FACILITY FOR ADVANCED FUELS THROUGH THE SOL-GEL METHOD

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Abstract. Advanced fuel forms need to be developed for use with the evolving nuclear fuel cycles. The fabrication of sphere-pac fuel pins that employ microspheres of U,Pu mixed oxide (MOX) or microspheres containing the oxides of Minor Actinides (MA) prepared through the internal gelation process are particularly relevant in this context. Since the sol-gel process used in the fabrication of these microspheres offers significant advantages over the conventional powder metallurgical processes used in the fabrication of pellets, efforts are underway at IGCAR in collaboration with the Bhabha Atomic Research Centre (BARC), Mumbai in order to establish a remote handling facility suitable for fabricating a sphere-pac fuel pin containing MOX microspheres. This paper describes the details of a facility that is being created at IGCAR to accomplish the above and the recent experience on the fabrication of sphere-pac fuel pins for test irradiation.

This facility comprises a jet-entrainment facility for the preparation of fine fraction UO_2 microspheres (115 ± 10 μm), a column gelation facility for the preparation of the coarse fraction U, Pu MOX (53 mol% Pu) microspheres (775 ± 75μm) through column gelation method and equipment for characterization of the microspheres prepared in our laboratory. In addition a glove box train comprising facilities for handling the microspheres, vibro-packing, fuel-pin welding and decontaminating the fuel pin was commissioned and qualified for handling MOX microspheres.

As many as 75 runs were carried out for the production of UO_2 microspheres (115 ± 10 μm) with a jet entrainment set-up, earlier, in order to optimize the process parameters viz., size of the nozzle, temperature of gelation, composition of the broth, washing routine as well as the conditions for calcination and sintering. Both the MOX as well as the UO_2 microspheres were checked for their physical integrity, dimensions and were found to conform to the desired chemical composition stipulated for the test irradiation in FBTR. Conditions for vibro-compaction were optimized. Quality control checks were performed on the fuel pins after the fabrication.

The viscosity of a broth containing both U and Pu was measured in order to establish the optimum conditions for gelation of the broth. This is a "first of its kind" measurement, made in a custom-made facility created for this purpose.

Key Words: Sol-gel, Sphere-pac fuel pins, irradiation in fast reactors, remote fabrication.

1. Introduction

Fabrication of U,Pu mixed oxide fast reactor fuels is conventionally carried out by the powder metallurgical (PM) route which is well established, and commercially proven process. Even though, this process is well established, the steps in the PM process that involve milling, grinding, pre-compaction and granulation generate aerosols that enhances the radiotoxic burden to the operating personnel. Hence, there is a need to develop an advanced process which would be devoid of this limitation. The sol-gel process is one such method which predominantly uses fluids that could be handled remotely[1]. This method would be most suited for the fabrication of advanced fuel forms containing minor actinides as well as ^{232}U. The sol-gel process is particularly attractive, for it uses the solutions of nitrates derived from the reprocessing plant directly into the process stream and avoids the "reconversion" step. Sphere-pac fuel pins could be fabricated with the "hard" sintered microspheres produced

through the sol-gel process by using vibro-compaction. In addition, the "soft" microspheres produced through this process could be deployed in the PM method. The latter method termed as Sol-Gel Microsphere Pelletization (SGMP) route [2], couples the advantage of both the sol-gel process and the conventional PM process. Test irradiations on "sphere-pac" fuel pins have demonstrated that these pins show superior performance in-pile performance (both with respect to fuel clad chemical interaction (FCCI) and fuel clad mechanical interaction (FCMI)) [3].

At IGCAR a fuel fabrication facility based on the sol-gel process is being set up. In the first phase, a fabrication line suitable for the fabrication of the fuel pins through vibro-packing the microspheres has been established. The salient features of this facility are explained in this paper.

The target smear density specified for the sphere-pac test fuel pin was 80±1% theoretical density (TD). The fuel column comprised microspheres of two different diameters viz., 775 ± 75 μm (MOX) and 115 ± 10 μm (UO_2) taken in the volume ratio 3:1 and packed in a clad tube with an internal diameter of 5.7 mm. The vibro-packed fuel pin represents a system of restrained packing of spheres. The choice of the sizes and the vibropacking process are explained in Section 2.

