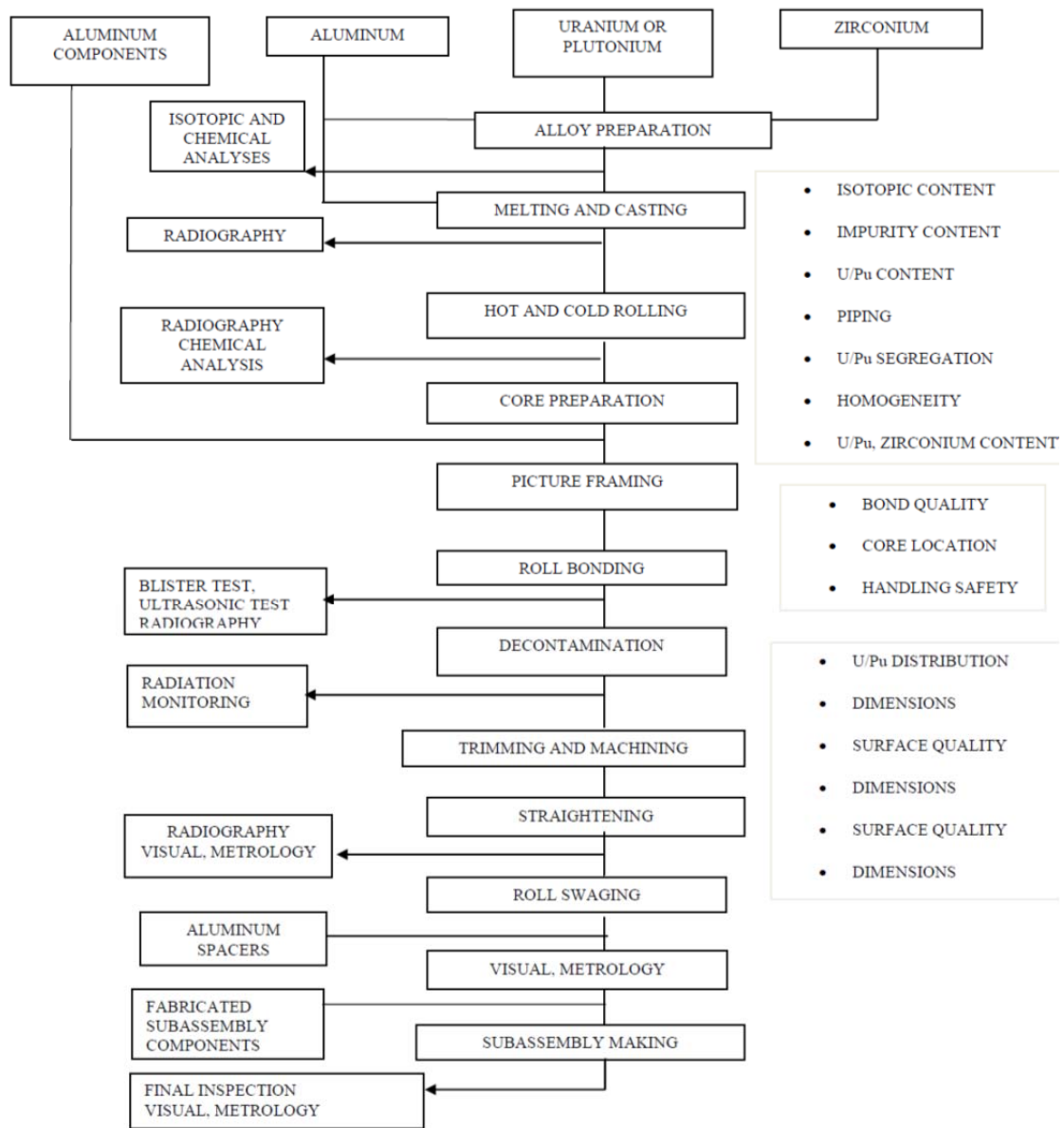


FIG. 54. Process Flowsheet with Quality Control steps for Manufacturing Al Clad, Al-20%  $^{233}\text{U}$  Plate Fuel Elements Assemblies for KAMINI reactor in India.

Four full-sized plates fabricated by CERCA in France with up to  $6.0 \text{ gU/cm}^3$  were successfully irradiated in the SILOE reactor to a burnup of 53–54% of the initial  $^{235}\text{U}$ . A full-sized fuel assembly with  $\text{U}_3\text{Si-Al}$  fuel and  $6.0 \text{ gU/cm}^3$  was also fabricated by CERCA and irradiated in SILOE to 55%  $^{235}\text{U}$  burnup. However, conclusive evidence indicating that  $\text{U}_3\text{Si}$  becomes amorphous under irradiation convinced the RERTR Programme that this material as then developed could not be used safely in fuel plates beyond the limits established by the irradiation tests in SILOE [236].

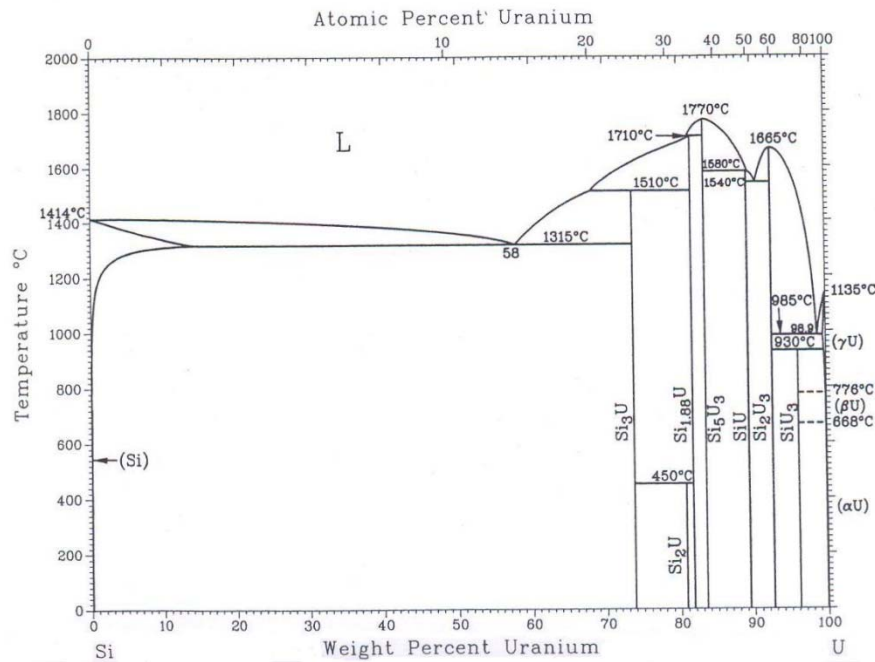


FIG. 55. Uranium silicon binary phase diagram showing  $U_3Si_2$  and  $U_3Si$  phases.

