CrossMark

Synthesis of thorium sol for fabricating fuel kernels

Feng-Xia Wang[1,2] · Chao Yan[2] · Chang-Qing Cao[2] · Peng Wang[2] ·
He Huang[2] · Hai-Tao Jiang[2] · Jun Lin[2] · Zhi-Xuan Cheng[1] · Zhi-Yong Zhu[2]

Abstract To fabricate thorium-based fuel kernel for solid fuel molten salt reactor, a component of tri-structural isotropic fuel particles is mostly based on sol–gel method. The preparation of thorium sol is an important step for fabrication of thorium-based fuel kernels, such as thorium carbide and thorium oxide. The gel quality affects the gel particle dispersion and the final products. In this work, thorium sols were prepared using $Th(NO_3)_4$ and $NH_3·H_2O$ by sol–gel method. The effects of thorium concentration, mole ratio of NH_4^+/NO_3^- and reaction temperature on the pH, viscosity, turbidity, particle size and the thorium sol distribution were investigated. The results show that the viscosity and turbidity increased with the NH_4^+/NO_3^- ratio; the turbidity and colloidal particle size increased with the reaction temperature, which affected little the sol viscosity; the sol viscosity increased with the thorium concentration, which virtually did not change the turbidity; and the particle size decreased and the size distribution narrowed with increasing thorium concentration. The sol could be stored at room temperature for one day without significant property changes. Thorium gel spheres of good quality were prepared at 60 °C with the NH_4^+/NO_3^- ratio of 75–85% and the thorium concentration of 1.2–1.4 mol/L.

Keywords Thorium sol · Sol–gel method · PH · Viscosity · Turbidity · Particle size distribution

1 Introduction

With the increasing demand of world energy and the rising concern about the sustainable development of nuclear energy in the future, thorium, which is 3–4 times more abundant than uranium, has been considered as a potential alternative fuel material. The development and utilization of thorium-based fuels for future Generation IV nuclear reactors have drawn more and more attention worldwide, especially in recent years [1–3]. A Th-based fuel is the tri-structural isotropic (TRISO)-coated particles embedded in graphite matrix. The TRISO-coated particles consist of spherical fuel kernels and four coating layers expected to retain fission products efficiently [4].

There are several types of fuel kernel under development, such as oxide, carbide and oxycarbide. Spherical kernels can be obtained by wet chemical routes called sol–gel method [5] in general. The sol–gel process for the nuclear fuel fabrication involves the following steps: preparation of sol from precursor solutions, gel particle forming, aging and washing of the gel particles, and thermal treatment of the gel particles [5]. As a prospective method for preparing ceramic nuclear fuels, the sol–gel process has attracted a good deal of attention because of its advantages of simple process, handling no radioactive powders, high-quality products and the ease of remote automation [6]. Effort were made in developing sol–gel technique for fabricating ThO_2 [7–9] and

✉ Zhi-Xuan Cheng
cnzxcheng@shu.edu.cn

✉ Zhi-Yong Zhu
zhuzhiyong@sinap.ac

1   Shanghai University, Shanghai 200444, China

2   Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Jiading Campus Shanghai, Shanghai 201800, China

(Th,U) O$_2$ [10–13] kernels. And carbon blacks were dispersed into the thorium sol for producing ThC$_2$ kernel [14]. Note that the same and basic step in fabrication of ThO$_2$ and ThC$_2$ kernel is the preparation of thorium sol, the property of which affects directly the gel particle dispersion and the final products.

The sol forming is a complicated dynamic process closely related to the reaction conditions. The sols were prepared bathwise by adding gaseous or aqueous ammonia to the heavy metal nitrate solution [15]. The additives could also be urea and ammonium nitrate, and the urea was decomposed into NH$_3$ by heating the solution [16]. All the systems for sol preparation go through the same reaction, namely, by neutralizing Th(NO$_3$)$_4$ solution with ammonia.