The larger size fraction MOX microspheres were fabricated at the Bhabha Atomic Research Centre, Mumbai by the column gelation method. This method is not suitable for making the smaller microspheres of UO_2. Hence, a separate process known as the jet-entrainment technique was used for preparing the latter, the details of which are described here.

The "gelation process" is strongly influenced by many process parameters which include, the concentration of the metal ions, gelating agents and heating rate. Often the appropriate recipe for the gelation is arrived at by trial and error. In order to identify the exact condition at which gelation takes place, an appropriate parameter that would serve as an indicator needs to be monitored. The refractive index of the mixture as well as the viscosity of the "borth" are among such indicators. In order to map the concentration regimes over which the gelation takes place, the viscosity of the broths need to be monitored. An abrupt change in the viscosity is indicative of the onset of gelation. To carry out such experiments on the broths that contain Pu, a special viscometry set up was established in a glove box. The gelation temperature of broth containing uranium with 21% Pu was measured using this facility.

2. Preparation of fine fraction (115 ± 10 μm) UO_2 microspheres by using the jet-entrainment set-up

The internal gelation process involves controlled in-situ gelation brought about by warming of the "borth" by dispersing it in the form of droplets into an oil bath. The method used in the preparation of the coarser microspheres by using a column-gelation set-up is described elsewhere [5]. In this process a pre-cooled broth is dispersed through a vibratory nozzle into a vertical glass column in which hot silicone oil is circulated. The column is so designed that from their point of discharge to the bottom of the oil column, the droplets flow counter current to silicone oil. Upon reaching the bottom of the column, the droplets flow co-current with the silicone oil and exit the column along with it. These droplets undergo gelation during its residence within the column of hot silicone oil. The finer fraction (115 ± 10 μm) of microspheres could not be prepared using such a column gelation set up; because owing to their lower density these finer droplets (400 μm) dispersed from a fine bore (200 μm) nozzle tend to remain on the surface and do not sink in and flow down the column. Further, their increased number density within a given area over which they were dispersed, led to their coalescence before gelation, impairing the control of size.

To circumvent these difficulties, a set-up based on the jet-entrainment technique was established (Fig.1). It essentially comprised a hot silicone oil jet that flew through the air and carried the droplets discharged from a 200 μm nozzle as and when they came in contact with the former. The broth was held in a pre-cooled tank from which it was fed to the nozzle through pressure transfer. The pressure in the feed tank is kept constant throughout the course of the experiment by using the pressure indicator/controller. The nozzle was vibrated using an electromagnetic vibrating diaphragm. The hot silicone oil was circulated from a hot (85°C) thermally insulated reservoir (40 L) fitted with a temperature controller. We observed that the linear flow velocity of the oil should be greater than 1.6 m/s in order to prevent the dispersed droplets from coalescing. The jet of hot silicone oil acts as both the hydrophobic medium as well as the source of heat.

The process parameters for the preparation of the UO_2 microspheres (115 ± 10 μm) were optimized through several trial runs (Table 1). An optimum size of the nozzle was found to be 200 μm. Acid deficient uranyl nitrate (ADUN) was used to calibrate the flow through the nozzle, for its density approximated that of the broth. After establishing the laminar flow rate with an appropriate pressure differential, the number of droplets that would be dispersed per minute was calculated. The fact that in a stream with laminar flow through a nozzle, the natural distance at which the stream breaks of would be 4.5 D (where D is the diameter of the nozzle) and therefore used in arriving at the mean droplet volume. From the above parameters the desirable frequency of vibration was arrived at. Subsequently the gelled spheres were dried in an oven at 373 K, and calcined at 573 K in air, reduced at 1073 K in flowing Ar + 8% H_2 and finally sintered at 1573 K under reducing atmosphere. The sintered UO_2 microspheres prepared by using these optimized parameters, exhibited good physical integrity and are shown in Fig. 2.

Table 1. Optimized parameters used in the jet entrainment experiments

Parameter	Differential Pressure	Broth Flow rate	Droplet Volume	Vibrator Frequency
Optimized Value	1500 mm H_2O	8.33 mL / min	3.76 x 10^{-5} mL	3700 Hz.