The conventional method of synthesis of  $U_3Si_2$  is by vacuum induction melting or arc melting in inert atmosphere of elemental buttons. In arc melting, multiple meltings are needed to get a good homogeneous product. Another disadvantage of arc melting is the pick up of impurities from crucible and electrode material. After melting the bulk uranium silicide is crushed and sieved to have  $U_3Si_2$  particles with 50 to 150  $\mu m$  size. Next, the silicide particles are mixed with fine Al or Al alloy powder (< 45  $\mu m$ ), compacted, picture framed in Al alloy clad, and hot-rolled to have metallurgical bonding between the mating surfaces of the Al plate containing the fuel meat and the top and bottom Al cover plates. In India, the powder metallurgy route has been followed for preparing  $U_3Si_2$  clinkers, using elemental powders of aluminium and silicon as feed materials. Thus it was possible to synthesize pure  $U_3Si_2$  at temperatures way below their melting points. In the Republic of Korea, atomized powder of uranium silicide is prepared by centrifugal atomization by melting uranium and silicon and then subjecting the molten metal to atomization by a rotating disk as shown in Fig. 56 [237]. The molten metal heated to approximately 200 K higher than the melting point is fed through a small nozzle onto a rotating disk in an argon atmosphere. Alloy melt droplets, which are formed from melt by centrifugal force, were spread from the disk toward the atomizing chamber wall by flowing argon gas during flying. Atomized powder of  $U_3Si$  and  $U_3Si_2$  have been fabricated by centrifugal atomization and the particles produced by rotating disk atomization appeared to be spherical in shape and smooth in surface as shown in Fig. 57.

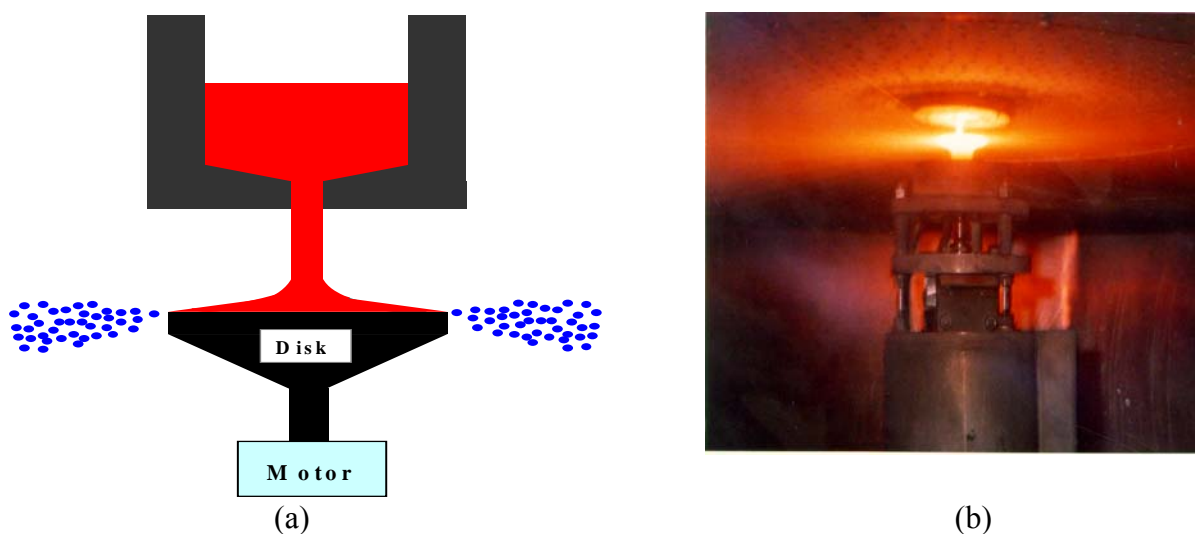


FIG. 56. (a) A schematic illustration and (b) a picture of a centrifugal atomization process

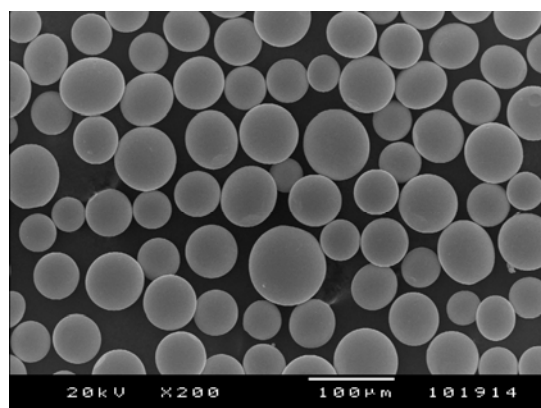


FIG. 57. Morphology of atomized powder of a U-Mo alloy.

### 6.4.3. Al matrix, U-Mo dispersion fuel

Though Al matrix- $\text{U}_3\text{Si}_2$  dispersion fuel with uranium density  $4.8 \text{ g/cm}^3$  is presently the reference LEU based fuel for non-power research reactor, with a well mastered production process on the industrial scale and a good behaviour profile under irradiation, its density is clearly not sufficient for the conversion of some of the more demanding research reactors having high neutron fluxes with LEU fuel.

Uranium metal has high density ( $19.05 \text{ g/cm}^3$ ) but  $\alpha$  uranium with orthorhombic structure up to  $660^\circ\text{C}$  is anisotropic and associated with thermal and irradiation growth. The  $\beta$  uranium has a tetragonal structure and is stable between  $660\text{--}760^\circ\text{C}$ . The  $\gamma$  uranium phase, stable from  $760^\circ\text{C}$  to melting point of uranium, has a BCC structure and is malleable and ductile. The  $\gamma$  phase also has high irradiation stability. The  $\gamma$  phase can be stabilized at room temperature by addition of alloying elements like Mo, Nb, Pt, Ru, V, etc. Molybdenum is the best choice for stabilizing  $\gamma$  uranium because it has higher solubility range in uranium. The U-Mo phase diagram is shown in Fig. 58. The U-Mo alloy containing 10% Mo has a density in the range of  $17\text{--}18 \text{ gU/cm}^3$ .