In this paper, thorium sols were prepared using Th(NO$_3$)$_4$ and NH$_3$·H$_2$O by the external sol–gel method, and the effects of thorium concentration, mole ratio of NH$_4^+$/NO$_3^-$ and reaction temperature on the viscosity, turbidity, pH, particle size distribution of the thorium sol were investigated. The reaction conditions were optimized to prepare thorium sols that could be transformed into uniform gel spheres. A method for evaluating the quality of sol was established through characterization of viscosity, turbidity and pH value.
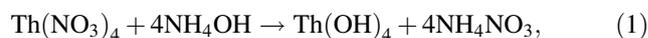
2 Materials and methods

2.1 Materials

Thorium nitrate hexahydrate, Th(NO$_3$)$_4$·6H$_2$O, was obtained from Changchun Institute of Applied Chemistry, Chinese Academy of Sciences. Concentrated ammonia and acetic acid, of analytical grade, were supplied by Sinopharm Chemical Reagent Company (Shanghai, China). Deionized water was obtained from laboratory.

2.2 Preparation and characterization of thorium sols

The synthesis pathway used is based on the classical hydrolysis–polymerization reaction starting from thorium nitrate and ammonia. The solutions of thorium nitrate (0.6–1.6 M) were prepared by dissolving a certain amount of Th(NO$_3$)$_4$·6H$_2$O powder in deionized water at 30 °C. The mixture was stirred (800–1000 r/min) in a thermostatic water bath at temperatures of 20–95 °C. Concentrated ammonia was injected into the mixture at 30 mL/h first and 5 mL/h when pH of the solution was close to 3.0. The whole reaction process was monitored by a pH meter (Metrohm pH-827). The viscosity was measured by a viscometer (Brookfield LVDV-II) and the turbidity by a desktop turbidimeter (Hach 2100AN). All

the measurements were carried out at room temperature (~22 °C). Sols, colorless and transparent, were obtained at pH 3.4–3.8. The density of the sols was measured by a densimeter (Rudolph DDM 2911). The particle size and size distribution of the sols were analyzed by a laser diffraction particle size analyzer (Brookhaven Zeta PALS/90 plus) at room temperature. The NH$_4^+$/NO$_3^-$ mole ratios were calculated according to the adding amount of NH$_3$·H$_2$O and Th(NO$_3$)$_4$. The reaction may be as follows [17].

$$Th(NO_3)_4 + 4NH_4OH \rightarrow Th(OH)_4 + 4NH_4NO_3, \qquad (1)$$

$$\cdots\cdots\text{---}\underset{\underset{\textstyle OH}{|}}{\overset{\overset{\textstyle OH}{|}}{Th}}\text{---}O\text{---}\underset{\underset{\textstyle NO_3^-}{\overset{(+)}{}}}{\overset{\overset{\textstyle OH}{|}}{Th}}\text{---}O\cdots\cdots, \qquad (2)$$

3 Results and discussion

3.1 Effect of NH$_4^+$/NO$_3^-$ mole ratio on thorium sol properties

The thorium sol was prepared by neutralizing 1.2 mol/L Th(NO$_3$)$_4$ solution with concentrated ammonia at 60 °C. The change of pH, turbidity and viscosity of the mixed solution in the ammonia neutralization is shown in Fig. 1. The pH increased abruptly as the NH$_4^+$/NO$_3^-$ mole ratio increased from 0 to 30%, where it began to increase in a much lower rate. The pH was around 3.5 at the NH$_4^+$/NO$_3^-$ mole ratios of 75–85%. The viscosity and turbidity of the solution showed almost no change before the NH$_4^+$/NO$_3^-$ mole ratio increased to 75%, where they began to increase dramatically. We found that sol could be prepared when the abrupt growth of viscosity and turbidity started and the pH was over 3.4, at the NH$_4^+$/NO$_3^-$ mole ratio of <75%. When the NH$_4^+$/NO$_3^-$ mole ratio was over 90%, the sol would become gel and lose mobility, but it could be reversed to sol again by adding of a small amount of acetic acid. The viscosity of the sol is a crucial parameter determining size distribution of the emulsion drops [18]. The present work revealed that for dispersion of gel particles, the NH$_4^+$/NO$_3^-$ mole ratio should be 75–85%, while the viscosity could be adjusted according to gel particle size requirement.

