

Behavior of Fission Products in Sulfide Reprocessing Process

Akira Kirishima,* Yuuki Amano and Nobuaki Sato

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 1-1 Katahira, 2-chome, Aoba-ku, Sendai 980-8577, Japan

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For the recovery of nuclear materials from spent fuel with more effective and convenient methods comparing with conventional process, the sulfurization and dissolution behavior of fission products, such as rare-earths, alkali, alkaline-earth and platinum group elements were studied. The sulfurization experiment was carried out using tracer doped U_3O_8 . The samples were reacted with CS_2 at temperatures from 573 to 773 K for 1 hour followed by dissolution with 1M nitric acid solution for 1 hour at 323 K. The dissolution ratio for each element was obtained by α - and γ -ray spectrometry. The alkali and alkaline-earth elements show higher dissolution ratios as well as trivalent lanthanide elements. On the other hand, U, Zr, Ce, and Ru showed lower dissolution ratios. These results were in good agreement with those expected from the thermodynamic consideration.

1. Introduction

For the recovery of nuclear materials from spent fuel with more simple and cost effective process comparing with the conventional wet process, the sulfide reprocessing process has been proposed and studied.^{1,2} In this process, nuclear materials are recovered as the oxides by a selective sulfurization of FPs and selective dissolution of the sulfurized FPs. The points of this process are, 1) sulfurization treatment at relatively low temperature, 2) reduction of uranium oxide by CS_2 , 3) less consumption of chemical reactants, 4) recovery of the fuel materials as oxides. In our previous studies,²⁻⁴ the phase analyses of U, Nd and Eu after the sulfurization treatment by CS_2 were conducted using XRD and thermogravimetric analysis where the starting materials were U_3O_8 , Nd_2O_3 and Eu_2O_3 respectively. The results indicated that CS_2 reduced U_3O_8 to UO_2 and sulfurized Nd_2O_3 and Eu_2O_3 to NdS_2 and Eu_3S_4 , respectively in the range of sulfurization temperature 573 to 773 K. This result reflects a unique and useful chemical property of CS_2 , that is, CS_2 works as a reducing agent for U_3O_8 while it works as a sulfurizing agent for trivalent lanthanide. After the sulfurization treatment, trivalent rare-earths were separated from the uranium matrix by the dissolution with a dilute nitric acid solution, while UO_2 was recovered as a solid phase by utilizing the low solubility of UO_2 for the dilute acid solution. The behavior of minor actinides as well as Pu was reported in the previous works.^{4,5} In this paper, therefore, the sulfurization

and dissolution behavior of fission products, such as rare-earths, alkali, alkaline-earth and platinum group elements was investigated using the tracer doped U_3O_8 with the help of thermodynamic consideration.

2. Experimental

2.1. Sample Preparation. The U_3O_8 was obtained by the oxidation of U metal turnings in air at 1073 K. Then the tracer doped U_3O_8 was synthesized as follows. A nitric acid solution of FP tracers, *i.e.*, ^{152}Eu , ^{141}Ce , ^{95}Zr and ^{103}Ru were mixed with uranyl nitrate solution. Then, it was co-precipitated as a tracer doped ammonium di-uranate (ADU) by adding adequate amount of ammonia solution. This ADU was calcined to U_3O_8 in air at 1273 K for 8 hours. The nitric acid solution containing ^{137}Cs and ^{89}Sr tracers was then added to the above mentioned U_3O_8 powder and calcined in air again at 1073 K for 8 hours to avoid the volatilization of ^{137}Cs . The chemical abundances of Cs, Sr, Eu, Ce, Zr and Ru in the tracer doped U_3O_8 sample were in trace levels which were chemically ignorable. Analytical grade of CS_2 having the boiling point 46-47 °C and maximum water content of 0.02% (Wako Pure Chemicals Co., Ltd.) and Argon gas of 99.99% purity (Nippon Sanso Co., Ltd.) were used as received.