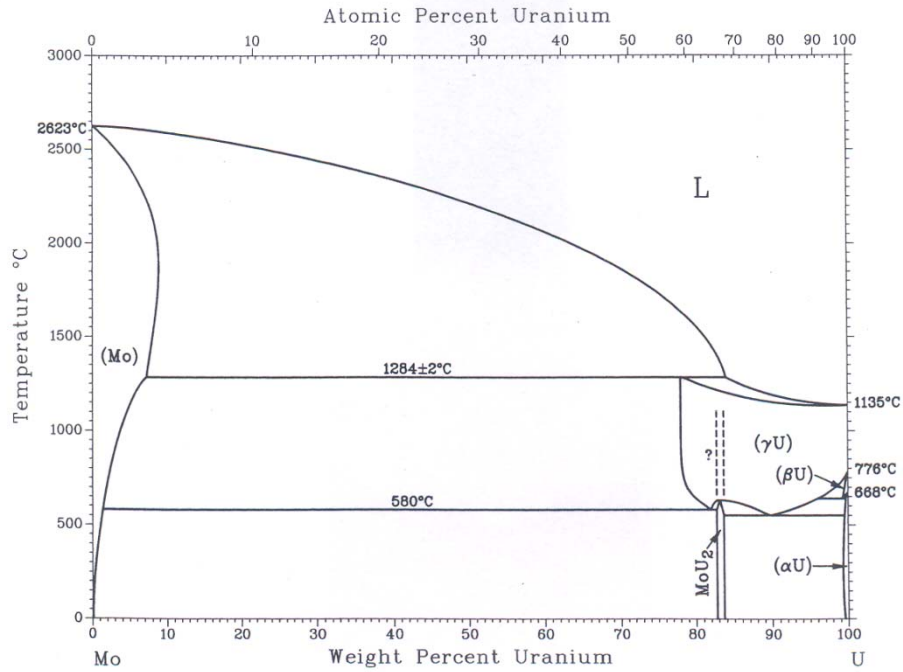


FIG. 58. Uranium-Molybdenum phase diagram showing single phase  $\gamma$ -U in the uranium rich region.

In KAERI, ROK, rotating disk atomization technology has been utilized effectively for preparation of spherical  $\gamma$  U-Mo alloy containing 7–10 wt% Mo. The process is simple and suitable for mass production with high yield and purer product [238].

Centrifugal atomization was adapted in the Russian Federation [239] using a rotating consumable electrode for preparation of spherical particles of U–10% Mo alloy in the size range of 60–160  $\mu\text{m}$ . These particles are coated with a thin layer (1–3  $\mu\text{m}$ ) of zirconium nitride using the plasma-arc method. Next, the coated particles are dispersed in aluminium alloy matrix containing 2–13% silicon and consolidated in the form of tubular and pin fuel elements and successfully irradiated in MIR. Figure 59 shows the microstructure of Al matrix U-Mo dispersion fuel with the uranium density  $\sim 6.0 \text{ gU/cm}^3$ .

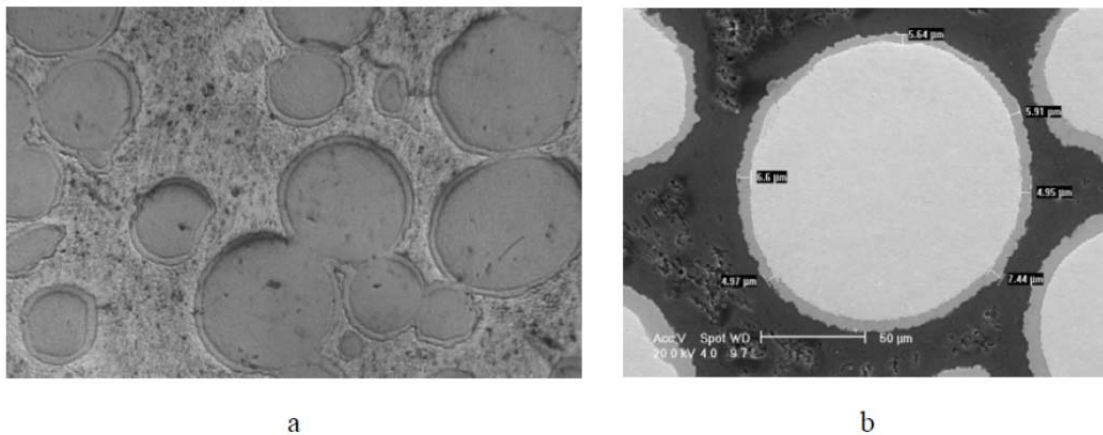


FIG. 59. Typical microstructure of dispersion fuel showing dispersed coated spherical particles of U–Mo fuel in undamaged aluminium matrix containing silicon.



Argentina [239] has developed the hydriding-milling-dehydriding (HMD) process for preparation of  $\gamma$ U–Mo powder containing 5–8% Mo. Figure 60 shows the microstructures of U–7% Mo powders after hydriding and dehydriding, and the Al matrix dispersion fuel with the U–Mo powder thus produced. China has prepared U–10% Mo alloy powder, in batches of 5 kg by vacuum melting in induction furnace followed by HMD process. The hydriding was carried at 100–250°C at hydrogen pressure of 0.1–0.4 MPa for 10–15 hours. The U–Mo hydride was mechanically crushed into powder, then subjected to dehydriding at 300–500°C for 2–6 hours to obtain U–Mo coarse particles in the size range 44–150  $\mu\text{m}$ . The fuel particles were mixed with aluminium powder containing silicon and compacted into slabs at 6–10 MPa. The fuel slab was degassed at 350–500°C for 2–4 hours. The fuel meat was encased in aluminium cladding plate by picture frame technique and subjected to roll-bonding at 480°C.

