Challenges in the Fabrication and Recycling of Mixed Carbide Fuel

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Abstract.

Mixed ($U_{0.3,}$ $Pu_{0.7}$)C fuel is the driver fuel for Fast Breeder Test Reactor (FBTR) at Kalpakkam, India. This fuel is being fabricated at Radiometallurgy Division, Bhabha Atomic Research Centre (BARC). The reactor was made critical with Mark-I fuel having composition ($U_{0.3,}$ $Pu_{0.7}$)C in year 1985. The fuel has seen a maximum burn up of 165GWd/t. The carbide fuel is phyrophoric in nature and very much susceptible to hydrolysis. Hence the handling of fuel is done inside alpha leak tight glove-boxes having N_2 as cover gas. The fuel is fabricated by classical powder pellet route. In the recent past a new fuel fabrication facility has been commissioned and improvement over the existing equipments and process steps have been carried out to make the fuel fabrication process more efficient resulting in higher productivity and lesser contact between personnel and radioactive powder. The use of liquid binder and lubricant has eliminated dewaxing step from the process flow sheet for UC pellet fabrication. Dry recycling of the fuel is carried out on regular basis by oxidizing the mixed carbide powder. Chemically accepted pellets having physical defects are directly recycled by crushing and milling the pellets to powder form and subsequently following other regular process steps to produce sintered pellets.

Key Words- mixed carbide, powder-pellet, liquid binder and lubricant, dry recycling

1. Introduction

Three stage nuclear power programme pursued by India aims to utilize judiciously limited reserve of uranium and vast reserve of thorium. In accordance with this programme natural uranium is used in operating pressurized heavy water reactors (PHWRs) in first stage. In second stage plutonium obtained from the reprocessing of PHWR spent fuel is planned to be used along with uranium as fuel and thorium as blanket material in fast breeder reactor. In fast reactor plutonium breeding takes place with simultaneous conversion of thorium into U^{233} which shall be used as Th-U^{233} fuel in thermal reactors in third stage [1].

Fast Breeder Test Reactor (FBTR) situated at Kalpakkam in India is a front runner for making the base of fast reactor technology in India. Commercial fast reactor named Prototype Fast Breeder Reactor (PFBR) presently under construction will be in operation in near future.

Liquid metal cooled fast breeder test reactor (FBTR) commissioned at IGCAR, Kalpakkam in mid 80's uses plutonium - uranium mixed carbide (MC, M=Pu+U) of composition ($Pu_{0.7}$ $U_{0.3}$)C – MK-I as driver fuel. This fuel of unique composition has been developed at Radiometallurgy Division, BARC and the first criticality of the reactor was made with 23 MK-I fuel subassemblies [2]. The fuel has already performed extremely well up to a cumulative burn up of more than 160,000 MWd/t. Further, over a period of time, mixed carbide fuel subassemblies of fuel composition ($Pu_{0.55}$ $U_{0.45}$)C – MK-II were also introduced in the reactor to expand the FBTR core. In recent past a new fabrication facility has been commissioned in BARC with sate of art equipment to produce MC fuel for FBTR

2. Fabrication

2.1.Challenges involved in fabrication of Mixed carbide fuel

2.1.1 Pyrophorocity

Mixed ($U_{0.3}$,$Pu_{0.7}$)C is pyrophoric material and is highly susceptible to oxidation and hydrolysis. The fabrication of carbide is therefore done in inert atmosphere inside glove box. The glove-box atmosphere is constantly monitored for oxygen and moisture and each one is maintained ≤ 25 ppm during fabrication process [2].

2.1.2 Control of C Stoichiometry

Plutonium when reacts with carbon it forms hypostochiometric compound. Therefore with higher Pu containing mixed carbide fuel, control of C stoichiometry becomes difficult. In the mixed carbide composition the non-stoichiometric carbon forms higher of M_2C_3((M=U+Pu) phase which has potential to carburise clad in the reactor. So control of C percentage in the mixed carbide composition is important to avoid formation of higher sesquicarbide(M_2C_3). This is done by restricting C addition in the initial oxide feed to about 98% of stoichiometric carbon value needed for feed preparation for carbothermic reduction [2].

2.1.3 Large number of process steps

Number of steps required for fabrication of mixed carbide fuel is more because of extra step of carbothermic reduction required for conversion of oxide to carbide. Therefore extra process control steps need to be introduced in the flow sheet to assure good quality of the product. Extra process step is time consuming and may increase chances of impurity pick during fabrication process.