2.2. Sulfurization. The sulfurization experiments were carried out using a quartz apparatus shown in Figure 1. After the weighed sample was placed on the quartz boat in a quartz tube,

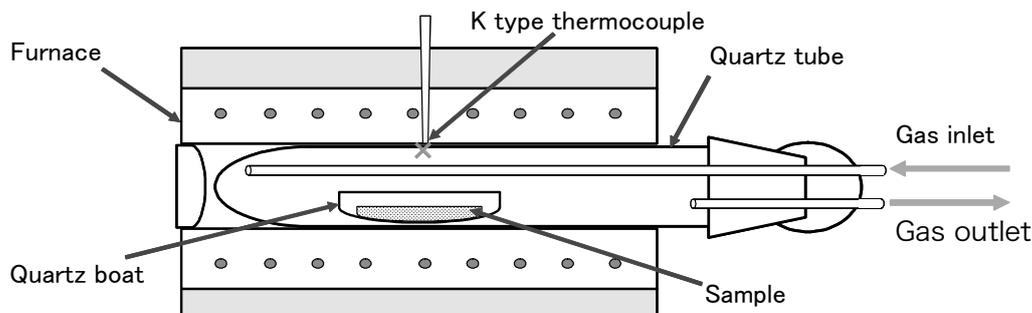


Figure 1. Schematic drawing of sulfurization apparatus.

*Corresponding author. E-mail: kiri@tagen.tohoku.ac.jp

the inside of the reaction system was evacuated by a rotary pump followed by the refilling with argon. Then the temperature of the furnace was raised to an intended temperature at a heating rate of 10 °C/min. At the intended temperature, the mixed gas of CS₂ with Ar, which was obtained by bubbling Ar gas through a bubbler containing liquid CS₂, was introduced into the quartz tube by a flow rate of 5 ml/min of CS₂ and 30 ml/min of Ar. The flow rate of Ar gas was controlled using a digital mass flow meter (Kofloc Model DPM-2A). The sulfurization time was set to 1h, hence, the temperature and mixed gas flow rate were kept constant during the sulfurization for 1 h. After that, the supply of the mixed gas was stopped, and then the inside of the quartz tube was flashed and cooled down by Ar gas.

2.3. Dissolution. After the sulfurization treatment, the RI tracer doped U₃O₈ sample was immersed into 100 ml of 1 M nitric acid solution and shaken for 1 hour at 323 K by an air bath shaker. Then, the solution and residue were separated by suction filtration to determine the dissolution ratio of U, Eu, Ce, Zr, Ru, Cs and Sr to the acid solution by α - and γ -ray spectrometry.

2.4. α - and γ -ray spectrometry. For the determination of the dissolution ratio of each element, α - and γ -ray spectrometry was applied by a surface semiconductor detector (Canberra, model-7401) and a coaxial Ge semiconductor detector (Canberra, model-GC1318), respectively. The isotopes used for analysis were ²³⁸U, ¹⁵²Eu, ¹⁴¹Ce, ⁹⁵Zr, ¹⁰³Ru, ¹³⁷Cs and ⁸⁵Sr. The half life and γ -ray energy of tracers used for the calculation of the distribution ratio between solution fraction and residue fraction are given in Table 1. As an example, the γ -ray spectrum of the sample is shown in Figure 2. For the quantitative α spectrometry of U, the samarium co-precipitation method⁶ was employed in this study, where a natural radionuclide ¹⁴⁷Sm is used as the inner standard for the counting efficiency calculation. The detail of the α spectrometry is described in our previous work.⁵ For the analysis of U, the α peak of ²³⁸U at 4.20 MeV in the obtained spectrum was used. The dissolution ratio (D_R) of U, Eu, Ce, Zr, Ru, Cs and Sr is derived by the following equation.

$$D_R = \frac{\text{Activity of tracer in solution (cps)}}{\text{Activity of tracer in solution and residue (cps)}} \quad (1)$$