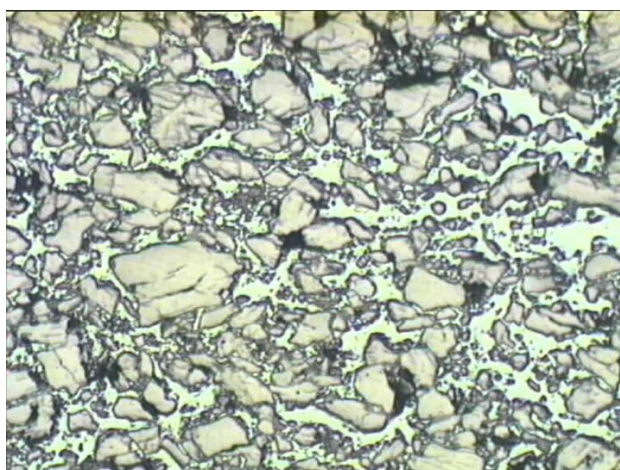


FIG. 60. Microstructure of Al matrix dispersion fuel with U–Mo powder obtained by hydriding and de-hydriding.

Powder metallurgy route is also a viable option that has been explored in laboratory-scale in India for preparing coarse U–10 wt% Mo alloy powder starting from high purity uranium metal and molybdenum metal powders. The elemental powders are mixed in required proportion, cold compacted and heat treated at 1050°C for 6 hours to get homogeneous, easily friable and single phase  $\gamma$  intermetallic of composition  $\text{U}_2\text{Mo}$ . The  $\text{U}_2\text{Mo}$  clinkers, thus prepared, are crushed and sieved to  $\sim 400 \mu\text{m}$  size, mixed with fine aluminium powder and compacted to obtain the Al matrix  $\text{U}_2\text{Mo}$  dispersion fuel meat.

The in-pile behaviour of Al matrix  $\text{U}_2\text{Mo}$  dispersion fuel has not been very satisfactory and the Al matrix is found to react with the U–Mo alloy and the reaction product was apparently amorphous causing blistering of the plate and its ultimate rupture. The addition of 2–5% of Si either in the Al matrix or in the U–Mo alloy leads to the formation of a silicon-containing phase at the interface between U–Mo and Al which acts as a diffusion barrier.

## 6.5. MANUFACTURING EXPERIENCE OF MONOLITHIC U–Mo FUEL

During the last few years the primary focus of RERTR fuel development has shifted from Al matrix dispersion fuel to monolithic U–10% Mo fuel of high uranium density, in the range of 15–16  $\text{gU}/\text{cm}^3$ , with the objective of converting all non-power reactor core to LEU based fuel without loss of performance. This will significantly enhance proliferation resistance of fissile material in non-power reactor which has been the main objective of RERTR programme.

In USA, the Y-12 National Security Complex (Y-12) at Oak Ridge and Idaho National Laboratory have jointly developed the flow sheet, shown in Figure 61, for manufacturing Al alloy (6061) clad [241], monolithic U-10% Mo alloy fuel plates with zirconium barrier layer, by melting and casting of the alloy, covering the same with a thin barrier layer (25  $\mu\text{m}$ ) of zirconium and encasing the coated fuel plate in Al alloy sheet by friction bonding or hot isostatic pressing (HIP). First, in the Y-12 facility, the U-10% Mo alloy is cast into plates by double melting U bulk metal with Mo powder and casting in a multicavity mould where some 20 plates could be cast. Figure 62 shows the melting and casting facility and representative castings of U-10%Mo alloy plates. Next, the cast alloy slabs are hot-rolled and subjected to cold-rolling annealing cycle to obtain the plates of desired thickness. The plates are then sheared to size  $\sim 75\text{ mm} \times 100\text{ mm} \times 3.25\text{ mm}$ . At INL [242], the U-Mo fuel plates are encased in Zr foil and subjected to hot co-rolling to form a zirconium barrier layer of some 25  $\mu\text{m}$  on the U-Mo fuel plate. Figure 63 shows a coated fuel plate thus prepared and section of the fuel element showing the zirconium protective layer. The Zr acts as a diffusion barrier and prevents the chemical interaction of the fuel with Al cladding during in-pile operation. The coated U-Mo alloy plate is encased in Al alloy cover plates and bonded to the plates by friction bonding or hot isostatic pressing (HIP). The friction bonding process makes use of thermo-mechanical energy imparted via the application of a contacting rotary tool. The HIP process involves simultaneous application of heat and pressure upon a hermetically sealed, evacuated sample canister containing a stack of cladding/fuel foil sheets.

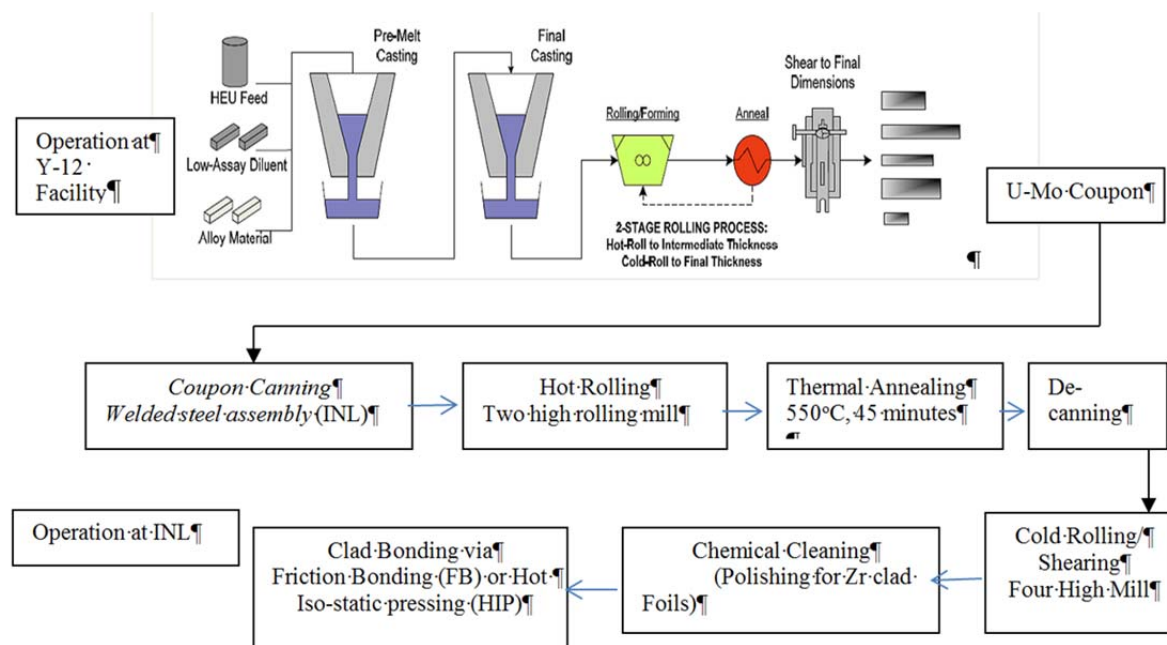


FIG. 61. Flow sheet developed in USA for monolithic Al alloy clad U-Mo plate fuel.