2.1.4 Stringent Control of oxygen and nitrogen

Pick up of oxygen from the unreacted feed material and nitrogen from the glove-box cover gas may lead to excess presence of these elements in the product. Presence of oxygen and nitrogen in the matrix of fuel act as carbon equivalent. These elements replace C in the carbide lattice resulting in formation of higher carbides in the fuel matrix which may become potential source for clad carburization at higher temperature in the reactor [3].

2.1.5 High Pu evaporation loss

Pu loss due to high vapour pressure increases with increase of temperature. The carbide product with lesser O_2 content is obtained with higher temperature of carbothermic reaction. So optimization of carbothermic reduction temperature is an important step to avoid Pu loss and maintain O_2 within specified value.

2.2. Fabrication Process

The carbide fuel is fabricated using classical powder metallurgy technique involving mixing of feed powder, carbothermic reduction of the mixed powder to obtain carbide clinker. The clinker is crushed and milled to obtain fine sinterable grade powder followed by precompaction, granulation and final compaction to get green pellets. The fabrication of carbide fuel for FBTR started in early 1980's [2]. Since then till recent past the process flow sheet being followed is shown in the Fig. 1. The mixing of feed powders namely graphite, UO_2 and PuO_2 is done in planetary ball mill. It takes almost 12 hrs to get the powder properly homogenized. The mixed powder is subjected to process control check like determination of Pu/U ratio by XRF and C analysis by carbon determinator. The powder is tableted at 60 MPa and loaded in to all metal bell type furnace of capacity 600 gms for carbothermic reduction under vacuum of the order of 10^{-3} mbar. The carbothermic reduction takes place as per following equation.

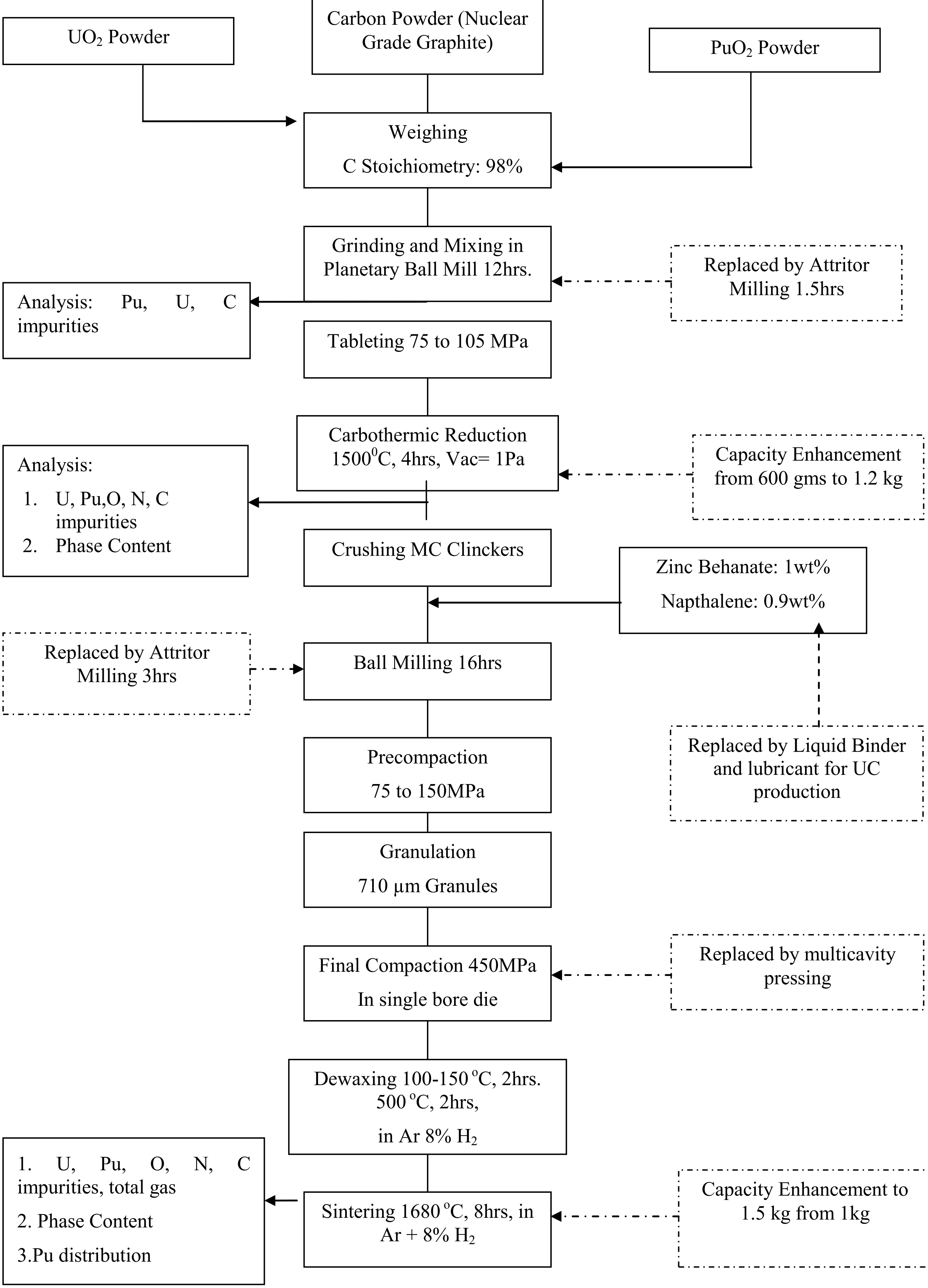
$$0.3UO_2 + 0.7PuO_2 + 3C \leftrightarrow (U_{0.3}Pu_{0.7})C + 2CO\uparrow$$