3.2 Effect of reaction temperature on thorium sol properties

The effect of reaction temperature on properties of the sol was studied at 20–95 °C and thorium concentration of 1.2 mol/L. Thorium sols could be obtained below 80 °C,

Fig. 1 pH value (**a**) and viscosity/turbidity (**b**) of the mixed solution as a function of NH_4^+/NO_3^- mole ratio
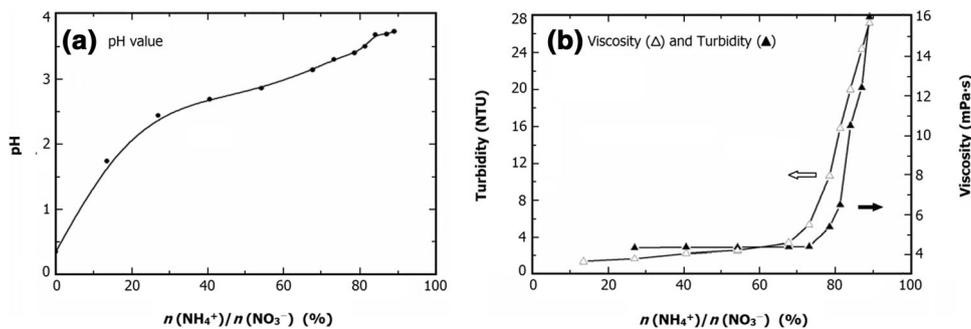
while the milky suspension was obtained at <80 °C. The reaction time required for preparing the sol deceased with increasing temperature, from 80 h at 20 °C to 8 h at 60 °C. This is due to that the peptizing process of precipitation is relatively slower at lower temperatures. Figure 2a shows the room-temperature turbidity and viscosity of the final products prepared at different reaction temperatures and NH_4^+/NO_3^- mole ratio of ~82%. The room-temperature viscosity increased with the reaction temperature below 60 °C, but greatly reduced at >80 °C. Anyhow, the variation was relatively small with all the viscosities being in the range of 4–7 mPa·s. The slightly increasing viscosity at 20–60 °C is probably due to the longer chain of polymers formed at higher reaction temperatures. The decreasing viscosity above 80 °C is attributed to the formation of suspension. The turbidity increases lightly with temperature below 60 °C, when it began to increase sharply. Above 80 °C, the increase trend slowed down to some extent. The increasing turbidity below 60 °C should be due to the size increase in colloidal particles in the solution.

Figure 2b shows the colloidal particle size distribution of the final sols prepared at 20, 40 and 60 °C. The average size of colloidal particle increased with the reaction temperature. As known, the sol formation is a thermodynamic process. The colloidal particles got more energy and became unstable with the rise of temperature. Colloidal particles grew without coagulation through collision as long as the temperature was not high enough. If the reaction temperature was sufficiently high, the violent movement of particles would cause coagulation of the solution, thereby forming a milky suspension. This is why the sol could not be obtained at >80 °C. The present work revealed that the optimum reaction temperature for forming the thorium sol is about 60 °C in consideration of the reaction time and the sol quality.

3.3 Effect of thorium concentration on thorium sol properties

The starting thorium concentrations should affect the sol properties of spherical degree and density. In the present study, the thorium sols were prepared by sol–gel method with the starting thorium concentrations of 0.6–1.6 mol/L at 60 °C and ~84% of NH_4^+/NO_3^- mole ratio. Figure 3a shows the density of the final sols as a function of starting thorium concentration. As expected, the sol density increased linearly with the thorium concentration. As shown in Fig. 3b, both the viscosities of thorium nitrate solutions and the final sols increased with the thorium concentration. The viscosity of thorium sols is larger than that of the thorium nitrate solutions at the same thorium concentration. The sol turbidity did not change much as the thorium concentration increased.