3.0 Vibro-compaction

The vibratory compaction involves dynamic consolidation of a system of spheres in a confined volume. While we consider the packing of mono-dispersed hard spheres, the maximum packing fraction achievable would be limited to about 64% of the volume [4], if they adopt the close packed structure. The "sphere-pac" process involves packing of the spheres in a limited volume. Thus smear densities of the order of 80 % TD cannot be achieved with a system of single fraction of mono-disperse spheres. Hence, multimodal packing is often resorted to. It was observed that for achieving the smear density mentioned above, at least two size fractions need to be used. The interspaces created by the coarser fraction would be filled by the finer spheres. In order to facilitate effective infiltration and space filling the relative ratios of the sizes had to be maintained such that the finer fraction has just $1/7^{th}$ the diameter of the coarse fraction. Further, they need to be used in the volume ratio as, coarse : fine = 3:1 [5]. Owing to the difficulties involved in the preparation of the fine fraction MOX microspheres, we chose to use a coarse fraction comprising the U, Pu mixed oxide (MOX) and a fine fraction that was UO_2.

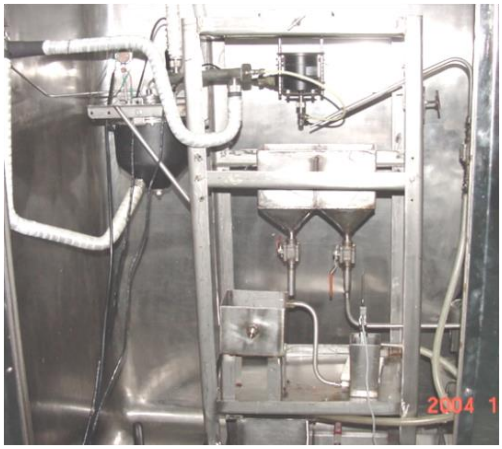

Fig. 1. Jet-entrainment facility

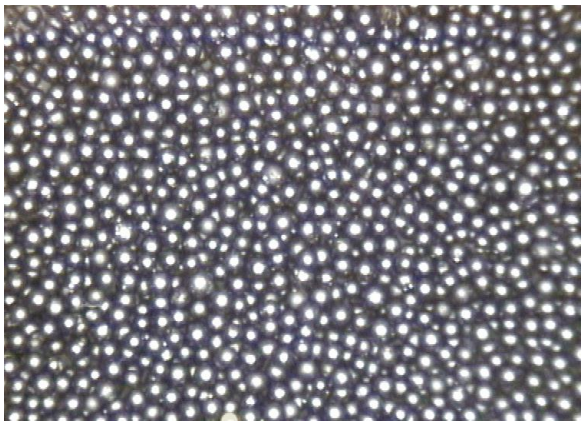

Fig. 2. Sintered fine fraction UO_2 microspheres (magnification: X16)

We tried two different methods in the vibrocompaction. In the first, the clad was filled with the coarser fraction, which was followed by the infiltration of the finer fraction. This method did not yield the desired density as the infiltration was incomplete. Hence, a second method was devised in which the clad was filled with a small aliquot of the coarse microspheres following which the finer spheres were allowed infiltrate by vibrocompaction. The clad was thus filled in multiple steps. The second method called the "batch infiltration method" yielded the desired result. The frequency of the vibration for the coarse fraction was varied from 10 – 500 Hz and that for the infiltration of fine fraction was varied from 100 – 3000 Hz. The relative displacement (amplitude) was indexed by using the current flowing through the electromagnetic vibrator. Without the vibration the coarser fraction, the finer fraction was packed at a frequency of 1000 Hz to ensure complete infiltration.

The uniformity of the packing (± 1%) was ascertained by measuring the axial density profile by using gamma scanning system (Figs. 3 & 4).

