

## **Supercritical Fluid Extraction of Silicone Oil from Uranate Microspheres Prepared by Sol-gel Process**

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Supercritical fluid extraction of silicone oil from urania microspheres prepared through sol-gel route was investigated. The influence of pressure, temperature, and flow rate on the extraction efficiency was studied. Experimental conditions were optimised for the complete removal of silicone oil from urania microspheres.

### **1. Introduction**

Supercritical fluids provide faster, cleaner, and efficient extractions. The low viscosity, high density, low surface tension, and better diffusive properties help supercritical fluids to easily penetrate through the pores of a sample matrix and extract the components of interest efficiently.<sup>1-3</sup> Supercritical fluid extraction (SFE) results in little or no waste. Carbon dioxide as supercritical fluid is non-toxic and inexpensive, making it an attractive candidate as a solvent for extraction. The extraction power of supercritical carbon dioxide (SC-CO<sub>2</sub>) depends on its density which can be altered by varying the pressure/temperature.

Conventionally used techniques for the removal/recovery of materials from different waste matrices e.g. from nuclear waste, generate relatively large amount of secondary liquid waste with proportional consumption of solvents. But the supercritical fluid extraction technique enables the same task with minimum or no waste since the fluid escapes as a gas after extraction, thus reducing the burden of secondary waste generation considerably. This is obviously an attractive feature especially in nuclear industry where the main concern is accumulation of radioactive waste. In addition, the SFE technique obviates in many cases the cumbersome pre-treatment of waste matrix. Application of SFE technique for radioactive materials using modified SC-CO<sub>2</sub> demonstrated the feasibility of efficient extraction.<sup>4-10</sup> The SFE of uranium from tissue paper waste was also demonstrated from our laboratory.<sup>11-12</sup> This paper presents an important application related to the removal of silicone oil from urania microspheres produced by sol-gel process wherein silicone oil is employed as the gelation medium.

Sol-gel process for the production of nuclear material offers the advantages such as amenability for remotisation and elimination of powder handling leading to less man rem problems. Hence, it is being considered for the development of future fuel cycles by international initiatives such as INPRO by IAEA.<sup>13-14</sup> Internal gelation process is one of the important sol-gel routes for the preparation of microspheres of nuclear fuel materials in which in-situ homogeneous release of ammonia by decomposition of hexamethylenetetramine (HMTA) is used for the conversion of solution droplets into hydrous gel particles.<sup>15</sup> In this process, silicone oil is used as the gelation medium. After the completion of gelation, the silicone oil is removed from the micro-spheres by washing with carbon tetrachloride. This leads to a generation of large amount of radioactive liquid waste. To obviate this disadvantage, extraction of silicone oil using SC-

CO<sub>2</sub> was investigated.

The extraction of silicone oil was initially studied using SC-CO<sub>2</sub> as a function of its pressure, temperature, and flow rate. Subsequently, silicone oil present in urania microspheres was extracted. The influence of various SFE parameters was investigated and the results are discussed.

### **2. Experimental**

**Preparation of microspheres.** The urania gel preparation was carried out in an assembly described elsewhere.<sup>15</sup> The broth was prepared by mixing desired quantities of acid-deficient uranyl nitrate and HMTA-urea mixture pre-cooled to -2°C and charging into the feed tank. The broth was fed into the gelation column in the form of droplets. The droplets slowly traveled down into the wider limb of the column with the hot silicone oil flowing upwards. As the droplets reached the bottom of the column, the oil flow carried them up to the narrow limb. The gelled droplets were transferred to the oil-separator assembly for separating the silicone oil.

**Removal of silicone oil.** The gelled spheres were separated into two equal lots. The first lot of the spheres was washed by the conventional method, i.e. initial wash with carbon tetrachloride to remove oil and with 5% NH<sub>4</sub>OH solution to remove ammonium nitrate and residual gelation agents. During each batch of ammonia wash, 10 minute period was given for each rinse with 500 mL of 5% NH<sub>4</sub>OH, the electrical conductance of the wash solution was measured using conductivity meter. The washing was continued until the conductivity of the wash solution reduces to the background values of 5% NH<sub>4</sub>OH solution. The second lot of the spheres was subjected to SFE using SC-CO<sub>2</sub>.

