Korean J. Chem. Eng., **26**(1), 165-167 (2009)

SHORT COMMUNICATION

Microwave-assisted dissolution of UO_2 with TBP-HNO_3 complex

Yunfeng Zhao and Jing Chen†

Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 102201, China
(*Received 27 February 2008 • accepted 10 June 2008*)

Abstract−The direct dissolution of UO_2 in TBP-HNO_3 complex by microwave heating in this study suggests the possibility of dissolving spent nuclear fuels. This new technique offers many benefits for reduction in aqueous and organic waste generation and improved efficiency of chemical processing. The dissolution rate of UO_2 particles with TBP-HNO_3 complex by microwave assisted heating is highly dependent on the temperature and the particle size.

Key words: Uranium Dioxide, Dissolution, Microwave Heating, Tri-n-butylphosphate

INTRODUCTION

In order to develop the head-end process of nuclear spent fuel, data on the dissolution of UO_2 particles are essential. Some studies on the dissolution of UO_2 particles or powders in HNO_3 have been reported [1,2]. But some problems emerged during the HNO_3 dissolution procedure, such as difficulty of complete recovery of uranium and some metals, and generation of a relatively large amount of organic solvent and aqueous liquid waste and NO_X gases. Therefore, searching for new, effective techniques for reprocessing of spent fuels is a challenging task in the future. In evaluating any acceptable new techniques for reprocessing of spent nuclear fuels, minimizing waste generation is an important criterion for consideration [3].

Microwave-assisted leaching has been studied to improve the yield of extracted metal and reduce the process time. The unique microwave heating advantages such as short processing time, direct, selective and volumetric heating, and a more controllable heating process [4] are the main drivers for potential implementation in metal extraction. For the consideration of reducing waste generation and to explore a new concept of head-end process, the dissolution of UO_2 particles with TBP (tri-n-butyl phosphate)-HNO_3 complex by microwave heating is considered. Microwave energy can give a selective and rapid volumetric heating. Meanwhile, the direct dissolution of UO_2 with TBP-HNO_3 complex could offer many benefits such as promoting the dissolution process, reducing waste generation, etc. In this paper, the dissolution of the UO_2 particles with TBP-HNO_3 complex by microwave heating has been studied fundamentally to determine the applicability of this process in reprocessing.

EXPERIMENTAL

A MARS 5 (Microwave assisted reaction system) with an airtight Teflon vessel [5] was used to study the dissolution of UO_2 particles under 100 W, 2.45 GHz microwave field. The temperature of the solution in the vessel was automatically controlled by regulating the microwave power output according to a temperature feedback signal. The volume of the vessel was 5 ml and it was transparent to microwaves so that the reactants could absorb the maximum amount of microwave energy.

TBP is known to form complexes with aqueous HNO_3. The TBP-HNO_3 complexes also contain water with different hydration numbers [6]. In this study, the TBP-HNO_3 complex was prepared by mixing 100 ml of an anhydrous TBP and 23.4 ml of 69.5% (15.6 mol ml^{-1}) HNO_3 and shaking the mixture vigorously in an extraction tube with a stopper for 30 min. The HNO_3 concentration of the remaining aqueous phase was determined to be 0.42 M by titration, indicating that most of the HNO_3 had reacted with TBP to form the TBP-HNO_3 complex. The molar ratio of TBP/HNO_3 can be determined to be 1 : 1 by the method of titration and ICP-AES (inductively coupled plasma atomic emission spectrometry) [6].

Ceramic UO_2 particles with a diameter of 450-550 μm were crushed and sieved to the sizes of <75 μm, 150-250 μm, 250-350 μm and 350-450 μm. These UO_2 particles were made from the $UO_2(NO_3)_2$ solutions by the method of total-gelation process (TGU) [7]. The UO_2 samples are in pellet form with a diameter of 450-550 μm. The density is ≥10.4 $g \cdot cm^{-3}$ and the element ratio of O and U is 1.99-2.01.

Three ml of TBP-HNO_3 complex was transferred into the vessel; then UO_2 particles were weighed out accurately and put into the vessel. The solution could be rapidly heated to a designated temperature by microwaves. The temperature of the solution was detected by fiber thermometer, which does not absorb the microwave energy and with an accuracy of ±1 °C. The UO_2 particles were dissolved and then the solution was filtrated by the filter paper to separate the residual particles. The concentrations of UO_2^{2+} in the complex [4] were determined by spectrophotometer [8].

RESULTS AND DISCUSSION

The heating of TBP-HNO_3 complex, H_2O, 69.5%HNO_3 and pure TBP by microwaves is shown in Fig. 1. The data were obtained by the heating of 30 ml reactants in Teflon vessels by 300 W microwaves. The results suggest that the reactants could be heated very fast by microwaves. The heating speed of TBP-HNO_3 complex is the quickest of the four. Within 30 seconds, the temperature of TBP-HNO_3 complex can be heated to above 100 °C.