Melting-casting of U-10% Mo alloy



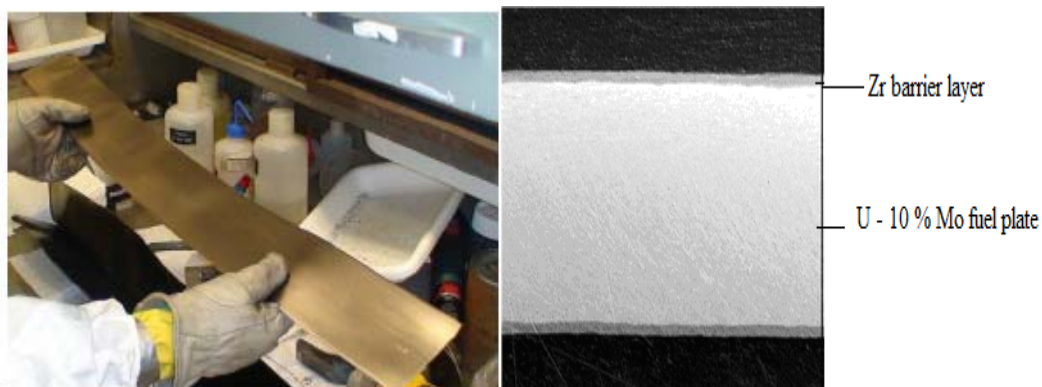
U-10% Mo alloy castings

*FIG. 62. Multi cavity mould for casting twenty U-10% Mo alloy plates at a time [240].*

ROK has prepared rod-type monolithic, multi-wire U-7% Mo fuel by injection casting. In order to establish the fabrication process of a multi-wire fuel, an injection casting technology using quartz moulds. U-Mo wires of diameter 1.95 mm were produced and inserted into four 2 mm round machined grooves and swaged [242]. Figure 64 shows the U-Mo wires and the swaged assembly containing four wires.

#### Natural 'U' metal fuel

India has two of the largest research water cooled research reactors namely the 40 MW (t) CIRUS and the 100 MW (t) Dhruva. The 40 MW (t) CIRUS reactor is similar to the NRX reactor at Chalk River, Canada. Both CIRUS and DHRUVA reactors use natural uranium metal rod clad in 1S Aluminium as fuel.



*FIG. 63. Co-rolled Zr and U-Mo alloy fuel foil and SEM picture of the cross section of a Zr co-rolled U-10Mo fuel foil showing the barrier layer [241].*

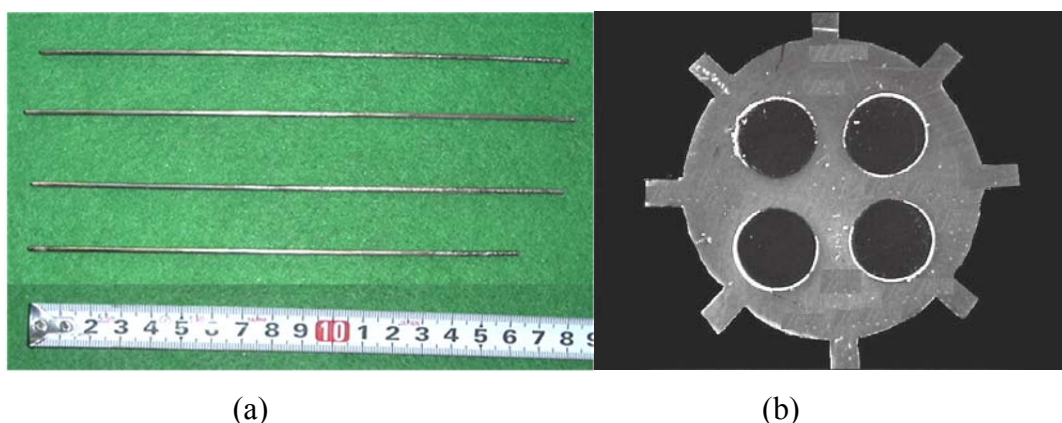


FIG. 64. (a) U-7 wt% Mo wires, 1.95 mm in diameter, produced by an injection casting method (b) Macroscopic cutting view (x20) of the irradiated U-Mo multi-wire fuel [242].

Whereas the CIRUS uses rigid single fuel element, the fuel element for Dhruva is a cluster of 7 uranium metal pins. The starting material for fuel fabrication is uranium ingots of nuclear grade purity prepared by magnesio-thermic reduction of  $UF_4$ . The melting and casting of uranium is carried out in vacuum induction furnace with alumina-coated graphite crucible and mould. The molten metal is heated to about  $1400^\circ\text{C}$  and cast into billets of 75 mm diameter and 900 mm length. Next, the casting is subjected to hot rolling at  $620^\circ\text{C}$ . After this the rolled rod is heated to the beta phase at  $720\text{--}740^\circ\text{C}$  in a molten salt and water quenched. This cause randomization of the grains and avoids irradiation growth during in-pile operation because of the anisotropy of orthorhombic uranium. The heat treated rod is straightened, ground, cleaned and canned in aluminium finned tube by drawing the assembly on a draw bench through a special die to ensure excellent mechanical bonding between the uranium fuel and the aluminium cladding [243].

#### 6.6. DISPERSION TYPE MULTILAYER COATED FUEL PARTICLES IN GRAPHITE MATRIX FOR HIGH TEMPERATURE GAS COOLED REACTORS (HTGRS)

Experimental and prototype high temperature gas cooled reactors (HTGR) were built and operated from the 1960s through the 1980s in the USA and Europe with block-type and pebble bed core designs respectively. Several IAEA documents have summarized the status of HTGR and related fuel cycle [244–245].

So far, five prototype HTGRs were constructed in the past. These are the 20 MW(t) Dragon reactor in the United Kingdom, the 40 MW(e) Peach Bottom and 330 MW(e) Fort St. in the USA and the 15 MW(e) AVR and the 300 MW(e) thorium high temperature reactor (THTR) power plants in Germany.