**SFE system.** The SFE system (M/S Jasco, Japan) used in the present studies consisted of a solvent delivery system, a constant temperature oven ( $\pm 0.1^\circ\text{C}$ ) and a back pressure regulator. Extraction vessels (EV) of 10 mL and 50 mL capacity were employed for the studies. Carbon dioxide used in the SFE was of supercritical grade (99.99%).

**Silicone oil collection and assay.** The extracted silicone oil was collected either in an empty flask or in a flask containing small quantity of *n*-heptane. It was assayed by weight and also using IR spectroscopic technique (with BOMEM FTIR MB 100 spectrophotometer) when present in smaller quantities (ppm levels). After the extraction, the spheres were shaken with known volume of *n*-heptane, and an aliquot was used for the IR analysis. Calibration graph for the IR determination was prepared for the range 5 to 75 ppm with a detection limit of 1 ppm.

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**SFE of silicone oil.** The silicone oil and the same present in uranate micro spheres were subjected to SFE in 10 and 50 mL extraction vessels. The extraction was studied as a function of pressure in the range of 100–300 bar and in the temperature range of 308–323 K. The influence of silicone oil content in the microsphere, extraction vessel capacity and SC-CO<sub>2</sub> flow rate was investigated.

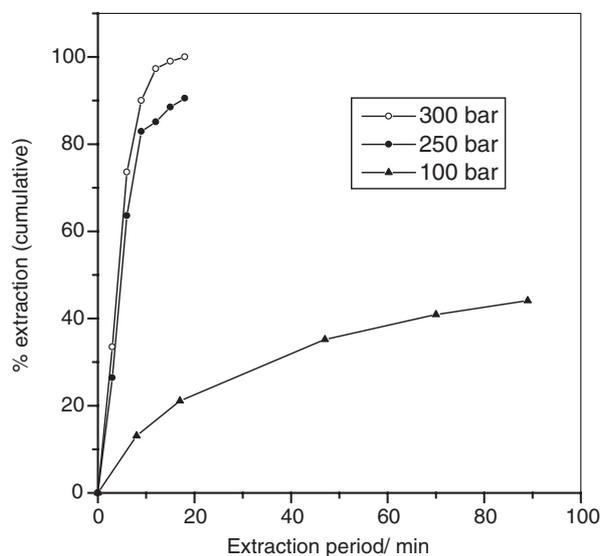
**Preparation of simulated samples of silicone oil in urania microspheres.** A batch of samples were prepared by equilibrating urania microspheres of about 5–10 g with 1 g of silicone oil in *n*-hexane followed by evaporation of the volatile solvent. Another batch of samples were prepared by equilibrating about 10 g of urania microspheres with different amounts of silicone oil in *n*-hexane followed by evaporation of the volatile solvent, *n*-hexane.

### 3. Results and Discussion

**Extraction of silicone oil.** The results on the extraction of silicone oil (5 g) with no matrix present in the 10 mL extraction vessel for various operating pressures using SC-CO<sub>2</sub> are shown in Figure 1. A SC-CO<sub>2</sub> flow rate of 5 mL/min was employed. Complete extraction was observed in about 20 min when the pressure was about 300 bar. It was about 90% at 250 bar for a similar extraction period. The extraction kinetics was, however, found to be slow at a lower pressure of 100 bar, and about 45% extraction only for a period of 90 min. Increase in pressure leads to higher CO<sub>2</sub> density resulting in better solubilisation of silicone oil, thus enhancing the extraction kinetics. Accordingly higher pressures are required for faster and complete extraction of silicone oil.

When the same experiment was carried out using 50 mL extraction vessel under similar conditions for the same quantity of oil, extraction was found to be slower and about 100 min extraction period was required for complete removal of silicone oil at a pressure of 250 bar and a flow rate of 5 mL/min with a 50 mL extraction vessel (Figure 2). However, the trend in extraction behavior with pressure variation remains the same, as in the case of 10 mL extraction vessel.

