

REMOVAL OF URANIUM FROM WASTE CATALYST OF ANTIMONY-URANIUM COMPOSITE OXIDE BY SUPERCRITICAL FLUID EXTRACTION COMBINED WITH CHLORINATION PRETREATMENT

Kayo Sawada* and Youichi Enokida

Nagoya University, Furo-co, Chikusa-ku, Nagoya, 464-8603

E-mail k-sawada@nucl.nagoya-u.ac.jp, Fax +81-52-789-5936

To remove uranium from a waste catalyst, in which uranium forms the stable composite oxide with antimony, uranium extraction with supercritical carbon dioxide (SC-CO₂) containing tri-*n*-butylphosphate (TBP)-nitric acid complex was conducted following a chlorination treatment to volatilize antimony in the catalyst. By the chlorination pretreatment with hydrogen chloride gas at 1173 K, 89% of antimony was removed from the catalyst, and uranium converted to uranium oxide, U₃O₈. By the extraction with SC-CO₂ and the TBP complex following the chlorination, 95% of uranium was removed from the waste catalyst.

INTRODUCTION

In 1960s, a catalyst of antimony-uranium composite oxide was invented by a team that developed a famous acrylonitrile synthesis process, the SOHIO Process, in U.S.A. [1-4] The catalyst was in a form of that the composite oxide of antimony and uranium was supported on porous silica beads. The contents of antimony and uranium in the catalyst were approximately 30 and 15% in mass, respectively. Several Japanese chemical companies employed the catalyst to synthesize acrylonitrile until the early 1980s. Then, they changed the catalyst to uranium-free one, such as a molybdenum-bismuth-iron composite oxide, *etc.*,. The composite oxides are so chemically stable that it is difficult to dissolve uranium from the catalyst by acids, such as nitric acid, hydrochloric acid *etc.* In Japan today, 200 tons as metallic uranium are estimated as waste catalyst stored without any treatment in the several companies with the rigid managements under Japanese legislation.

In order to remove uranium from the waste catalyst, we applied the uranium extraction with supercritical carbon dioxide (SC-CO₂) containing tri-*n*-butylphosphate (TBP)-nitric acid complex following a chlorination treatment to volatilize antimony in the catalyst. The extraction with SC-CO₂ is known to be effective to extract uranium from uranium oxides [5-9], on the other hand, antimony (III) chloride is known to have relatively low boiling point at 497 K [10]. In this study, the feasibility of the proposing treatment was confirmed by using a real waste catalyst sample. The samples were treated with hydrogen chloride gas employed as

a chlorination reactant at 1173 K, and then, they were conducted to the supercritical fluid extraction (SFE).

MATERIALS AND METHODS

Materials

The real waste sample was obtained from 3R Corporation, Japan. To clarify the elemental contents in the sample, the element concentration in the solution was measured by inductively-coupled plasma atomic emission spectrometry (ICP-AES) (ICPE-9000, Shimadzu, Japan) following the dissolution of the sample with alkali fusion.

The TBP complex was prepared as follows: TBP (99.93%, Wako Pure Chemical Ind., Ltd., Japan) and concentrated HNO_3 (69% HNO_3 ; 31% H_2O , *ibid.*) were well mixed in a test tube. The complex was obtained as the upper organic phase after centrifugation.

Chlorination Procedure

Figure 1 illustrates the experimental apparatus. Approximately 30 mg of each sample was placed in a platinum sample cell whose diameter was 1.5 cm and volume was 0.7 cm^3 . The cell was hung in a quartz tube reactor equipped in an electric furnace (ARF 30K, Asahi Rika Seisakusho, Japan). With purging air inside of the reactor with argon gas, the reactor was heated up to 1173 K. After the temperature of the reactor became stable, 1 vol% hydrogen chloride gas diluted with argon (Japan Fine Products Co. Ltd., Japan) was introduced into the reactor at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ for 1 h.

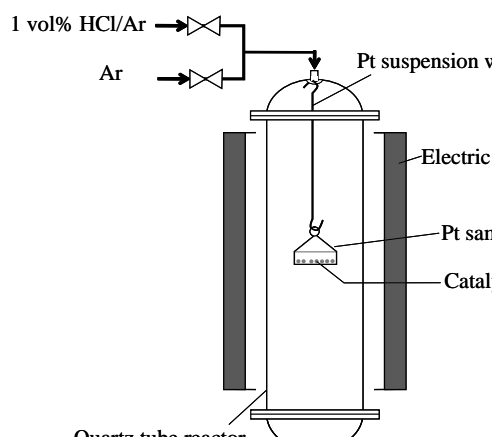


Fig. 1 Apparatus for chlorination.

SFE Procedure

The supercritical fluid extraction apparatus used is illustrated in **Fig. 2**. A 0.5 cm³ of the TBP complex was placed in reaction vessel 4. In the reaction vessel 5, 77 mg of pretreated catalyst was placed. The total volume of the two vessels 4 and 5 was approximately 5 cm³. Pressurized CO₂ was introduced from a cylinder to the experimental system via a syringe pump (260D, ISCO, U.S. A.). The complex was well mixed with SC-CO₂ in vessel 4 before the valve between vessels 4 and 5 was opened to mix the catalyst with the mixture of complex and SC-CO₂. The two reaction vessels were kept at 323 K and 25 MPa, because the complex became miscible with SC-CO₂ above 24 MPa [11]. After static extraction for 1 h, SC-CO₂ was introduced to the vessels at 1 dm³ min⁻¹, at 25 MPa for 1 h.