Fig. 2 (Color online) The temperature effects on viscosity/turbidity (**a**) and particle size distribution (**b**) of the thorium sols
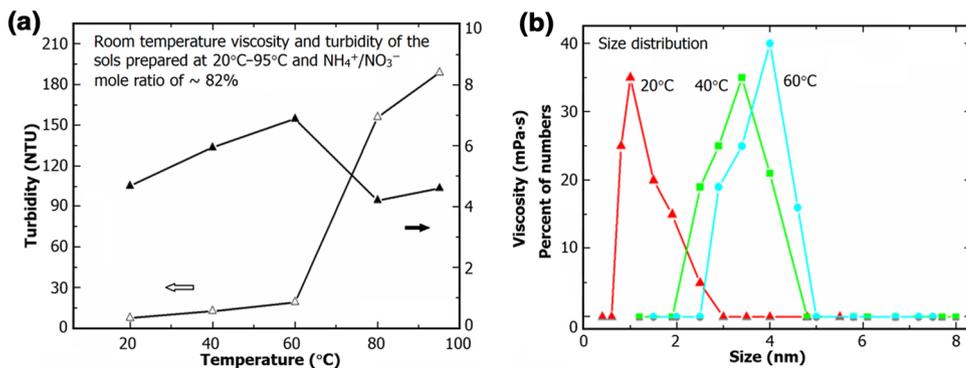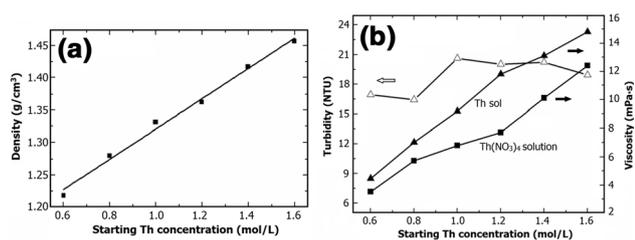
Fig. 3 The density (**a**) and viscosity/turbidity of thorium sol (**b**) versus the starting Th concentration, together with viscosity of $Th(NO_3)_4$ solutions
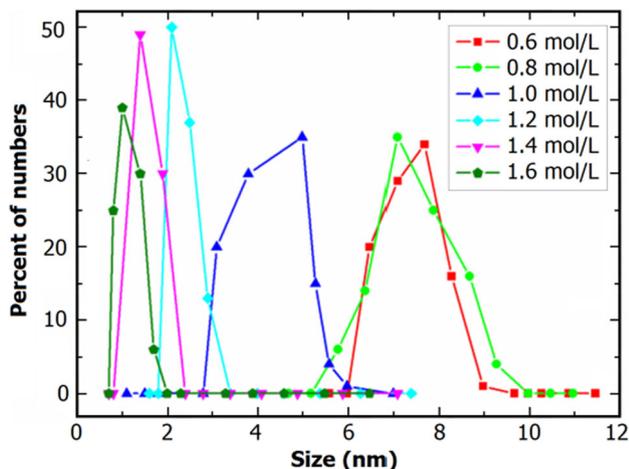

Fig. 4 (Color online) Particle size distribution of the final sols prepared at different thorium concentrations

The particle size distributions of final thorium sols prepared at different thorium concentrations are shown in Fig. 4. The size of colloidal particles decreased with the increasing thorium concentrations, and the size distribution narrowed. These are consistent with the classical nucleation theory. According to the theory of Weimarn, the formation of colloidal particles can be divided into two stages. The first stage is nucleation, and the second stage is the growth of the crystal nucleus [19]. The nucleation and growth rates are all proportional to the supersaturation, but the nucleation rate is more strongly dependent on both supersaturation and suspension density. In the sol-forming process, as the precursor concentration increased, the nucleation rate was faster than growth, hence the formation of more crystal nucleuses, which led to smaller colloidal particle size. So, the sol particle size decreased with the increasing thorium concentrations.

The sol particles can be well dispersed at lower thorium ions concentration, as the sol viscosity is smaller. But the spheres would become too soft and easily deformed during the heat treatment when thorium ions concentration is too low. When the thorium concentration is too high, it is hard to disperse the sol because of the large sol viscosity. To achieve good sphericity and high density of the

microspheres, the initial thorium concentration of 1.2–1.4 mol/L is suggested.

3.4 Stability of the sol

The sol obtained at 60 °C, NH_4^+/NO_3^- mole ratio of 81.5% and the initial thorium concentration of 1.2 mol/L was tested after storing at room temperature for up to 744 h. The results are given in Table 1. The storing time had a great impact on the thorium sol. The pH, viscosity, turbidity and particle size of the thorium sol increased with the storing hours. It seems that further condensation had occurred during the storing. If the storing time is over 1 month, the sol will easily turn into gel of three-dimensional network structure. It is confirmed that the sol can be stored at room temperature for 24 h with only minor changes in the thorium sol properties.