Presently, there are only two small experimental HTGRs in operation. The first is the 30 MW (t) high temperature engineering test reactor (HTTR) of Japan which was put in service in 1999 with an outlet helium temperature of  $850^\circ\text{C}$ . The second is the HTR-10 at the Institute of Nuclear and New Energy Technology (INET) of Tsinghua University in China. The project on pebble bed modular reactor (PBMR) by South African utility ESKOM has been discontinued.

The modified version of HTGR known as very high temperature gas cooled reactors (VHTR) has been considered as one of the GenIV reactor system for producing electricity with high conversion efficiency and supplying process heat above  $600^\circ\text{C}$ . The GenIV VHTR is expected to cogenerate steam, hydrogen and heat.

Regarding the fuels for HTGR, two types of advanced coated fuel particles have been developed, namely, TRISO and BISO. A TRISO coating contains three types of coating in four layers, namely, low density pyrocarbon around the fuel kernel to act as a buffer, inner and outer pyrolytic carbon with SiC layer in between for retention of solid fission products. A BISO coating contains two layers, namely the low density pyrocarbon buffer and high density isotropic pyrocarbon to retain the fission products.

Dispersion fuel consisting of multilayer coated fuel particles in graphite matrix is the reference fuel for HTGR. The dispersion fuel is consolidated in the form of 60 mm diameter 'spherical shell' in the AVR and THTR pebble bed reactors of Germany and in the shape of 'prismatic rod' in the Dragon and Peach Bottom reactors of UK and USA respectively.

The high density ( $\geq 94\%$  T.D) spherical oxide or dicarbide fissile fuel particles are prepared from sol gel derived hydrated oxide and oxide plus carbon microspheres. For preparing dicarbide microspheres, the oxide plus carbon gel microspheres are subjected to vacuum-carbothermic reduction at 1800–2100°C. During carbothermic reduction reaction sintering takes place simultaneously leading to densification of the fuel particles.

Fabrication of the fuel form consists of three major steps: preparation of spherical fuel particles usually by the sol-gel process, multilayer coating of fuel particle and consolidating the fuel particles in graphite matrix and shaping into spherical shells or prismatic blocks.

The fissile fuel particles are around 200  $\mu\text{m}$  in diameter and are coated with three layers of pyrolytic carbon and one layer of SiC and are known as TRISO. The high density fertile dicarbide particles are made similarly. These are 500  $\mu\text{m}$  in diameter and are coated with two layers of pyrolytic carbon and are known as BISO (buffer isotropic). The inner low density non graphitized coating of around 85  $\mu\text{m}$  for both BISO and TRISO provides void volume for fission gases, accommodates any swelling of the fuel or shrinkage of the outer coating and attenuates fission recoil. The coating is made by depositing carbon from acetylene between 1000–1300°C. In BISO, the outer, dense, isotropic pyrolytic carbon coating of around 75  $\mu\text{m}$  acts as a pressure vessel to retain gaseous fission products and also forms a relatively impermeable barrier to the diffusion of non-gaseous fission products. In TRISO, the inner high density isotropic pyrolytic carbon coating of 25  $\mu\text{m}$  protects the SiC layer from detrimental reactions with fuel and fission products and the outermost high density isotropic carbon layer of 35  $\mu\text{m}$  provides mechanical support for the SiC layer and protects the SiC from damage during handling. The high density pyrolytic carbon layers, lamellar or random isotropic, are formed by cracking  $\text{CH}_4$  in the temperature range of 1500–1800°C. The 10  $\mu\text{m}$  SiC layer is deposited by chemical vapour deposition from methyl trichlorosilane in hydrogen at 1500°C and acts as a crack arrestor and limits diffusion of uranium and some of the metallic fission products namely Sr, Ba, Cs and Ce which are not so effectively retained by pyrocarbon layers alone.

The coated particles are consolidated in a graphite matrix in the form of spherical shell or prismatic rod. The spherical graphite fuel elements of 60 mm diameter for pebble bed reactors are fabricated by mixing a powder of 70–80% well crystallized natural graphite flake, 10–20% graphitized petrol coke and 10% binder with the coated fuel particles and pressing the same in a silicone rubber die. In a subsequent second pressing stage, a fuel free shell of 10 mm diameter is pressed on to the core. The shell assembly is then sintered in two steps at 800°C and 1800°C.

The prismatic bars for the HTGRs in UK and USA are prepared similarly by mixing coated carbide fuel particles with graphite flour and a pitch binder and subjecting the mixture

to a) hot pressing and sintering; b) extrusion and sintering; or c) isostatic pressing (at 70 MPa) and sintering. Final Sintering and graphitization is done at 1800°C in vacuum.

## 6.7. SUMMARY

The main focus of research reactor fuel development has been ‘proliferation resistance’ of fuel. Accordingly, the main objective of the USA-led RERTR programme initiated in 1978 was to develop a LEU based fuel of high uranium density in order to replace all HEU core exported from USA. The Russian Federation joined this programme and a joint US-Russian Federation collaboration is underway to convert HEU cores exported from the Russian Federation to LEU based fuel. The RERTR programme has been successful in developing and qualifying Al-matrix dispersion fuel with  $\text{U}_3\text{Si}_2$  dispersion with uranium density of  $4.8 \text{ g/cm}^3$ . The silicide fuel is now being manufactured on an industrial scale in several countries and several research reactors are now in operation with this LEU based silicide fuel. However, reprocessing of spent uranium silicide fuel is still a challenge.

R&D efforts are underway to develop LEU based fuel that are easy to reprocess and have higher uranium density. U-Mo alloy with high uranium density is emerging as a strong candidate. The targeted density of Al-matrix U-Mo dispersion fuel is  $6\text{--}8.5 \text{ gU/cm}^3$  and for monolithic alloy, the target density is between  $15\text{--}16 \text{ gU/cm}^3$ . In the Al-matrix dispersion fuel, the problem of chemical interaction between aluminium and U-Mo phases has been resolved by coating of U-Mo alloy particles with a thin layer of ZrN and adding 2–6% Si to the matrix. For the monolithic fuel, initial trials have been successful. Friction bonding and hot isostatic pressing are used for metallurgical bonding between the core aluminium alloy plate containing the monolithic U-10% Mo fuel and the Al alloy cover plate. Zr diffusion barrier between the U-Mo fuel and Al alloy cladding prevented fuel-cladding chemical interaction. The U-Mo monolithic fuel is likely to be qualified shortly and pave the way for conversion of all research reactor fuel to LEU core without compromising on the neutron flux. Industrial scale manufacturing of U-Mo monolithic fuel is expected in coming years.