Fig. 3. Axial gamma scanning equipment

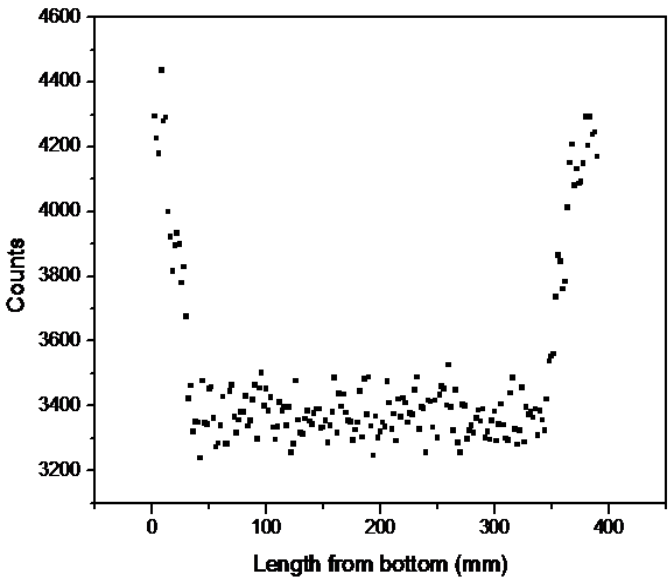

Fig. 4. Axial density profile of the vibro-packed fuel pin

4.0 Fabrication of sphere-pac fuel pins and test irradiation in fast reactor

4.1 Salient features of the glove box facility

The schematic of the sol-gel fuel fabrication facility is shown in Fig. 5. The photographs of the sphere-handling facility and the fuel pin welding facility are shown in Fig. 6 and 7, respectively. Facilities for degassing the microspheres, their transfer into the clad tube, vibro-compaction and welding of the fuel pin were housed in these glove boxes.