Extraction profiles of 5 g of silicone oil both in 10 and 50 mL capacity extraction vessels were compared. The 10 min extraction with the flow rate of 5 mL/min in 10 mL vessel (five changes of fluid) caused complete extraction whereas the 10 min extraction with the same flow rate in 50 mL extraction vessel (one change of fluid) effected only about 20% extraction. Even though in both the cases, the total amount of CO<sub>2</sub> was maintained same i.e. 50 mL in 10 min, it had 5 incremental

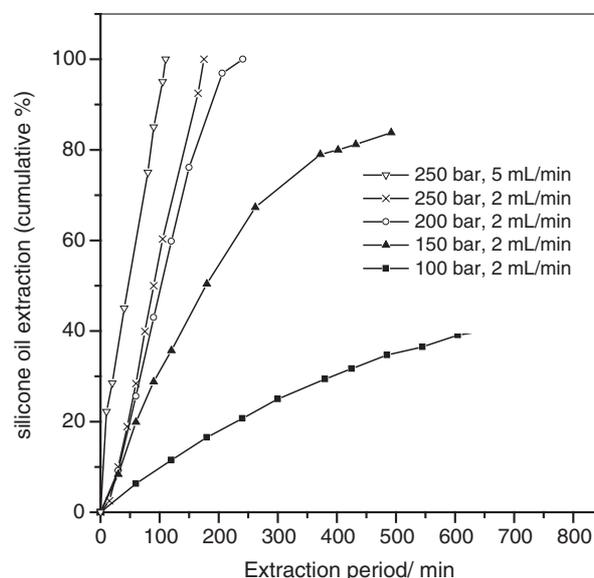


**Figure 1.** Extraction of silicone oil (no matrix) using SFE. Experimental conditions: SC-CO<sub>2</sub> *P*: 100–300 bar, flow rate: 5 mL/min, *T*: 308 K, EV: 10 mL, silicone oil content: 5 g.

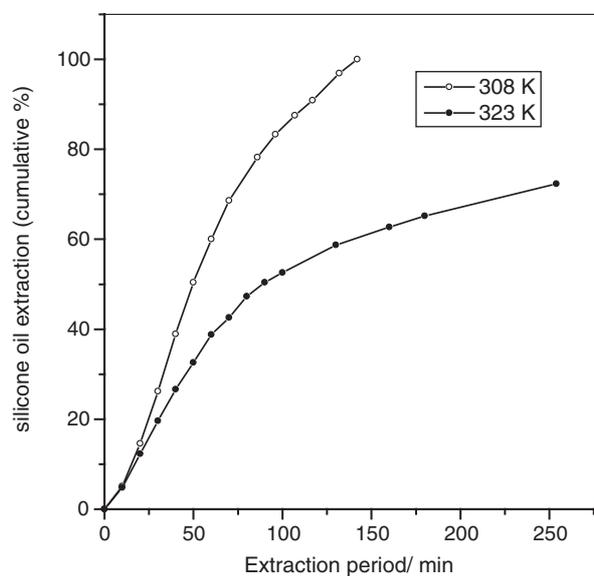
extractions in 10 mL EV but only 1 extraction in 50 mL EV in the given 10 min. This observation agrees well with the established fact in the conventional solvent extraction technique that the higher incremental extractions always lead to better extraction efficiency. Hence it suggests that the minimum capacity extraction vessel for the given amount of solute is always preferred for the more efficient and economical supercritical fluid extraction technique.

Better extraction behaviour was observed at lower temperatures i.e. 308 K compared to higher temperature i.e. 323 K (Figure 3). For example, complete extraction of about 1.3 g of silicone oil was observed at 308 K for an extraction period of 140 min. However, only 60% extraction was observed when the extraction temperature was kept at 323 K for the same period. This behaviour is explained by the fact that the density of SC-CO<sub>2</sub> is high only at lower temperatures and density decreases with raise in temperature. Hence the solubility of silicone oil in SC-CO<sub>2</sub> decreases with raise in temperature.

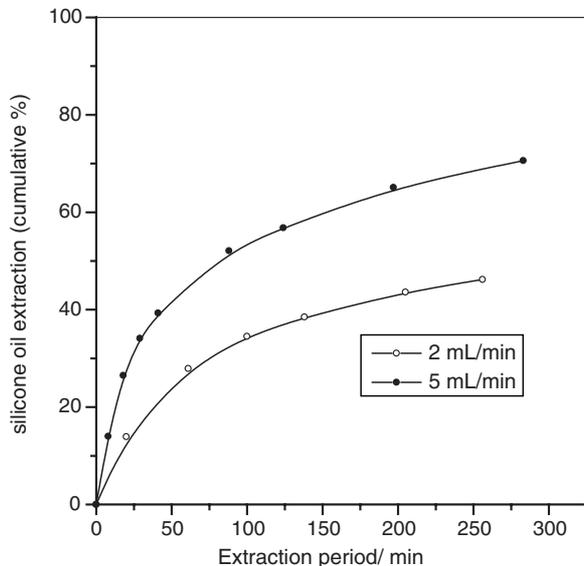
The extraction of silicone oil was also studied as a function of SC-CO<sub>2</sub> flow rate (Figure 4). Better extraction behaviour was observed at higher flow rates. For example, at 100 bar and 308 K, extraction of about 70% and 45% were observed