The carbide clinker thus obtained is subjected to process control step for determination of C, O, Pu/U ratio N and M_2C_3 in the product. After completion of reduction of one more set of 600 gms of mixed powder, the milling of total carbide clinker (20% loss in form of CO and CO_2) is done in planetary ball mill for 16hrs. This is followed by addition of zinc behenete and naphthalene as lubricant and binder respectively in the milled powder. Naphthalene being a pore former helps in lowering the density of sintered pellet. The normal pressure during precompaction is maintained at 150 MPa. The powder is subjected to final compaction where pressing is done using single bore die to fabricate green pellets of dia 4.65mm and height between 7 to 8mm. The final compaction pressure is maintained at 450 MPa .The green pellets thus produced are stacked in tungsten trays and subjected to dewaxing followed by sintering at 1680°C in Ar+8% H_2 atmosphere.

2.3. New Fabrication Facility

Recently a new fuel fabrication facility of mixed carbide has been set up. This facility houses indigenously developed state of the art equipment. Significant modifications have been done in the process steps like introduction of attritor for mixing and milling, higher capacity all metal furnaces for carbothermic reduction (CR) and sintering, use of liquid binder and lubricant, double bore die for final compaction etc. The changes in the flow sheet in Fig.1 have been shown by dotted line boxes. As per the modified process flow sheet mixing of feed oxide and graphite powders and milling of carbide powder is done in attritor machine. Graphite being lighter in density it tends to segregate during mixing with UO_2, PuO_2 powder. Addition of little amount of oleic acid during mixing of oxide and graphite was found helpful in avoiding the segregation of graphite and resulting in uniform mixing of the different components of the fuel. Further during mixing slow speed of attritor helps in better homogenization of the powders. The design of the attritor is modular, so that it could be easily dismantled and assembled inside the glove-box. The separation of ball and powder takes place automatically during discharge by opening the bottom ball valve. In planetary ball mill intermittent stirring is required and separation of ball and charge is done manually.

Fig.1 Flow sheet for fabrication of (U, Pu) C pellets for FBTR



Because of high energy mixing effect in the attritor, the time for mixing and milling as well as the contact time of personnel with equipment has reduced significantly. The presence of oxygen in the glove box is monitored with digital display monitor. The sudden rise in the reading of digital oxygen monitor indicates presence of tiny hole or some damage of gauntlet of the glove-box. Results of carbon analysis and Pu/U ratio of co-milled oxide–graphite powders in the attritor is shown in the Table-1. As observed from the table, the homgenised mixing of UO_2, PuO_2 and graphite powder occurs in one and half hour of mixing which otherwise used to take 12 hrs by ball milling.