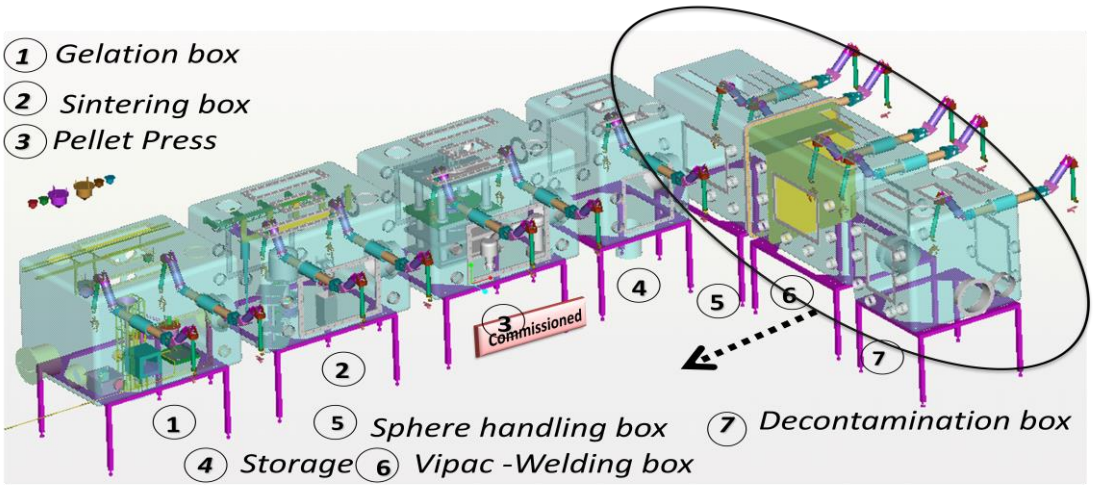

Fig. 5. Schematic of the fuel fabrication facility by sol-gel process

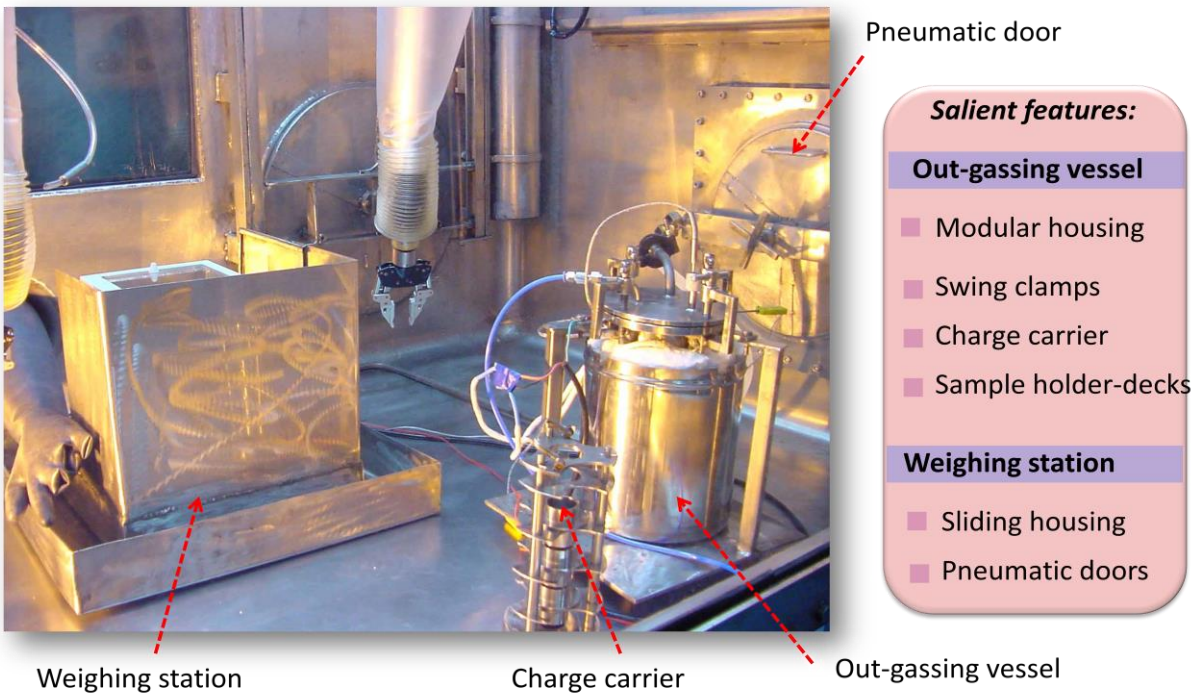

Fig. 6. Photograph showing the microsphere-handling unit inside a glove box

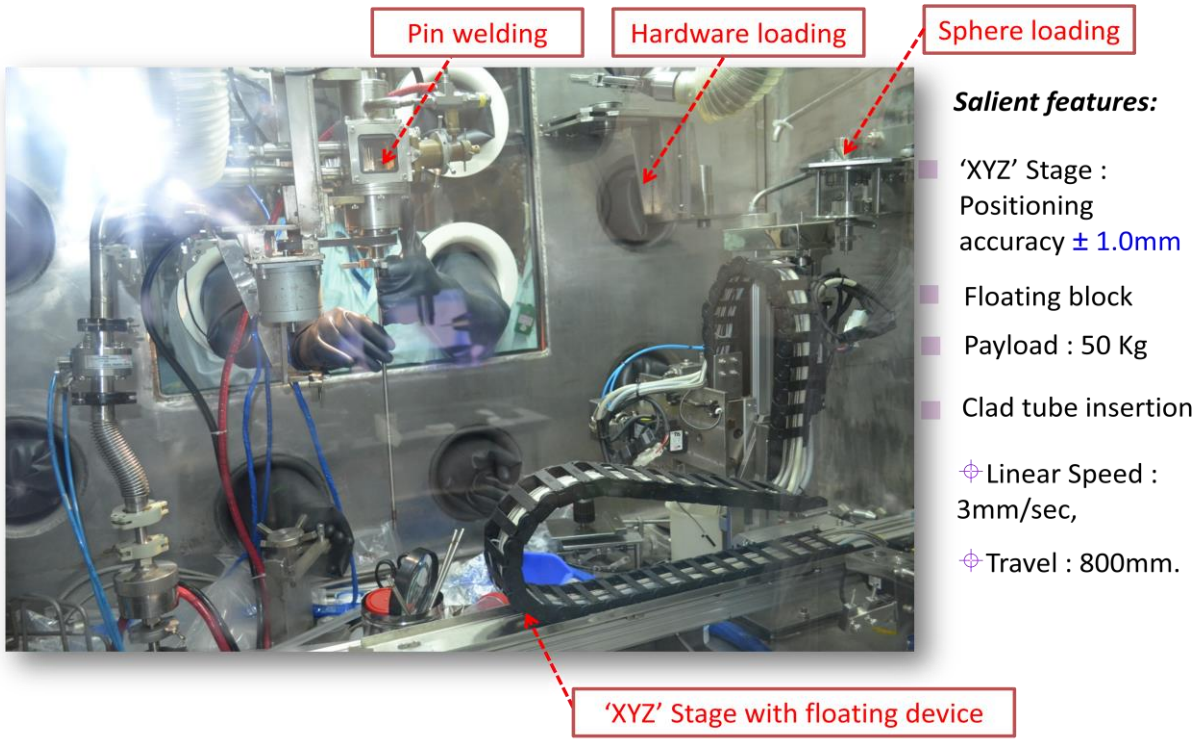

Fig. 7. Photograph showing the fuel pin welding facility inside a glove box.