3.5 Gelled microsphere formation

For preparing the thorium gelled spheres, sols were obtained at 60 °C, NH_4^+/NO_3^- mole ratio of 82.5% and initial thorium concentration of 1.2 mol/L. Urea and polyvinyl alcohol were used to adjust performance of the sol. After the mixed sol was prepared, it was slowly sprayed through a vibrating nozzle, during which the sol droplet was first formed in the air followed by pre-consolidation in NH_3 gas before eventually falling into ammonia solution [20]. As shown in Fig. 5, the gelled spheres are of good sphericity, without any cracking.

4 Conclusion

The preparation of thorium sol is an important step for fabrication of thorium carbide and thorium oxide kernels. It affects directly the dispersion of gel particles and quality of products. In this work, thorium sols were prepared using $Th(NO_3)_4$ and $NH_3 \cdot H_2O$ as main reactants by sol–gel method. The effects of thorium concentration, mole ratio of NH_4^+/NO_3^- and reaction temperature on the pH, viscosity, turbidity, and particle size and distribution of the thorium sol were investigated, and the optimum reaction conditions were determined. The results show that viscosity and turbidity of the sol increased with the NH_4^+/NO_3^- mole ratio. The turbidity and colloidal particle size increased with the reaction temperature, whereas the viscosity of the sol changed very little. The viscosity of sol increased with the initial thorium concentration, while the turbidity showed almost no change. The particle size decreased and the size distribution narrowed with increasing initial thorium concentration. A method for evaluating the quality of sol was established through characterization of viscosity, turbidity

Table 1 Changes in physical properties of the thorium sol stored at room temperature for different hours

Time (h)	pH	Viscosity (mPa s)	Turbidity (NTU)	Surface tension (mN/m)	Particle size (nm)
0	3.7	9.7	18.1	66.0	1.2
5	3.7	9.7	19.2	68.0	1.1–1.7
20	3.8	11.2	19.7	67.6	2.0–2.7
72	3.9	19.9	21.4	72.9	2.3–2.4
144	3.9	24.3	22.8	63.1	2.0–4.0
216	3.9	28.2	22.5	67.0	3.2–5.6
504	3.9	168.5	29.5	75.4	4.5–9.9
744	4.1	645.3	33.2	–	–
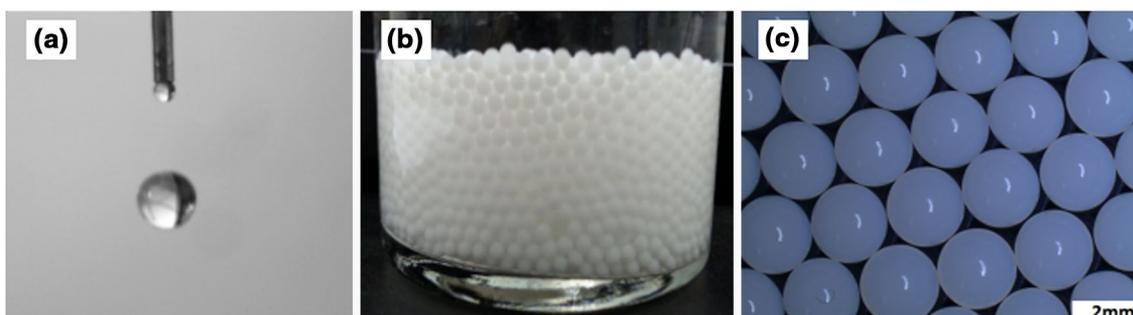
Fig. 5 (Color online) The sol droplet (**a**) and gelled spheres (**b–c**)

and pH. Thorium sols of good quality could be obtained at 60°C with the mole ratio of NH_4^+/NO_3^- of 75–85%. The sols can be stored at room temperature for 24 h with only minor changes in the thorium sol properties, which is beneficial for production of thoria matrix microspheres. Gel spheres of good sphericity without any cracking were prepared at initial thorium concentration of 1.2–1.4 mol/L.