**Figure 2.** Extraction of silicone oil using SFE from a larger capacity vessel. Experimental conditions: SC-CO<sub>2</sub> *P*: 100–250 bar, *T*: 308 K, flow rate: 2–5 mL/min, EV: 50 mL.



**Figure 3.** Influence of temperature on the extraction of silicone oil. Experimental conditions: SC-CO<sub>2</sub> *P*: 150 bar, flow rate: 2 mL/min, EV: 10 mL, silicone oil taken: 1.29 g.



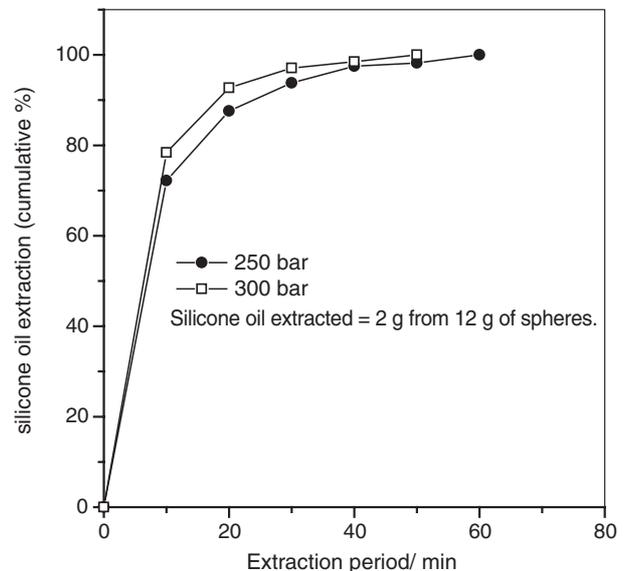
**Figure 4.** Influence of SC-CO<sub>2</sub> flow rate on the extraction efficiency of silicone oil. Experimental conditions: SC-CO<sub>2</sub> *P*: 100 bar, *T*: 308 K, EV: 10 mL, silicone oil employed: 3.5 g.

for a flow rate of 5 and 2 mL/min, respectively. Thus higher operating SC-CO<sub>2</sub> flow rate is essential for faster removal of silicone oil. It is also illustrated (Figure 2) with a 50 mL capacity extraction vessel.

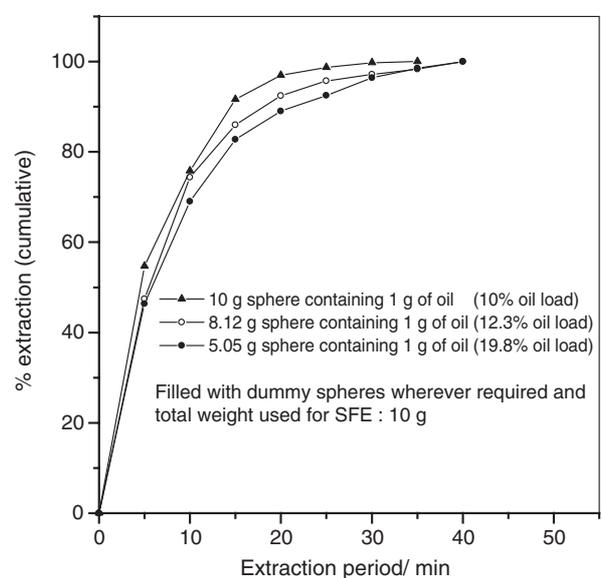
**Extraction of silicone oil from spheres.** Initially the gelled spheres were directly subjected to SFE extraction in the pressure range of 73–300 bar at 308 K. It was observed that the spheres in the extraction vessel crumbled during extraction. Initially this was assumed to be due to the extraction of the residual gelation agents, HMTA-urea along with the silicone oil from the soft wet gels. Subsequently, the gelled spheres were washed with 5% NH<sub>4</sub>OH solution and the complete removal of gelating agents was ensured by measuring the electrical conductance of the wash solution. It was observed again that the spheres got crumbled during the extraction despite ammonia wash. Thus it is evident from these studies that the wet gels are not suitable for extraction under the SFE conditions. The microspheres prepared are intended to be used for the fabrication of sphere pac fuel pins for the fast reactors. The crack or crumbling of spheres is undesirable as it will create small particles or powders and thereby we lose one of the main advantage of the sol-gel process i.e. elimination of powder handling. Thus it is essential to maintain the integrity of spheres during extraction.

