SOL-GEL PROCESS FOR CERAMIC NUCLEAR FUELS

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Introduction

Processing of ceramic materials is known to mankind from very early ages. The first products were the baked earthen pots and later the sophisticated china pottery. Generally, the ceramic materials are associated with high chemical stability at elevated temperatures without large change in the physical properties. These properties associated with ceramic materials make them highly attractive for their use as nuclear fuel materials. Oxides, carbides, nitrides, silicides of uranium, thorium and plutonium and their mixtures fall in this category. Powder metallurgical routes have been established for the production of oxide, carbide and nitride fuels. The established procedures have been used industrially for the production of UO$_2$, (U,Pu)O$_2$, (U,Pu)C pellets successfully. Fabrication of UO$_2$ pellets using powder metallurgical process for the power reactors is a very well established route. However, the following problems are associated with the fabrication of Pu or U-233 fuels using powder metallurgical route.

1. Handling of large quantity of highly toxic radioactive powders.
2. Large number of mechanical steps in the fuel fabrication flow sheet.
3. Difficulties in remotisation of the process as a consequence of the above.
4. Increase in the man-rem problems with the aging of the fabrication facility because of $^{241}$Am built up.

Sol-Gel Processes

For the above reasons, the powder metallurgical routes are considered not ideally suited for the fabrication of Pu or $^{233}$U bearing fuels as they involve fabrication facility to be housed in glove-boxes and remote handling. In early sixties, attempts were made to develop solution-based fuel fabrication processes for the production of Th-$^{233}$U fuels. Solution-based routes were first investigated for the production of spherical coated particle fuel for
the High Temperature Gas cooled Reactors (HTGR). The coated fuel microspheres (UC\textsubscript{2}, UThC\textsubscript{2}) were manufactured by using new solution/sol-based routes called Sol-Gel process. The name Sol-Gel process is a generalized heading for chemical routes which involves the gelation of a droplet of sol or solution of the desired fuel material into a gel microsphere. These are washed, dried and heat treated to obtain high density microsphere. These processes offer a large number of advantages over the conventional powder route. Sol-gel processes do not require handling of radioactive powders and involve handling of fluids or fluid like materials which are ideally suited for the remote handling. These processes also minimize the number of mechanical operations and thus reduce the man-rem problems.

Various countries having plutonium fuel development programme developed different versions of sol-gel processes. At ORNL, USA, a sol dehydration process was developed. The process was demonstrated for the production of ThO\textsubscript{2}, UO\textsubscript{2}, (U,Pu)O\textsubscript{2}, and (Th,U)O\textsubscript{2} microspheres. Another sol-based process was developed at CNEN in Italy called SNAM process. The process was a combination of external gelation of sol droplets in organic medium. At KFA, Germany, a solution-based process called 'external gelation (KFA) process' was developed for ThO\textsubscript{2} and UO\textsubscript{2} microspheres. At Harwell, UK, another version of external gelation called 'gel supported precipitation' was developed for UO\textsubscript{2}, (U,Pu)O\textsubscript{2} microspheres. KEMA process, also known as Internal Gelation process, was developed at KEMA laboratories in Netherlands and in many other laboratories like at ORNL, KFA, in Russian labs, in Czechoslovakia labs, at Wurenlingen in Swiss labs, BARC, India, etc.

The sol-gel routes are designed to use the output of reprocessing plant in the form of solutions and convert them into consolidated gel particles, thus eliminating the powder handling and the associated hazards. Vibro- compaction of multiple sizes of high density microspheres in fuel pin cladding has been used to fabricate VIPAC type fuel pins. The history of irradiation behavior of power reactor fuels favour pellet fuel. Thus, a hybrid process involving the sol-gel process in the front end of fuel fabrication merged with the pellet making process called Sol-Gel Microsphere Pelletisation (SGMP) process was developed to get the best of the two processes.

**Internal Gelation Process**

Internal Gelation Process (IGP) is one of the well studied process in BARC for the preparation of gel microspheres of UO\textsubscript{2}, ThO\textsubscript{2}, (U,Pu)O\textsubscript{2}, (Th,U)O\textsubscript{2}, etc. The process uses the solutions of the nitrates of uranium, thorium and plutonium or their desired mixtures. The cooled (~0°C) metal nitrate solutions

![Fig. 1 Flow Chart for Internal Gelation Process](image)
are mixed with urea and HMTA (hexamethylenetetramine) solution in cooled condition (~0°C). The droplets of this mixture are contacted with hot oil (silicone oil ~90 °C) to make gel microspheres. These gel microspheres are washed first with CCl₄ to remove the silicone oil and then with NH₄OH solution to remove excess gelation agents — HMTA, urea and ammonium nitrate. The washed particles are dried at 150°C in air and then calcined up to 500°C to remove residual organic matter and ammonium nitrate. The calcined microspheres are then reduced in N₂+H₂ mixture at 600°C. The UO₂ microspheres thus produced are sintered at 1200°C for 3 hrs to produce >99% TD microspheres. The flow chart of the Internal Gelation Process is given in Figure 1.

The gelation behaviour of feed solution comprising of metal nitrate solution, HMTA and urea is the deciding factor for the properties of the gel particles.

Studies have been carried out in FCD, BARC, to establish the gelation behaviour of the feed solution as a function of gelation temperature and the quality of resultant gels.

Results of these studies for feed solution containing uranium and thorium solution as a function of feed composition have been consolidated to yield gelation field diagram.