The dispersion type HTGR fuel has been prepared in the past on a semi-industrial scale for experimental and prototype reactors. The technology of manufacturing coated fuel particles and consolidating them in graphite matrix in the form of spherical shell and prismatic block has been developed and demonstrated. This technology will be available for VHTR fuel in the future.

## 7. CONCLUSIONS

$^{235}\text{U}$ , the only fissile isotope in nature, is the fuel for most operating power and research reactors. Water cooled nuclear power reactors account for more than 90% of the operating reactors. LWRs are the most dominant followed by PHWRs. They will continue to be the mainstay in the commercial nuclear power market for several decades. LWRs and PHWRs use LEU containing up to 5%  $^{235}\text{U}$  and natural uranium respectively as fuel in the form of high density  $\text{UO}_2$  pellets, clad in zirconium alloy. The target of fuel development programme for research reactors is LEU based fuel with  $^{235}\text{U}$  enrichment  $<20\%$  to ensure proliferation resistance.

$\text{UO}_2$  fuel is being manufactured on an industrial scale for more than five decades for use in LWRs, PHWR, AGR and RBMK and has attained a high level of industrial maturity. Likewise, MOX fuel is also being manufactured on an industrial scale for the last forty years

for use in LWRs. The present focus is on high performance and high burnup oxide and mixed oxide fuels for LWRs. For this, pellets with tailored characteristics (large grain size, controlled microstructure, minimum surface defects, etc.) are being manufactured. The recent trend in quality control in fuel manufacturing has been towards process control of each manufacturing step, in addition to inspection of the final product, to ensure high fuel performance.

The burnup of LWR fuel has doubled during the last three decades and the present average burnup is in the range of 50 GW d/t. It can be expected that this burnup will be increased further. Uranium fuel cycle facilities, including manufacturing plants, are presently licensed for  $^{235}\text{U}$  enrichment level of 5% maximum. Increasing the enrichment limit of  $^{235}\text{U}$  could be required to meet future demands.

Regarding  $\text{Gd}_2\text{O}_3$  bearing  $\text{UO}_2$  fuel, the  $\text{Gd}_2\text{O}_3$  content is usually up to 7% today. This is expected to be increased to around 10% for higher burnup fuel. Since addition of  $\text{Gd}_2\text{O}_3$  lowers thermal conductivity of oxide fuel, metallic fiber phase in radial direction of pellet could compensate for reduction in thermal conductivity. Alternatively, higher number of poisoned rods per fuel assembly could be used without increasing the  $\text{Gd}_2\text{O}_3$  content.

The plutonium by-product from operating thermal reactors is subjected to mono-recycling in nearly 40 LWRs in the form of mixed uranium plutonium oxide (MOX) fuel containing depleted uranium and <12%  $\text{PuO}_2$  in Belgium, France, Germany, Japan and Switzerland, thereby improving utilization of natural uranium resources. There are some trends in Europe to recycle REPU in LWRs either after re-enrichment or after blending with HEU. Some countries are also considering REPU in PHWR for better resource utilization.

Presently, the natural uranium resource utilization in operating thermal reactors is <1% and most of the uranium is locked as  $^{238}\text{U}$  in the tailings of  $^{235}\text{U}$  enrichment plant, REPU and in spent fuel. Plutonium is the best fissile material in fast reactors. Hence, it is desirable to recycle Pu in SFRs, in combination with depleted uranium for breeding more plutonium than what is consumed. Thus, multiple recycling of plutonium will increase utilization of natural uranium resource by a factor of at least 60. The minor actinide by-products from the thermal reactors and SFR could be burnt in SFR along with the plutonium, thus minimizing volume, radiotoxicity and decay heat of the high level waste for permanent disposal in repositories. SFRs and related closed fuel cycles are therefore essential for long term sustainability of nuclear power.

The semi-industrial scale production experience of MOX fuel for SFR is available in several countries. Advanced SFR fuels, namely, carbide, nitride and metallic fuels, have so far been fabricated only on a pilot plant scale, mainly for irradiation testing experiments and to a limited extent for use as a driver fuel in experimental fast reactors. MA bearing oxide, carbide, nitride and metallic fuels are being prepared only on a laboratory scale in France, Germany, Japan USA and the Russian Federation for out-of-pile property evaluation and irradiation testing.

One of the major challenges in the manufacture of Pu,  $^{233}\text{U}$  (always associated with  $^{232}\text{U}$ ) and MA bearing fuels is the radiotoxicity and the high level of  $\beta$ ,  $\gamma$  and neutron radiations. For fabrication of ceramic nuclear fuels containing these materials, the challenges of radiotoxic dust hazard could be significantly minimized by using sol gel derived dust free process flowsheets that are amenable to remote and automated fabrication. The sphere-pac and SGMP processes are viable options.

The manufacture of U-Pu-Zr metallic fuel for fast reactors is relatively easy compared to those of ceramic nuclear fuels. The integration of pyro-processing plant of spent thermal and fast reactor fuels with manufacturing facility of metallic fuel will be relatively simple and would enhance proliferation resistance. The injection casting of metallic fuel pin is still the most viable route though alternative techniques based on continuous casting, arc melting and powder route are under development.

Proliferation resistance of fissile and fertile materials is of paramount importance in fuel fabrication plant since the critical mass of  $^{235}\text{U}$ ,  $^{239}\text{Pu}$ ,  $^{241}\text{Pu}$ ,  $^{237}\text{Np}$ ,  $^{241}\text{Am}$  is relatively low and in the range of tens of kilograms only. For Pu,  $^{233}\text{U}$  and MA based fuel, the isotopic barrier associated with  $^{238}\text{U}$ ,  $^{242}\text{Pu}$ ,  $^{233}\text{U}$  and MA isotopes could be effectively utilized to ensure 'intrinsic proliferation resistance' in the fast reactor fuel fabrication plant. For ensuring proliferation resistance, international efforts are underway in the following areas:

- (i) Conversion of HEU cores to LEU cores in research reactors by developing high uranium density fuel either in the form of aluminium matrix dispersion fuels like Al - (U, Mo) with U density in the range of 6–8.5 g/cm<sup>3</sup> or as monolithic U - (6–12%) Mo alloy with U density 15–16 g/cm<sup>3</sup>.
- (ii) Modifying the PUREX process in order to avoid separate plutonium and other fissile material streams, including minor actinides, by co-extracting uranium with plutonium and subjecting them to microwave de-nitration or co-precipitation in the form of mixed oxides. Likewise, efforts are underway to co-extract and co-precipitate minor actinides in combination with uranium and plutonium in the form of mixed oxide or as inert matrix (ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.) fuel.