3. Results and Discussions.

3.1. Behavior of rare earth oxides. In order to know the behavior of rare earth oxides in the U₃O₈ matrix, the effect of sulfurized temperature on D_R was investigated with dissolution time of 1 hour and nitric acid concentration of 1.0 M. The relation between sulfurization temperature and D_R of Eu was shown in Figure 3. The horizontal axis and vertical axis show the sulfurization temperature and D_R , respectively. The values of D_R for Cs, Sr, Eu and U are shown as \blacklozenge , \blacksquare , \blacktriangle , and \blackplus , respectively. It can be seen that the D_R of Eu is around 40 % at temperatures lower than 623 K, while Eu becomes soluble when the sulfurization temperature is higher than 623 K. The trivalent rare earth oxides are expected to show similar behavior to that of Eu, nevertheless, the heavy rare earth oxides are supposed to need higher sulfurization temperature to make them soluble than light ones by the sulfurization treatment. On the other hand, D_R of Ce was obtained as 6.2 % at sulfurization temperature 673 K as shown in Table 2. Since Ce forms stable tetravalent oxide CeO₂, this result suggests that tetravalent rare earth oxides are less soluble even after the sulfurization treatment. As seen in Figure 3, D_R of U is less than 5.5 % in the investigated temperature range, indicating that the insoluble U could be separated from rare earth oxides by the selective sulfurization and the acid dissolution procedures. Although the

TABLE 1: Half life and γ -ray energy of the FP tracers

Tracer	¹³⁷ Cs	⁸⁵ Sr	¹⁵² Eu	¹⁴¹ Ce	⁹⁵ Zr	¹⁰³ Ru
Half life	30.17 (y)	64.9 (d)	13.33 (y)	32.50 (d)	64.0 (d)	39.35 (d)
Analyzed energy (keV)	662	514	122	145	757	497

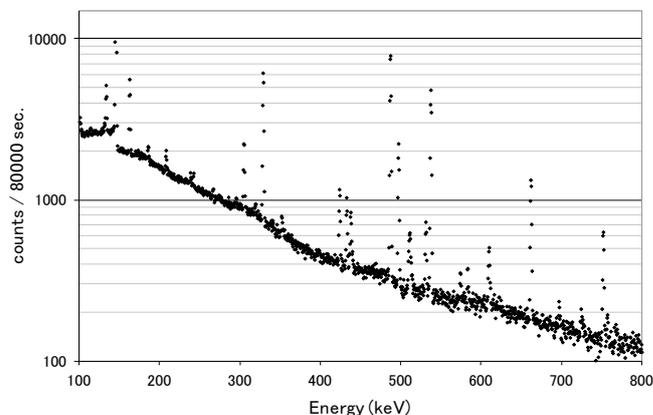


Figure 2. The γ -ray spectrum of the tracer doped U₃O₈.

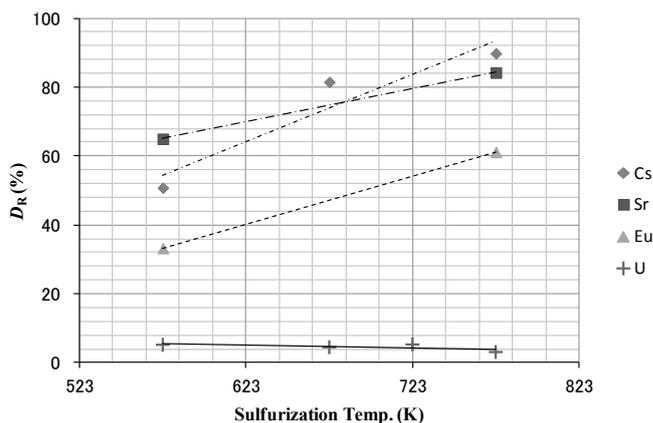


Figure 3. Dependence of DR for Cs(\blacklozenge), Sr(\blacksquare), Eu(\blacktriangle) and U(\blackplus) on sulfurization temperature. Dissolution Time: 1.0 hour with 1.0 M HNO₃.