References

1. M. Lung, *A Present Review of the Thorium Nuclear Fuel Cycles* (European Commission, Luxembourg, 1997) **(EUR-17771)**
2. IAEA, *Thorium Fuel Cycle-Potential Benefits and Challenges* (IAEA, Vienna, 2005). **(TECDOC-1450)**
3. NEA, *Introduction of Thorium in the Nuclear Fuel Cycle* (OECD, Paris, 2015). **(NEA 7224)**
4. M.P. Baker, J.C. King, B.P. Gorman et al., Selection and properties of alternative forming fluids for TRISO fuel kernel production. J. Nucl. Mater. (2013). doi:10.1016/j.jnucmat.2012.07.047
5. D.D. Sood, The role sol–gel process for nuclear fuels-an overview. J. Sol-Gel. Sci. Technol. **59**(3), 404–416 (2011). doi:10.1007/s10971-010-2273-y
6. K. Nagarajan, V.N. Vaidya, Sol-gel processes for nuclear fuel fabrication, in *Sol-Gel Processing for Conventional and Alternative Energy* (Springer, USA, 2012), pp. 341–373
7. S. Yamagishi, Y. Takahashi, Sol–gel method using carbon tetrachloride as drop-formation medium for producing large ThO_2-base microspheres. J. Nucl. Sci. Technol. **22**(12), 995–1000 (1985). doi:10.1080/18811248.9735755
8. M. Brykala, M. Rogowski, The complex sol–gel process for producing small ThO_2 microspheres. J. Nucl. Mater. **473**, 249–255 (2016). doi:10.1016/j.Jnucmat.2016.03.004
9. N. Mohseni, S.J. Ahmadi, S. Janitabar-Darzi et al., Sol–gel derived nanoscale ThO2 using nonionic surfactant agents. Ceram. Int. **42**(5), 6228–6235 (2016). doi:10.1016/j.Ceramint.01.005
10. C. Ganguly, H. Langen, E. Zimmer et al., Sol–gel microsphere pelletization process for fabrication of high-density ThO_2—2% UO_2 fuel for advanced pressurized heavy water reactors. Nucl. Technol. **73**, 84–95 (1986)
11. R.V. Pai, S.K. Mukerjee, V.N. Vaidya, Fabrication of (Th, U)O2, pellets containing 3 mol% of uranium by gel pelletisation technique. J. Nucl. Mater. **325**(3), 159–168 (2004). doi:10.1016/j.jnucmat.2003.11.010
12. R.V. Pai, J.V. Dehadraya, S. Bhattacharya et al., Fabrication of dense (Th, U)O2 pellets through microspheres impregnation technique. J. Nucl. Mater. **381**(3), 249–258 (2008). doi:10.1016/j.jnucmat.2008.07.044
13. T.R.G. Kutty, M.R. Nair, P. Sengupta et al., Characterization of (Th, U)O2, fuel pellets made by impregnation technique. J. Nucl. Mater. **374**(1), 9–19 (2008). doi:10.1016/j.jnucmat.2007.07.004
14. J.L. Kelly, A.T. Kleinsteuber, S.D. Clinton et al., Sol–gel process for preparing spheroidal particles of dicarbides of thorium and thorium-uranium mixtures. In. Eng. Chem. Process Design Develop. **4**(2), 212–215 (1965). doi:10.1021/i260014a016
15. S. Yamagishi, Y. Takahashi, Effect of thorium concentration on ThO_2 sol preparation under pH control by gaseous ammonia addition method. J. Nuc. Sci. Technol. **24**(9), 748–758 (1987). doi:10.1080/18811248.1987.9735875
16. P. Naefe, E. Zimmer, P. Naefe et al., Preparation of uranium kernels by an external gelation process. Nucl. Technol. **42**(2), 163–171 (1979)

17. Y. X. Zhu, Z. C. Xu. The Ceramic Fuel Kernel Prepared by Sol–Gel Method (Translated version). Atom Energy Press, pp 3–8 (1980)

18. M. Brykała, A. Deptuła, M. Rogowski et al., Modification of ICHTJ sol gel process for preparation of medium sized ceramic spheres (Ø < 100 mm). Ceram. Inter. **41**, 13025–13033 (2015). doi:10.1016/j.Ceramint.2015.07.002

19. H.B. Weiser, W.O. Milligan, Von Weimarn's precipitation theory and the formation of colloidal gold. J. Phys. Chem. **36**(7), 1950–1959 (1932). doi:10.1021/j150337a008

20. X.M. Fu, T.X. Liang, Y.P. Tang et al., Preparation of UO_2 kernel for HTR-10 fuel element. J. Nucl. Sci. Technol. **41**(9), 943–948 (2004). doi:10.1080/18811248.2004.9715568