Fig. 2 shows the heating of UO_2 particles with a diameter of 500

†To whom correspondence should be addressed.
E-mail: jingxia@tsinghua.edu.cn

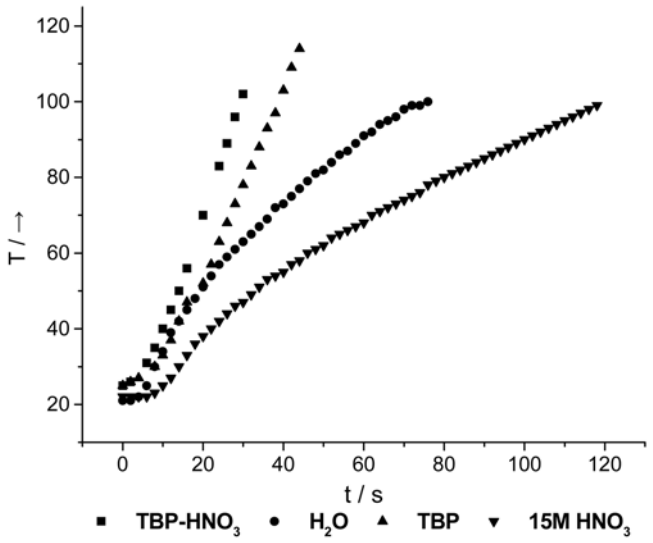

Fig. 1. Microwave heating of TBP-HNO_3 complex.

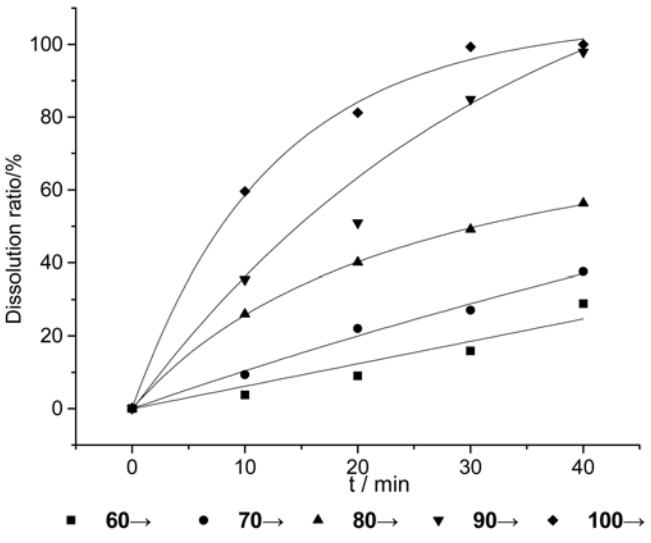

Fig. 3. Effect of temperatures on dissolution ratios.

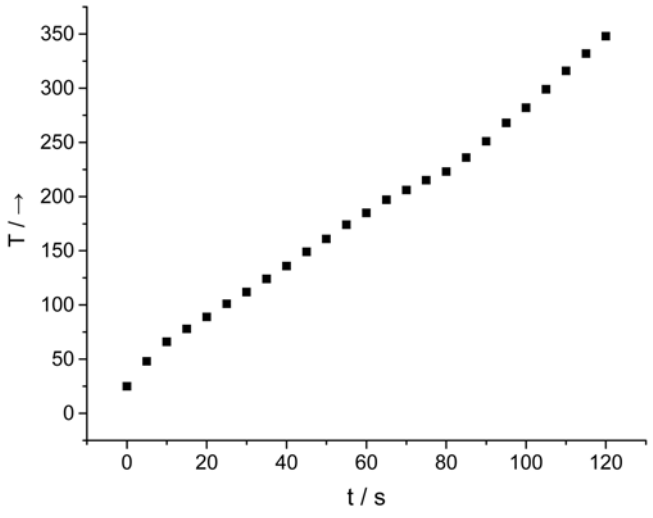

Fig. 2. Microwave heating of UO_2 particles.

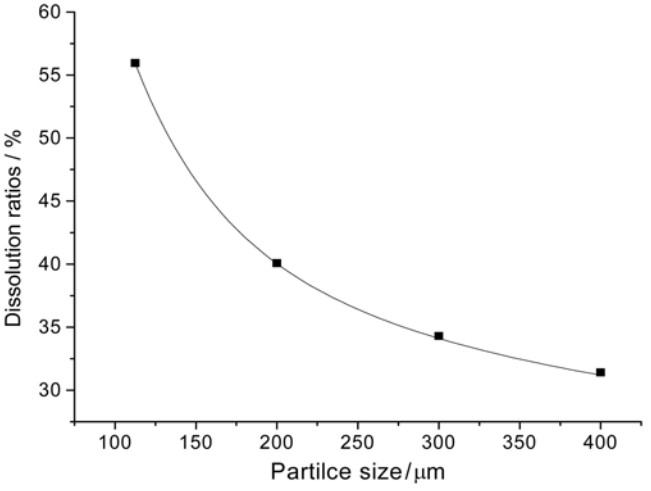

Fig. 4. Effect of particle size on dissolution ratios.