TABLE 2: Dissolution ratios of Ce, Zr and Ru at sulfurization temperature 673 K

Element	Ce	Zr	Ru
D_R (%)	6.2	5.2	1.1

acid concentration, the volume of the acid solution, the solution temperature and the shaking time were fixed in the dissolution treatment in this paper, the D_R of each elements are expected to depend on those conditions. The optimum dissolution condition will be sought in the future study. Figure 4 shows the Gibbs free energy for the reactions of UO₂, Eu₂O₃ and SrO with CS₂. According to our previous study,² U₃O₈ seems to be reduced to UO₂ by the reaction of CS₂ first. As can be seen in Figure 4, the ΔG^0 values for the sulfurization of UO₂ are positive showing that UO₂ does not react with CS₂. On the other hand, the ΔG^0 values for Eu₂O₃ are very negative. These thermodynamic tendencies agreed with the experimental results, i.e., Eu₂O₃ was sulfurized by CS₂ and forming soluble Eu₂O₂S

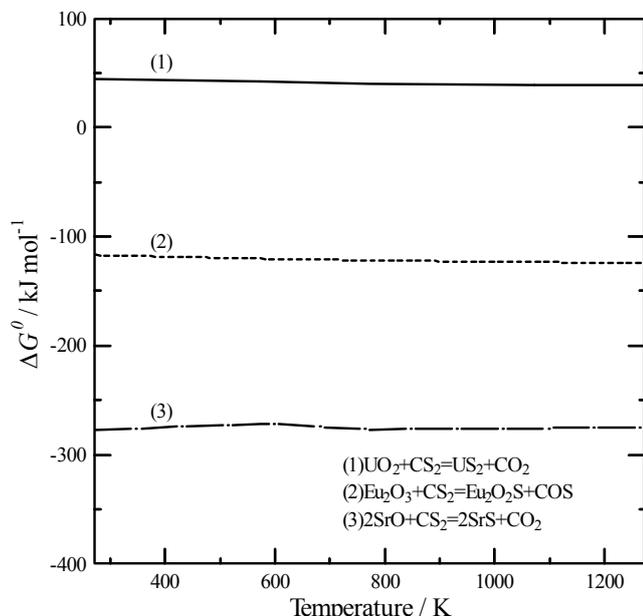


Figure 4. Gibbs free energy for the reactions of UO_2 , Eu_2O_3 and SrO with CS_2 .

and Eu_3S_4 while U_3O_8 was reduced to insoluble UO_2 .

3.2. Behavior of alkali and alkaline earth oxides. To investigate the behavior of alkali and alkaline earth oxides in the sulfide reprocessing process, the sulfurization and acid dissolution was examined for Cs and Sr. The D_R of Cs and Sr were shown in Figure 3. In both cases, their D_R values are much higher than that of U at the observed temperature range. Then the D_R values increases more than 80 % at 773 K, clearly showing that Cs and Sr dissolve into nitric acid after the sulfurization treatment. From the ΔG^0 values for the sulfurization reaction of SrO with CS_2 as given in Figure 4, SrO is thermodynamically easily sulfurized by CS_2 to SrS . Unfortunately, the ΔG^0 values for the sulfurization of Cs oxide and other alkaline metal oxides could not be obtained for the lack of thermodynamic data. The thermodynamic stability of the compounds in the $\text{Sr-O}_2\text{-S}_2$ system was discussed by using a potential diagram at 773 K constructed using the DATABASE MALT for Windows.⁷ The result of the calculation is shown in Figure 5, where the SO_2 , CS_2 and CO_2 of 1 atm are given as the dotted lines. The stable sulfide and oxide are indicated to be SrS and SrO , and the SrSO_4 phase appears at higher $\log P(\text{O}_2)$ and $\log P(\text{S}_2)$ region. When SrO react with 1 atm CS_2 gas at SO_2 pressure 1 atm, formation of SrS proceed along the dotted line. The cross point of the $\log P(\text{S}_2)$ and $\log P(\text{O}_2)$ lines locates in the SrS region. From these results, alkaline earth oxides are supposed to be easily sulfurized by CS_2 and separated from UO_2 by the acid dissolution.