Therefore the spheres were washed with NH<sub>4</sub>OH and then dried in an oven at 373 K for 12 hours and the dried spheres were then subjected to SFE. The sphere integrity was now observed to be intact under these experimental conditions. The results of the experiment on the extraction of silicone oil from microspheres are shown in Figure 5. About 2 g of oil was extracted completely in about 50 min at a pressure of 300 bar from about 12 g of spheres. Silicone oil content after extraction was found to be as low as 7 ppm in a typical run where 12 g of sphere was loaded in 10 mL extraction vessel with 5 mL/min CO<sub>2</sub> pumping. The typical extraction period was about 60 min. About 200 g of spheres were subsequently processed in three batches using 50 mL capacity vessel at a SC-CO<sub>2</sub> flow rate of 5 mL/min. Complete extraction of silicone oil from microspheres was ensured by IR spectroscopic analysis (< 7 ppm). The extracted quantity of silicone oil from the microsphere was found to be about 16%.

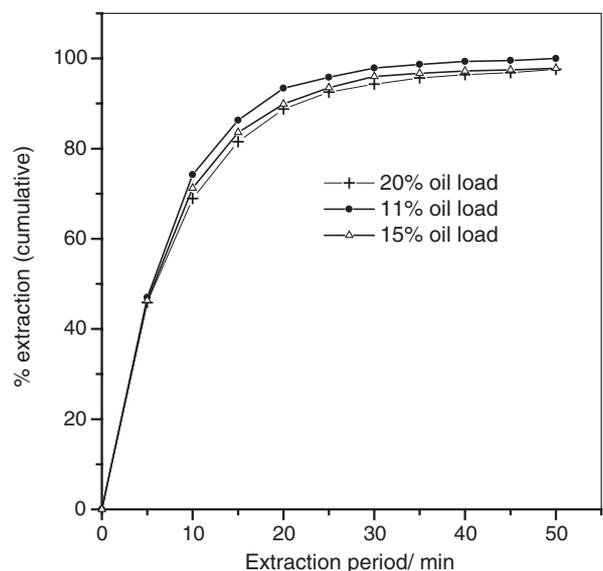
The results on the influence of silicone oil content in the microsphere (simulated samples) on the extraction efficiency are presented in Figures 6 and 7. A small variation in the rate of extraction was observed. For example, silicone oil from 10% oil loaded sample was extracted at a relatively faster rate



**Figure 5.** Extraction of silicone oil from urania microspheres. Experimental conditions: SC-CO<sub>2</sub> flow rate: 5 mL/min, EV: 10 mL.



**Figure 6.** Influence of silicone oil content in urania microsphere. Experimental conditions: SC-CO<sub>2</sub> *P*: 250 bar, flow rate: 5 mL/min, *T*: 308 K, EV: 10 mL.



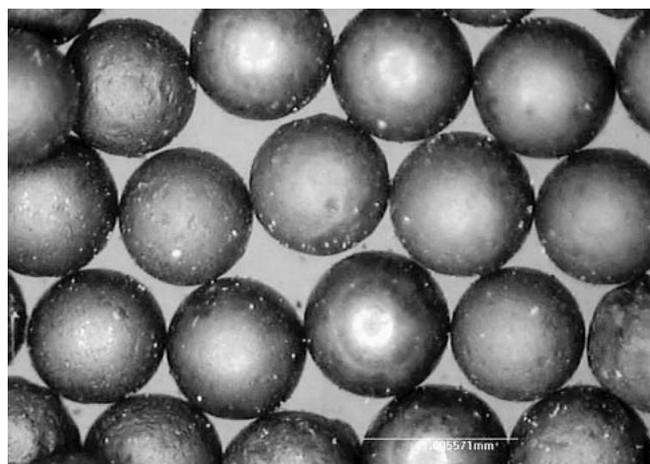
**Figure 7.** Extraction of silicone oil from urania microspheres. SC-CO<sub>2</sub> *P*: 300 bar, flow rate: 3 mL/min, *T*: 308 K, EV: 10 mL, 10 g of spheres employed.

compared to one corresponding to 12.3 and 19.8% oil loaded samples (Figure 6). However the difference in the rates of extraction were not significant. Data in Figure 7 also indicate that silicone oil from microsphere samples with lesser oil content could be extracted at a faster rates compared to samples with higher oil content.