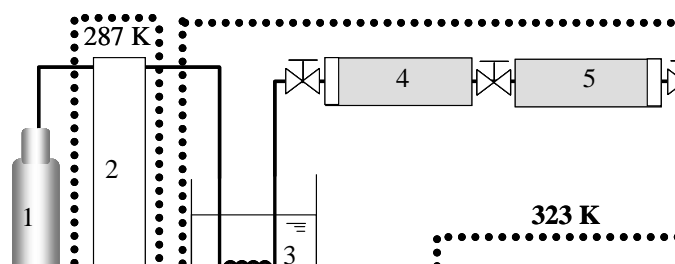


Fig. 2 Apparatus for SC-CO₂ extraction.

Analysis

The sample was conducted to the analyses; the identification of compounds by X-ray diffraction (XRD) (MiniFlex, Rigaku Co., Japan) and the chemical composition analysis by using ICP-AES following the dissolution of the sample with alkali fusion.

RESULTS

A photograph of samples before and after the chlorination treatment is shown in **Fig. 3**. After the chlorination, the color of the catalyst changed from brown to black. **Figure 4** shows XRD data of samples. In the sample after the chlorination, uranium oxide, U₃O₈, was identified as Fig. 4 (a). By the chlorination treatment, antimony in the composite oxide was volatilized, while uranium converted into uranium oxide, U₃O₈, which can be dissolved with nitric acid. On the other hand, the peaks of the uranium oxide disappeared after SFE as shown in Fig. 4 (b). **Figure 5** shows a photograph of samples before and after the

chlorination treatment and SFE. The color of the sample changed to white after the treatments.



Fig. 3 Photograph of samples (a) before and (b) after chlorination.

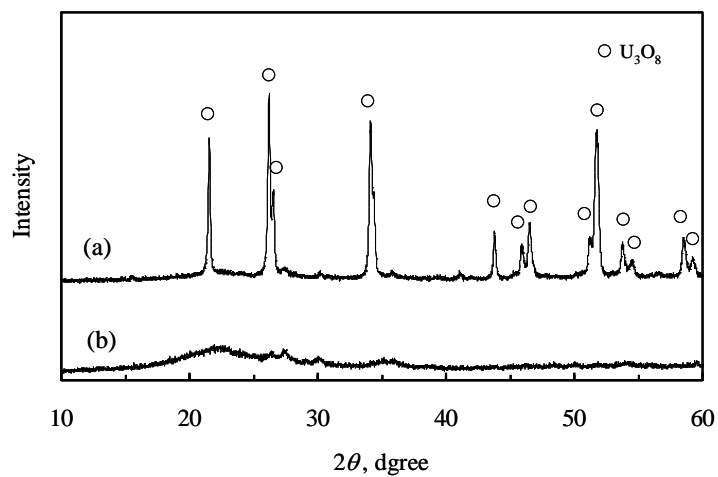


Fig. 4 XRD data of samples after (a) chlorination and (b) chlorination and SFE.

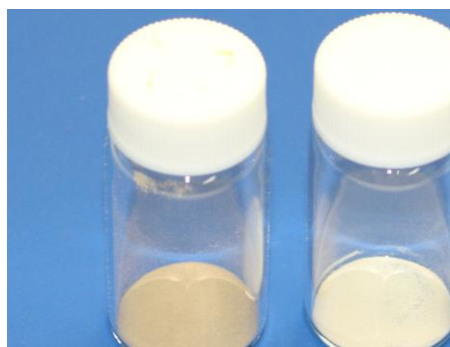


Fig. 5 Photograph of samples (a) before and (b) after chlorination and SFE.

The elemental contents in the samples are shown in **Table 1**. The antimony content decreased from 30 to 4.9 wt% by the chlorination, and the uranium and silicon contents increased up to 18 and 21 wt%, respectively. With the combination treatment of chlorination and SFE, uranium content decreased to 1.2 wt%. If the amount of silicon did not change during the treatments, the removal fraction of element i would be defined as follows:

$$(\text{Removal fraction, \%}) = 1 - \frac{(\text{Content of i, wt\%})_{\text{after}} / (\text{Content of Si, wt\%})_{\text{after}}}{(\text{Content of i, wt\%})_{\text{before}} / (\text{Content of Si, wt\%})_{\text{before}}} \quad (1)$$

The removal fraction calculated was included in Table 1. It was found that 90% of antimony contained in the catalyst was removed by the chlorination, in contrary, 95% of uranium was removed by SFE following the chlorination.

Table 1 Elemental contents in the samples

Sample	Content, wt% (Removal fraction, %)		
	U	Sb	Si
Non treated sample	13	30	15
Sample after chlorination	18 (1)	4.5 (89)	21
Sample after chlorination and SFE	1.2 (95)	5.9 (90)	30

CONCLUSIONS

The extraction with SC-CO₂ containing TBP-nitric acid complex was conducted following a chlorination treatment to volatilize antimony in the catalyst in order to remove uranium from the waste catalyst containing a composite oxide of uranium and antimony. The chlorination with 1 vol% hydrogen chloride gas at 1173 K for 1 hour could volatilize 89 % of antimony in the stable composite oxide, and convert uranium into uranium oxide, U₃O₈, which was easy to dissolve with nitric acid. By the extraction with SC-CO₂ after the chlorination, 95% of uranium was removed from the waste catalyst.

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