4.2 Fabrication of sphere-pac fuel pins

The microspheres were degassed to remove adsorbed moisture by heating it in the vacuum oven at 373 K under the vacuum of 10^{-3} mbar. An appropriate amount of degassed spheres was accurately weighed and transferred into the fuel pin directly held on to an electromagnetic vibrator placed in the vibropac –welding glove box. After the introduction of coarse MOX microspheres, the fine fraction of UO_2 microspheres were infiltrated in the bed of the coarse fraction by vibro-compacting using the optimized parameters of vibration. The total fissile column length in the fuel pin was 160 mm.

After completing the vibro-compaction the necessary hardware, viz., SS-frit, insulation pellet, spring retainer, spring and end cap were introduced into the fuel pin at the hardware loading station. The fuel pin was held vertically inside the welding chamber and was closed by ramming the top end plug on to the clad tube to make an interference with the latter at a He pressure 6.0-6.5 kg/cm^2. The end plug (AISI316L) was press fit into the clad tube (D9) and welded in the (2G) position by autogenously pulsed TIG welding process. The adverse effects of elevated pressure of He shielding gas during welding viz., onset of turbulence, arc instabilities, increased depth of penetration, narrow bead width and erosion of the tungsten electrode, were circumvented by optimizing the welding parameters. The welded fuel pin was decontaminated and subjected to quality control checks.

The welding procedure and fixture were qualified with the help of quality control protocols laid down for this process. These included visual examination, helium leak testing (HLT, 10^{-15} MPa m^3/s max), X-radiography and metallography. The quality of the weld, pressure and purity of the plenum bond gas were ascertained with the help of tests performed on set-up and process test pins that were welded prior to the actual fuel pin welding. The sphere-pac fuel pins containing MOX microspheres were subjected to dimensional inspection, HLT and full length 'X' radiography in order to ascertain the integrity of their internals (Fig. 8) as well as the weld joint. These quality control checks revealed that the pressure of helium is 6.1 kg / cm^2 and its purity 98% which were as per the

specifications. The axial density profile was measured by using gamma scanning (attenuation) method in order to check if the Pu distribution within the pin is homogenous. The variation was found to be within the acceptable value of ±1% and it was not adversely affected by thermal cycling (Fig.9).

4.3 Irradiation of the sphere-pac fuel pin in Fast Breeder Test Reactor (FBTR)

The qualified sphere-pac fuel pins and reference pellet fuel pin were then introduced into the irradiation capsule, TIG-welded and introduced into a special sub-assembly. The photographs pertaining to the fabrication of the capsule for test irradiation in FBTR is shown in Fig. 10.