TABLE-1: Analysis of oxide-graphite powder mixed in attritor

Batch No.	% C (after mixing) Control value11.60 to 12.00	Pu/U ratio Control value 2.40to 2.50
1	11.70±0.33	2.46
2	11.97±0.32	2.50
3	11.65±0.33	2.40
4	11.60±0.33	2.44
5	11.70±0.32	2.50
6	11.78±0.33	2.48
7	11.98±0.32	2.45

The carbothermic reduction (CR) is done in all metal furnace. The furnace has been indigenously developed. The furnaces use tungsten charge carrier and tungsten mesh heater. The CR temperature is maintained at 1500°C.The tabletting, precompaction and final compaction presses are operated through PLC and man machine interface (MMI). The tabletting and precompaction presses have die of bore dia 30mm.The operating pressure for tabletting press varies between 75 to 105 MPa .For fresh powder tabletting pressure required is low compared to recycled powder. Precompaction pressure is maintained between 150 to 270 MPa. The final compaction press has double bore die. The operating pressure varies from 300 to 450 MPa in order to meet specific mass to height ratio (linear mass).

Table-2 compares the total time taken for the production of sintered pellet as per old facility and new facility. It may be noted that time taken for mixing of powder and milling of clinkers reduces significantly to 1.5hrs & 3 hrs from 12 hrs and 16 hrs respectively. Because of the use of two bore die, the time period of final compaction reduces by half. All together the total time of production for a batch reduces by 30 %. Table -3 shows chemical analysis value of sintered carbide pellets made out of different batches.

TABLE-2: Comparison of the time required for different unit operation

	Fabrication time in old facility	Fabrication time in new facility
Mixing of the feed powder	12hrs	2hrs
Tableting	2hr	1hr
Carbothermic reduction	16hrs	16hrs
Milling of clinker	16hrs	3hr
Precompaction	1hr	0.5hrs
Final compaction	8hrs	4hrs
Dewaxing	20hrs	20 hrs
Sintering	18hrs	18hrs
Total Time	93hrs	64.5hrs

TABLE-3: Chemical analysis of sintered pellets

Chemical analysis for different batches	1	2	3	4	5	6	7	FBTR Carbide Pellet specification
Pu+U (wt %)	94.50	94.90	94.60	94.76	94.92	94.77	94.81	≥94
Carbon (wt %)	4.82	4.92	4.90	4.94	5.01	4.95	4.85	≤5.03
Oxygen (ppm)	6000	5300	5800	5800	5850	4338	4454	≤7500
Nitrogen (ppm)	280	350	200	794	400	142	160	
M_2C_3 (wt%) (by XRD)	18	19	17	16	19	17	16	5 to 20%
Total impurities (ppm)	<500	<500	<500	<500	<500	<500	<500	≤3000

2.4. Fabrication of UC Insulation Pellets

UC pellets are used as insulation material at both ends of FBTR fuel pin. UC pellets have been fabricated using liquid binder and lubricant. Polyethylene glycol (0.5 wt %) and oleic acid (0.3 wt %) was used as binder and lubricant respectively [4]. The use of liquid binder and lubricant obviates dewaxing step reducing the total production time by 50%.Green pellets were fabricated using two bore die of dia 4.65mm in double compaction mode. Aim was to achieve specified sintered density of 85 –90%TD with dia ranging from 4.10 to 4.22 mm. As observed from the Table-4 for batch no.1 with sintering temperature of 1680^0C, the sintered density of 92 to 93 %TD was achieved .The average dia of sintered pellet was 4.25 mm. In subsequent batches the sintering temperature was gradually reduced to 1550°C. As observed from the table-4, the density of the pellet reduced to 82 - 84%TD with sintered dia of 4.27 at 1550°C. As the sintered dia was not within the specified limit the die bore of dia 4.5 mm was chosen for further work. With change of tooling and maintaining a sintering temperature of 1600^0C the required dia and sintered density could be achieved

TABLE-4: Sintered density variation with temperature and bore dia

Batch No.	Bore dia of Die (mm)	Surface area m2/gm	Green density(%TD)	Sint. Temp(oC)	Sintered density (%TD)	Sintered dia of pellet(mm)
1	4.65	0.78	70 at 20 TSI	1680 for 5 hrs	92-93%	4.23-4.27
2	4.65	0.66	71-72 at 22 TSI	1660 for 4 hrs	92-93%	4.25-4.28
3	4.65	0.45	71-72 at 22 TSI	1625 for 4 hrs	92-93%	4.26-4.30
4	4.65	0.48	71-72 at 22 TSI	1600 for 4 hrs	91-92%	4.27-4.31
5	4.65	0.47	71-72 at 22 TSI	1575 for 4 hrs	87-89%	4.30-4.34
6	4.65	0.50	71-72 at 22 TSI	1550 for 4hrs	82-85%	4.39-4.46
7	4.50	0.52	71-72 at 22 TSI	1600 for 4 hrs	87-90%	4.15-4.18