The gelation behaviour of the feed solution is understood from the way urea and HMTA react with metal nitrate solutions. Urea (CO(NH₂)₂) reacts with the heavy metal ions U(VI), Pu(IV) and Th(IV) at low temperature ~0°C to form complexes which prevent hydrolysis at low temperature of these metal ions by HMTA ((CH₂)₆N₄). The metal ion complexes dissociate during gelation as they are unstable at higher temperatures. Metal ions hydrolyze as per reaction (1)

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(UO₂^{2+} + H₂O = (UO₂(OH))^{+} + H^+ \] (1)

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HMTA \text{ reaction: } \ (CH₂)₆N₄ + H^+ = [(CH₂)₆N₄] H^+ \] (3)

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(\text{NH}_₄)₆N₄H^⁺ + 9H₂O = 6HCHO + \text{NH}_₄^+ + 3 \text{NH}_₄OH \] (4)

Ammonium hydroxide generated reacts with hydrogen ion to neutralize and form the metal ion polymer \((UO₂ (OH))_{n}^{n-}\). The properties and molecular weight depends on the kinetics of reactions. Reaction (3) is ionic in nature and thus fast, and reaction (4) is comparatively slow. Thus, the properties of the gel depend on whether the hydrolysis is caused by reaction (3) or by reaction (4). When large molar ratio of HMTA/U is present, majority of hydrolysis is completed by the reaction (1). Resultant gel because of fast kinetics does not allow growth of crystallites and the gel formed is transparent or translucent.

![Fig.2 Gelation field diagram for uranium](image)

The gels formed with lower molar ratio of HMTA/U in the solution are predominantly formed by reaction 4 and thus the crystallites of the polymer are allowed to grow because of slow kinetics. These variations are clearly seen in the gelation field diagram as shown in Figure 2.
Feed compositions having uranium molarity between 1.0 to 1.4 M have been successfully used for the preparation of UO$_2$ gel particles. These gel particles have been sintered to make >99%TD UO$_2$ microspheres of 500 to 700 $\mu$m dia. Figure 4 shows sintered UO$_2$ microspheres. These microspheres are well suited for the vibro-compaction of fuel pins.

Regions involving lower molarity of uranium (0.7 to 0.9M) have been used for the preparation of UO$_2$ of smaller diameters between 70 to 100 $\mu$m dia. The regions involving higher molarity of uranium >1.35 M use lesser quantity of gelation agents HMTA and urea per kg of uranium processed. Using two sizes of microspheres, fuel pins can be vibro-compacted to give 82-83% smear density in the fuel pin. Such fuel pins have been fabricated and irradiated in Fast and Thermal Reactors in many countries. In pile and post irradiation examination, results of such experiments with mixed oxide and carbide fuels have been very encouraging.

**SGMP**

SGMP processes for the fabrication of UO$_2$ and (U,Pu)O$_2$ pellets have been studied in Fuel Chemistry Division and Radio Metallurgy Division of BARC. Originally, gel spheres containing carbon pore former were used for the process which required very long and highly controlled heat treatment schemes. The SGMP process was modified by the use of gelation field diagram. Compositions of feed solutions suitable for obtaining crushable UO$_2$ microspheres were identified by observing the regular change of dry gel properties as a function of feed composition.

The flow chart of SGMP for oxide pellets is given in Figure 5. Suitable feed compositions along with the calcination and reduction steps of heat treatment have been chosen to optimize the properties of the dry gel microspheres that do not shrink during further heat treatment and are soft. The compositions suitable for the SGMP are having higher molarity of uranium (>1.4 M) in feed solution. The pressed pellets are sintered at desired temperature to make high density pellets. Low Temperature Oxidative Sintering (LTS) procedure has been used to make UO$_2$ pellets suitable for PHWR. Figure 6 shows various stages of SGMP for making sintered UO$_2$ pellets.

Two fuel bundles using SGMP pellets have been successfully irradiated at MAPS.
A similar SGMP process has been optimized for the preparation of ThO$_2$ and (Th,2%U)O$_2$ pellets for their use in fabrication of fuel elements for AHWR. Various stages of SGMP for ThO$_2$ are seen in Figure 7.

![Fig. 7 Stages of SGMP for ThO$_2$ pellets](image)

A glove box facility for the preparation of (U,Pu)O$_2$ microspheres has been set up at FCD. Figure 8 gives the details of the gelation setup in a glove-box.

![Fig. 8 Gelation equipment in glove-box](image)
A fore-runner sol-gel facility has been set up at FCD. This setup is operated using a fully computerised control system. The setup has been used as a demonstration facility and has also been used for the qualification of equipment suitable for all future sol-gel facilities. The fore-runner facility is seen in Figure 9. A demonstration plant for sol-gel MOX microspheres is being set up at A3F Tarapur and another sol-gel facility is being set up at FCD, IGCAR at Kalpakkam.

The Sol-Gel Team

The team responsible for the development of sol-gel process comprises of following officers of FCD and RChD : Dr. S.K.Mukerjee, Mr R.V.Kamat, Mr S.Suryanarayana, Mr S.Venkateswaran, Mr S.B. Rajure, Mr J.K. Joshi, J. Radhakrishna, Mr N. Kumar, Dr J.V. Dehadraya, Dr. K.T. Pillai, Mr Ashok Kumar, Mr A.C. Deb, Mr Rajesh Pai, Mr V.R. Ganatra, Mr Y.R. Bamankar, Mr T.V. Vittal Rao, Mr L.B. Pable, Dr.D.D. Sood (IAEA), and Dr. V.N. Vaidya.

For Further Reading