μm by microwaves. The data were obtained by the heating of 30 g UO_2 particles in a quartz vessel with a diameter of 6 cm by 300 W microwaves. The surface temperature of the UO_2 particles was detected by infrared thermometer. It can be seen from the result that UO_2 could be heated quickly by microwaves. Within 60 seconds the surface temperature of UO_2 particles could reach almost 200 ºC.

The effect of temperature on the dissolution ratios of UO_2 particles is illustrated in Fig. 3. The experiments were performed under a 100 W microwave field, and the reaction temperatures were selected from 60 ºC to 100 ºC. The result showed that the dissolution ratios increased quickly with the increase of temperature. For example, only 15.9% of the UO_2 particles were dissolved at 60 ºC within 30 min; however, the dissolution ratio was improved to 84.8% when the temperature was increased to 90 ºC. And when the temperature increased to 100 ºC, the UO_2 particles could be dissolved completely within 40 min.

Fig. 4 shows the dissolution ratios of different sizes of UO_2 particles within 20 min at 80 ºC. The experiments covered a range of particle sizes from 75 μm to 450 μm. The numbers on the abscissa indicate the average particle size of UO_2. It can be found from the results that the dissolution ratios increased exponentially with the decrease of the particle sizes.

It can be seen from Fig. 3 and Fig. 4 that the dissolution ratios of the UO_2 particles are highly dependent on the temperature and particle size. The dissolution ratios increased quickly with the increase of the temperature and the decrease of UO_2 particle size. The results show that the dissolution ratios are comparatively high. In comparison with the dissolution rates reported by Samsonov [6], the results of the study were comparable to the dissolution of UO_2 in supercritical fluid CO_2 and showed even a faster dissolution rate. Almost the same amount of UO_2 particles was dissolved (about 9%) by microwave heating with UO_2 particle size of 150-250 μm and supercritical fluid CO_2 with UO_2 particle size of <150 μm. With the result that the dissolution ratio increased with the decrease of particle sizes, it can be concluded that the dissolution rate of UO_2 by microwave heating was faster than that obtained in supercritical fluid CO_2.

The dissolution of UO_2 may be represented by Eq. (1) assuming

the TBP-HNO_3 complex has a 1 : 1 stoichiometry:

$$UO_2(\text{solid}) + \frac{8}{3}\text{TBP-HNO}_3 \rightarrow UO_2(NO_3)_2 2\text{TBP} + \frac{2}{3}NO + \frac{4}{3}H_2O + \frac{2}{3}\text{TBP} \quad (1)$$

Because oxidation of UO_2 was required in the dissolution process, the diffusion of the oxidized products in the liquid phase could be a factor limiting the dissolution rate [4]. Eq. (1) shows that TBP will help NO_3^- react with UO_2 particles, so this will promote the dissolution of the UO_2 particles. In addition, the TBP-HNO_3 complex and the UO_2 are both polar molecules with high value of the dielectric loss factor and can absorb microwaves significantly [10]. The mixture of the reaction species can be heated rapidly. The difference of the heating rate between TBP-HNO_3 complex and UO_2 probably results in the large temperature gradient between solids and liquids, which will assist the mass transport from the reaction interface due to the generation of large thermal currents. This will markedly improve the reaction rate.

CONCLUSIONS

The dissolution rate of UO_2 particles with TBP-HNO_3 complex by microwave heating is highly dependent on the temperature and the particle size. The dissolution rate improved with the increase of the temperature and the decrease of the UO_2 particle size. The results of the study are comparable to the dissolution of UO_2 in supercritical fluid CO_2 and have shown even a faster dissolution rate.

The direct dissolution of UO_2 with TBP-HNO_3 complex by microwave heating in this study suggests the possibility of dissolving spent nuclear fuels with TBP-HNO_3 complex. The method is easy to accomplish, and without the use of conventional acid and organic solvents. Thus, this new technique could offer many benefits for reduction in waste generation and improved efficiency of chemical processing.

REFERENCES

1. F. Taylor, W. Sharratt, LEM. De Chazal and D. H. Logsdail, *J. Appl. Chem*., **13**, 32 (1995).
2. Y. Ikeda, Y. Yasuike, K. Nishimura, S. Hasegawa and Y. Takashima, *J. Nucl. Mater*., **224**, 266 (1995).
3. T. I. Trofimov, M. D. Samsonov, Y. M., et al., *C. R. Chimie*., **7**, 1209 (2004).
4. M. Al-Harahsheh, S. W. Kingman, *Hydrometallurgy*, **73**, 189 (2004).
5. J. H. Huang, N. A. Rowson, *Hydrometallurgy*, **64**, 169 (2002).
6. M. D. Samsonov, C. M. Wai, S.-C. Lee, et al., *Chem. Commun*., 1868 (2001).
7. T. Yaping, X. Zhichang, Z. Fuhong, et al., *Journal of Tsinghua University (Sci&Tech)*, **37**, 61 (1997).
9. G. Yifei, L. Junfu, J. Rongzhou and L. Xiuqi, *Atomic Energy Science and Technology*, **34**, 252 (2000).
10. P. A. Hass, *Am. Ceram. Soc. Bull*., **58**, 873 (1979).