2.5. Dry Recycling of Reject Pellets

Mixed carbide pellets at different stages get rejected in certain percentage. As these pellets contain high Pu in them it becomes important to recycle these Pu bearing material. This is done by dry recycling route. The chemically rejected pellets are sent for oxidation and subsequently used as oxide powder feed to be mixed with graphite for initial charge preparation for carbide production .Sintered pellets rejected due to physical defects are recycled directly avoiding long route of oxidation and carbothermic reduction. A brief description of the recycling process is given below.

2.5.1 **Chemically reject pellet**

About 15% sintered pellets get rejected due to non-compliance of chemical specification particularly in terms of oxygen , nitrogen , carbon or higher carbide phase. They are crushed into fine powder and in batch size of 200-300 gm taken for oxidation. The process starts at 280 to 300 ^{0}C with argon+5% oxygen gas flow. Temperature rises with flow of controlled oxygen as reaction is highly exothermic and it is maintained at $700\text{-}750^0$C. One important aspect of the process is to avoid very fine carbide powder for oxidation as probability of powder catching fire increases. Progress of the reaction is noticed by rise of temperature and when the reaction is over fall in temperature is observed. The oxidation is controlled to get mixed oxide powder with O / M ratio in the range of 2.17 to 2.20. After adjusting for Pu / U ratio, mixed oxide powder MO_2 (M = U + Pu) is co-milled with graphite powder and then processed to fabricate fuel pellets.

The process is simple and fast as it does not require continuous external heat input during oxidation. The process is used for safer storage of Pu bearing material after converting pyrophoric carbide to oxide

2.5.2 **Physically Reject Pellet**

To fabricate MC fuel pellets suitable for use in FBTR , process control parameters need to be followed strictly to comply with specifications e.g. carbon , oxygen , nitrogen , Pu / U , M_2C_3 (M = Pu + U) metallic and non metallic impurities have to be within specified limit. The flow sheet developed and followed for the fabrication of mixed carbide fuel pellets incorporating process control parameters is shown in Figure 1. The accepted sintered pellets are used for encapsulation and the pellets rejected due to off - dimensions and physical defects such as cracks, chips, surface defects etc. are normally crushed and oxidized before further processing into fuel pellets. With this approach, rejects are treated through entire process steps (Fig.1) as shown in the flow sheet. This leads to decrease in production throughputs and increase in radiation exposure to personnel. Direct reprocessing of reject pellets has also been carried out where step like oxidation of crushed pellet is avoided. The sintered pellets are crushed in jaw crusher to reduce the size to 0.5 mm. The crushed particle is milled in attritor to reduce the size further in range of 100 micron. The milled powder is precompacted at pressure of 150MPa and granulated using 30# size sieve. The minus 30# fraction is used for final compaction. The addition of the naphthalene and zinc behnete is done as binder and lubricant. The fine crushed powder has high bulk density, hence requires lesser compaction pressure to achieve specified linear mass as compared to the pressure applied for powder processed through regular route. As the pellets happen to see high temperature again precaution is taken to avoid pick up of O_2 and N_2 by maintaining the glove box under Ar atmosphere.

Direct processing of chemically accepted but physically rejected sintered pellets has the following advantages:

- Number of process steps is minimized.
- Mixing& milling of oxide – graphite mixtures, tabletting and vacuum carbothermic reduction are not required leading to almost 30% savings in time & energy
- Loss of plutonium is minimized
- Production throughputs is increased
- Radiation exposure to personnel is reduced

2.6. Conclusion

Fabrication of Mixed carbide fuel is a challenging work. It involves more number of process, quality control steps and inert atmosphere handling because of its pyrophoric nature. The issues have been taken care of by

1) Using better equipment consuming less time in process steps and facilitating production throughput. Mixing and milling time have reduced significantly with the use of attritor.

2) Use of liquid binder and lubricant which obviates the dewaxing step in UC fabrication.

3) Direct recycling of physically reject sintered pellets by crushing , milling and pellet fabrication avoiding longer route of carbide to oxide conversion and carbothermic reduction

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