3.3. Behavior of refractory metal oxides. Next, the behavior of refractory metal oxides was discussed. The D_R values of Zr and Ru sulfurized at 673 K for 1 hour and dissolved by 1 M HNO_3 at 323 K were given in Table 2. The D_R of Zr was 5.2 %, which was close to those of U and Ce. The thermodynamic stability of the compounds in the $\text{Zr-O}_2\text{-S}_2$ system at 673 K was discussed with using a potential diagram shown in Figure 6. In this figure, the dotted lines indicate 1atm of SO_2 , CS_2 and CO_2 . The potential diagram shows that the stable sulfide and oxide of Zr are ZrS_2 and ZrO_2 , then, the $\text{Zr}(\text{SO}_4)_2$ phase appears at higher $\log P(\text{O}_2)$ and $\log P(\text{S}_2)$ region. The crossing point of the $\log P(\text{S}_2)$ and $\log P(\text{O}_2)$ lines locates in the ZrO_2 region, suggesting that the formation of ZrS_2 seems not to proceed along the dotted line when ZrO_2 reacts with 1 atm CS_2 gas at SO_2 pressure of 1 atm. Due to this high stability of ZrO_2 , the D_R value of Zr became similar to

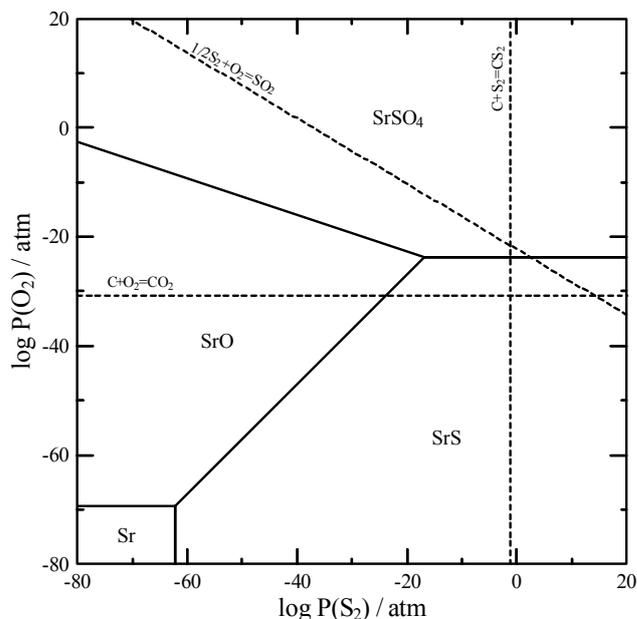


Figure 5. Stability diagram for the $\text{Sr-O}_2\text{-S}_2$ system at 773 K.

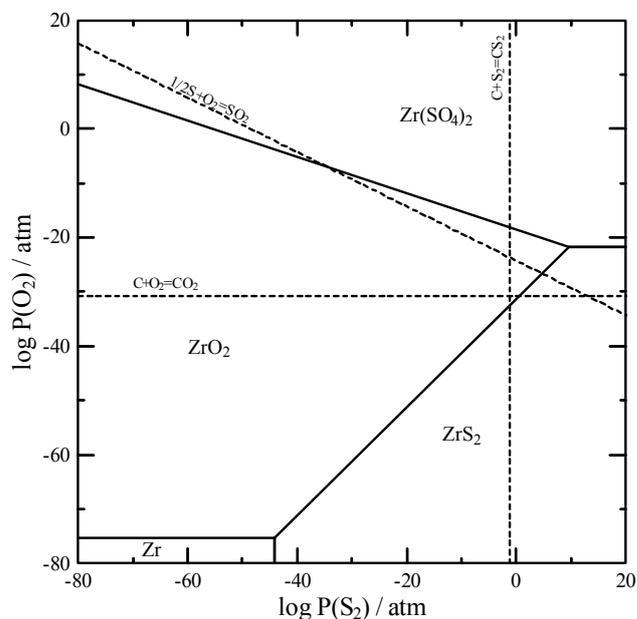


Figure 6. Stability diagram for the $\text{Zr-O}_2\text{-S}_2$ system at 673 K.