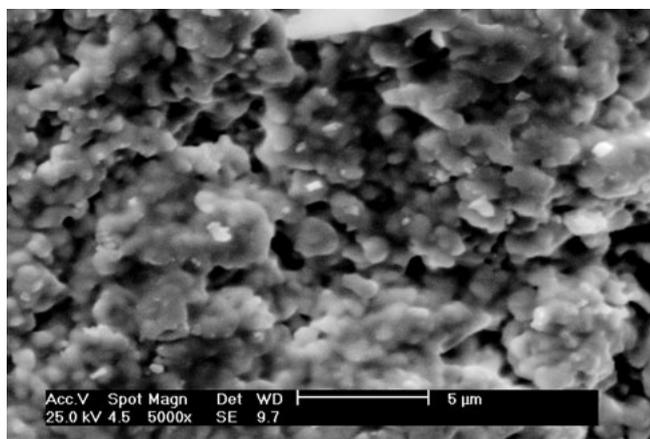
These spheres were subsequently subjected to heat treatments along with the spheres washed by conventional procedures i.e. these spheres were initially heated to 573 K for 4 hours, reduced under Ar + 8% H<sub>2</sub> at 1073 K for 4 hours and sintered at 1473 K for 4 hours.

The spheres obtained from SFE and the one prepared through conventional washing procedure were compared under microscope and found to be crack free. The microscopic image of the sintered microspheres, which underwent SFE, is shown in Figure 8. The density of the microspheres was measured using helium pycnometer. The average density of the sintered spheres which were subjected to SFE extraction was found to be 10.87 g/mL (99% TD) which is similar to the one obtained for the spheres which underwent CCl<sub>4</sub> wash.

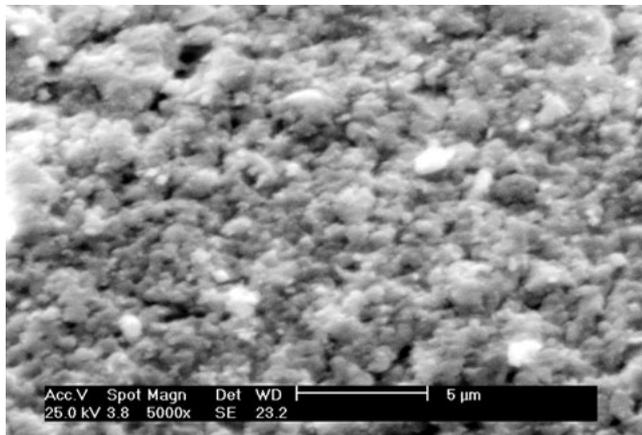
The SEM pictures under the same magnification of the sintered microspheres, prepared by washing under SFE and conventional methods are shown in Figures 9 and 10, respectively. The microstructure of both the spheres is flaky in nature. As seen in the figure the individual grain and pore size of spheres washed by SFE method appears to be an order of magnitude higher than that washed under conventional washing procedure. This may be due to extraction of certain residual gelating reagents by supercritical CO<sub>2</sub> after passing through the pores of matrix which might increase the pore size.



**Figure 8.** Microscopic image of urania microspheres after removal of silicone oil through SFE technique followed with heat treatment.



**Figure 9.** SEM of sintered microspheres subjected to SFE.



**Figure 10.** SEM of sintered microspheres wherein silicone oil has been removed by washing under conventional method.

#### 4. Conclusion

Silicone oil is extracted completely from uranate microspheres at 300 bar and 308 K. The microspheres after the extraction were found to maintain the integrity and similar to the conventionally washed spheres. They were also suitable for subsequent steps in the preparation of UO<sub>2</sub> spheres. The supercritical fluid extraction is thus an excellent alternate method with negligible generation of liquid waste for the removal of silicone oil from microspheres produced through sol-gel route.

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