The classical powder metallurgy process consisting of powder production followed by cold-pelletization and sintering is practised for ceramic nuclear fuel fabrication. Since U, Pu and MA are radioactive and hazardous to health in varying degrees, radiological safety is one of the main focus of attention in ceramic nuclear fuel fabrication. Apart from high  $\beta$ ,  $\gamma$  and neutron shielding, adequate arrangements should be made to take care of the high decay heat. In addition, some of the nuclear ceramics like carbides and nitrides of uranium and plutonium are highly susceptible to oxidation and hydrolysis and are pyrophoric in powder form, requiring inert atmosphere as cover gas. Further, most of the actinide compounds are non-stoichiometric. Hence, close control of oxygen, carbon and nitrogen stoichiometry are essential during the fabrication process. Finally, the criticality hazard associated with fissile isotopes has to be taken care of in the fuel manufacturing plant.

Dispersion type fuels used in research reactors are a judicious combination of radiation resistant matrix like aluminium and a dispersion phase consisting of the fissile and fertile material in certain proportions in order to ensure undamaged phase surrounding the dispersion particles. Currently, Al-U<sub>3</sub>Si<sub>2</sub> with U density of 4.8 g/cm<sup>3</sup> is the reference LEU based fuel. However, U-Mo fuels in dispersion and monolithic form for higher U density are being developed. These fuels are easier to reprocess compared to silicide fuels. U-Mo alloys containing 7–12% Mo are emerging as candidate fuels for dispersion and monolithic LEU based research reactors.

The development of nuclear fuel cycle on an industrial scale is essential in order to have a long term sustainability of nuclear power. In the front end, all activities including uranium mining, milling, refining, conversion, enrichment and fuel fabrication have reached a high level of industrial maturity. The identified uranium resources of ~6.3 million tons are

adequate to meet the annual uranium fuel demand for all foreseeable growth scenarios of nuclear power for the next 100 years. Added to this, undiscovered resources in the range of 10 million tons and unconventional uranium resources in phosphate rocks will further extend uranium availability.

In the back-end, spent fuel reprocessing and MOX fabrication have also reached a high level of industrial maturity during the last five decades. However, there is a need to develop advanced partitioning techniques, based on both aqueous and pyro-processing, to ensure proliferation resistance and efficient recovery and recycling of actinides.

Thorium resources are three times more abundant in nature, and compared to uranium and Th-based fuels have been manufactured in the past on a semi-industrial scale for use in water-cooled and gas-cooled reactors. Presently, there are no power reactors with Th fuel and the front and back ends of thorium fuel cycle are yet to be exploited on an industrial scale.

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## ABBREVIATIONS

ADU	Ammonium diuranate
ADS	Accelerator driven system
AFFF	Advance fuel fabrication facility, India
AFR	Away from reactor
AGR	Advanced gas cooled reactor
AHWR	Advanced heavy water reactor
ATR	Advanced test reactor, USA
AUC	Ammonium uranyl carbonate
AUPuC	Ammonium uranium plutonium carbonate
AVR	Experimental high temperature gas cooled reactor of Germany
BCC	Body centre cubic
BISO	Buffer isotropic
BOR – 60	Experimental fast reactor, 60 MW(t) at Dimitrovgrad, RIAR (Russian Federation)
CANDU	Pressurized heavy water reactor of Canadian design
CEFR	China experimental fast reactor
CIRUS	40 MW(t) research reactor in India (shut down)
COCA	Co-milling process at Cadarache, France
DC	Dry conversion process
DFR	Dounreay fast reactor, UK
DHRUVA	100 MW(t) research reactor in India
DOVITA	Dry processing, oxide fuel, vibro-compacted, integral, transmutation of actinides
DU	Depleted uranium
DUPIC	Direct use of PWR fuel in CANDU
EBR	Experimental breeder reactor, USA
EGT	External gelation of thorium

FBTR	Fast breeder test reactor, India
FFTF	Fast flux test facility, USA
HEU	High enriched uranium
HMTA	Hexa methylene tetra amine
HTGR	High temperature gas cooled reactor
HTTR	High temperature test reactor
HTR	High temperature reactor
IDR	Integrated dry route
IFR	Integral fast reactor
IMF	Inert matrix fuel
IMEF	Irradiated material examination facility
JAEA	Japan Atomic Energy Agency
JOYO	Experimental fast reactor, Japan
KAMINI	Kalpakkam mini reactor, India
LEU	Low enriched uranium
LTS	Low temperature oxidative sintering
LWR	Light water cooled reactor
MA	Minor actinide
MAGNOX	Uranium metal fuelled power reactor, UK
MC	Mixed uranium plutonium carbide
MDF	MOX fuel demonstration facility
MFFF	Mixed oxide fuel fabrication facility
MH	Microwave heating
MIMAS	Micronized master blend process
MN	Mixed uranium plutonium nitride
MOX	Mixed uranium plutonium oxide fuel
MTR	Material test reactor

NEXT	New extraction system for transuranium recovery
NRX	42 MW(th) research reactor in Canada
OCOM	Optimized co-milling
ORR	Oak Ridge research reactor, USA
PBMR	Pebble bed modular reactor
PHWRs	Pressurized heavy water reactors
PFR	Prototype fast reactor
PFPF	Plutonium fuel production facility
PIE	Post irradiation examination
PUREX	Plutonium uranium extraction
PWR	Pressurized water reactor
REPU	Reprocessed uranium
RBMK	Graphite moderated water cooled reactor
RE	Rare earth elements
RERTR	Reduced enrichment for research and test reactor
SBR	Short binderless route
SFR	Sodium cooled fast reactor
SGMP	Sol gel microsphere pelletization
SILOE	Research reactor, CEA - Grenoble (France)
SMP	Sellafield MOX plant, UK
THOREX	Thorium extraction process
THTR	Thorium high temperature reactor
TRIGA	Testing, research and isotope production reactors of General Atomics, USA
TRISO	Tri iso-structural
TRU	Transuranium elements
UNH	Uranium nitrate hexahydrate
UOX	Uranium oxide



WWER	Light water cooled reactor of Russian design
VHTR	Very high temperature reactor

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