those of U and Ce. From these results, refractory oxides are stable under CS_2 atmosphere at lower sulfurization temperature, and so they will be recovered with U and Ce as their oxides. The development of a separation method of Zr and Ce from U in the proposed sulfide process are one of the future subjects to be investigated. Besides, those elements could be fabricated as low decontamination factor UO_2 fuel without separation from U, since Ce and Zr can stably exist with UO_2 as the inert matrix.

3.4. Behavior of metal component. In a spent fuel, the metallic phase which consists of Mo and platinum group elements exists. This phase is chemically stable and remains as the insoluble residue during wet reprocessing process. The reaction between these metal components and CS_2 was discussed by using the thermodynamic data. Figure 7 shows the Gibbs free energy for the reactions of Pd, Rh, Ru and Mo with CS_2 . It can be seen that the ΔG^0 values for Mo, Rh and Ru are very negative in the above temperature range. In the case of Rh, the Rh_2S_3 was taken into account. It should be noted that the ΔG^0 values for the sulfurization of Pd changes from nega-

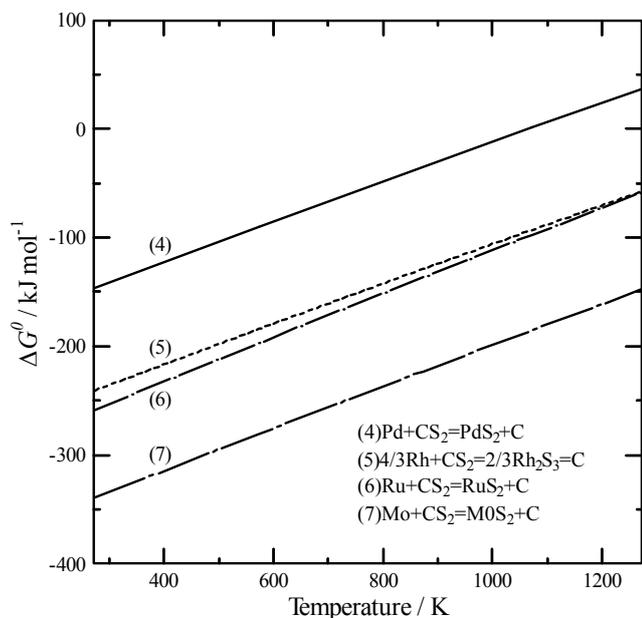


Figure 7. Gibbs free energy for the reactions of Pd, Rh, Ru and Mo with CS_2 .

tive to positive at 1100 K, meaning that the decomposition to Pd and S seems to occur over this temperature. According to the experimental results given in Table 2, the D_R value of Ru is about 1 %, which is smaller than those of U, Zr and Ce. This may be caused by the insoluble property of RuS_2 . From these results, the metal component is supposed to remain in the residue as sulfide after the sulfurization and the acid dissolution. Potential separation ideas of the platinum group elements from U are, 1) selective dissolution of platinum group to a molten metal, such as Cu, and 2) platinum group phase separation by utilizing the difference of specific gravities between platinum group and U oxide powders. It should be studied in the future work.

4. Conclusion

In order to know the behavior of fission products in the sul-

fide reprocessing process, the sulfurization and the dissolution treatments were carried out using the tracer doped U_3O_8 sample. The sample was reacted with CS_2 at temperatures from 573 to 773 K for 1 hour followed by the dissolution into 1M nitric acid solution. The alkali and alkaline-earth elements showed higher dissolution ratios as well as rare-earths excepting Ce that kept stable and insoluble tetravalent dioxide state. On the other hand, U, Zr, Ce and Ru showed lower dissolution ratio. These results were in good agreement with those expected from the thermodynamic consideration. These results suggest the separation of fission products by the sulfide process.

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