Fig. 8. X radiography of the sphere-pac fuel pins

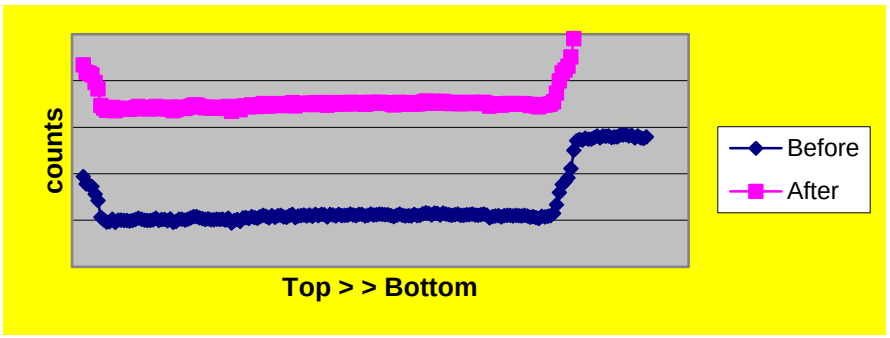

Fig. 9. Axial density profile by gamma scanning before and after thermal cycling

Fig. 10. Fabrication of irradiation capsule for test irradiation in FBTR

The design safety limit on linear power for sphere-pac fuel pins at the beginning of the life (BOL) was calculated to be 238 W/cm and the allowable linear power, based on 16% over power margin, is 205 W/cm. For the first 100 h the capsule containing the sphere-pac and reference fuel pins were irradiated at 205 W/cm. The restructuring after the initial irradiation is expected to increase the thermal conductivity of the sphere-pac fuel pin. Therefore, the capsule was irradiated at 260 W/cm for the next 200 h. The total burn up of the sphere-pac fuel pin is 1350 MWd/t. The post irradiation examination of these fuel pins has been recently completed.

5.0 Development of a plutonium solution handling facility and the determination of the gelation temperature of a broth containing U and Pu.

The equilibrium gelation temperature was determined by measuring the change in the viscosity of the broth upon heating. The time dependent change in viscosity was also measured under isothermal conditions. A special glove box facility was developed to accomplish the above. The glove box comprised two partially isolated chambers that communicated through a sliding window in-between. One part of this glove box was used for the dissolution of plutonium (Fig. 11) and the other for weighing, broth preparation and viscosity measurements (Fig. 12). The equipment required for carrying out these experiments were fabricated in-house and commissioned.

In a typical experiment, plutonium nitrate solution (1 M) was prepared by dissolving PuO_2 in concentrated nitric acid with HF as catalyst. This solution was heated under an IR lamp to remove the excess nitric acid. The plutonium nitrate crystals formed were dissolved in 0.5 M nitric acid and made up to a known volume in a volumetric flask. Acid deficient uranyl nitrate solution (ADUN), HMTA and Urea (HU) (gelating agent) were prepared

separately and transferred in to the glove box. Appropriate quantities of ADUN, HU and plutonium nitrate solution were taken and pre-cooled to 273 K. These solutions were mixed to obtain the broth. The latter was the introduced in to a pre-cooled sample vessel and the change in the viscosity of the broth was determined, by two methods.

Fig. 11. The plutonium nitrate preparation inside part of a glove box

Fig. 12. Broth preparation and viscosity measurement inside another part of the glove box

In the first (isothermal) method, the temperature of the water bath was maintained at 273 K and once the sample was introduced in to the test vessel the temperature of the bath was raised to 313 K at a heating rate of 0.3 K min^{-1} and then the temperature was maintained constant at 313 K for 3 h. In the second (dynamic) method, after the sample was introduced into the pre-cooled sample vessel the measurement of viscosity was carried out upon heating by using a temperature programmable furnace from 273 to 363 K at a heating rate of 3.6 K min^{-1}. The abrupt change in the viscosity as a function of temperature is shown in Fig. 13 The gelation temperature which is indicated by abrupt large change in the viscosity was observed at 313 K after 2 h in the isothermal method and at 348 K in the dynamic mode.

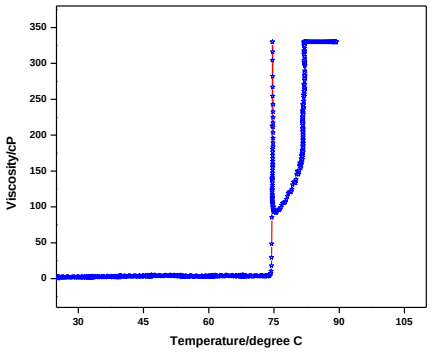

Fig. 13. Viscosity as a function of temperature (dynamic mode)

7.0 Conclusion

A facility was established for the fabrication of sphere-pac fuel pins. UO_2 microsopheres (115 +10 μm) were prepared through internal gelation in a jet entrainment set-up. This facility was designed, developed and commissioned in our laboratory. The microspheres were vibro-compacted and the test irradiation capsule was fabricated through trial runs and process optimization. Test irradiation of this capsule in FBTR was successfully completed. The post irradiation examination of the irradiated fuel pins has been completed

recently. A new facility was created for measuring the viscosity of Pu containing broths. For the first time the viscosity of Pu containing broths have been measured and reported.

8.0 References

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