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A basic study for radioactive nuclides recovery from spent PUREX solvent using adsorbents

Tsuyoshi Arai^{a*}, Fumiya Nakamura^a, Ryoji Abe^a, Fuga Ueno^a, Noriaki Seko^b, Yoichi Arai^c and Sou Watanabe^c

^a *Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo 135-8548, Japan;* ^b *National Institute for Quantum and Radiological Science and Technology, 1233 Watanukicho, Takasaki, Gunma 370-1292, Japan;*

^c *Japan Atomic Energy Agency, 4-33 Muramatsu, Tokai-mura, Ibaraki 319-1194, Japan*

Organic liquid waste such as extractants and solvents used in extraction tests at facilities that handle nuclear fuels such as U and Pu are stored in pails. Some of the extractants in these organic liquid wastes are stored with these nuclides extracted. For example, it is known that if radionuclides remain extracted in tributyl phosphate (TBP) used in the PUREX process, they will be decomposed by radiation to dibutyl phosphate (DBP) and monobutyl phosphate (MBP). As radiolysis progresses, these organic materials may gasify, leading to damage to pails, scattering of nuclides, and even fire or explosion at the facility. In particular, Pu(IV) is a nuclide that emits α -rays, which is a concern for accelerated degradation of extractants and organic solvents and generation of red oil. Therefore, it is necessary to promptly remove these nuclides from organic liquid waste containing Pu and other nuclides stored in the facility. However, DBP and Pu(IV) produced in these radiolysis form strong complexes, which are difficult to remove by normal back-extraction operations. Therefore, in this work, we have developed adsorbents to remove nuclides that are difficult to back-extract, such as Pu(IV), which is extremely strongly extracted into spent PUREX solvent (TBP and DBP mixed phase). Non-woven fabrics grafted with iminodiacetate, amidoxime, and phosphate groups, commercially available iminodiacetate chelate adsorbent (Muro-chelate), and the inorganic-organic hybrid chelate adsorbent (SIDAR) were used as adsorbent. Zr(IV) was used as the target element to simulate Pu(IV). These results indicated that the extraction rate of Zr(IV) increases significantly with increasing DBP content in spent PUREX solvent, and that all Zr(IV) is extracted at DBP contents of 10 % or more. This suggests that the removal of nuclides becomes more difficult as the amount of DBP produced increases with radiolysis. It was shown that Zr(IV) extracted in spent PUREX solvent could be effectively removed by adsorbents with IDA functional groups, and Muro-chelate and SIDAR could remove 17.0 % and 63.3 % of Zr(IV) from TBP-10%DBP (DSP-10). In particular, it was found that SIDAR have a fast adsorption rate, reaching adsorption equilibrium within about 30 minutes. Furthermore, it was shown that Zr(IV) extracted in spent PUREX solvent can be continuously adsorbed and removed by using the SIDAR packed column.

Keywords: *STRAD project; spent PUREX solvent; ion exchanger; chelate adsorbent; SIDAR*

1. Introduction

It is anticipated that decommissioning of nuclear facilities, hospitals, and laboratories that handle radioactive materials will increase in the future due to their aging. Especially in facilities that handle nuclear fuel materials such as U and Pu, these materials must be stored in an appropriate method. In addition, organic waste liquids including extractants and organic solvents used in extraction experiments of nuclear fuel materials such as U and Pu are stored in pails. Some of the extractants in these organic liquid wastes are stored in a state where Pu and other substances are extracted. An organic liquid waste containing extractants used in extraction experiments of nuclides may cause progressive deterioration of organic matter due to

residual Pu and other factors, leading to fire or explosion [1-3]. Furthermore, the generated gas which was degraded of the organic liquid waste may cause damage to the storage pails and scattering of the organic liquid waste including nuclides [4,5]. Therefore, it is necessary to remove Pu and other nuclides from stored organic liquid waste to reduce that risk. In general, it is possible to easily back-extract metal ions extracted by extractants and other agents by using distribution differences and complexation reactions [6-9]. However, it has been reported that it is difficult to remove Pu and other nuclides from degraded extractants by normal back-extraction operations because the nuclides form complicated complexes with the degraded extractants [10-14].

Against these backgrounds, Japan Atomic Energy Agency (JAEA), in collaboration with several organizations, initiated the STRAD project to establish appropriate

*Corresponding author. E-mail: t-arai@shibaura-it.ac.jp

treatment methods for complicated radioactive liquid waste generated from nuclear facilities, hospitals, and research laboratories [15-17]. The development of treatment technology for organic liquid waste containing radionuclides is one of the tasks of the STRAD project, and a special research team from JAEA, Ibaraki University, Shibaura Institute of Technology, and Research Institute of Quantum and Radiation Science is conducting basic research. In particular, our team is developing a method to efficiently remove and recover nuclides using solid adsorbents from organic liquid waste containing Pu and other nuclides that are strongly extracted by extractants degraded by radiation and other factors.

It has been reported that the extractant used in the PUREX process, tributyl phosphate (TBP), forms dibutyl phosphate (DBP) by radiolysis and hydrolysis, and that it is difficult to remove these nuclides from DBP in a normal back-extraction operation because DBP forms strong complexes with nuclides such as Pu(IV) [18,19]. In addition, Pu(IV) is a nuclide that emits α -rays, which is a concern for accelerated degradation of extractants and organic solvents and generation of red oil [1]. For this reason, in this work, we are developing adsorbents suitable for the adsorption and removal of Pu(IV) extracted in spent PUREX solvent (TBP and DBP mixed phase). The adsorbent was synthesized as the non-woven fabric type adsorbent and the inorganic-organic hybrid type adsorbent, respectively. The non-woven adsorbent was prepared with iminodiacetic acid groups, amidoxime groups, and phosphoric acid groups. The inorganic-organic hybrid chelate adsorbent was obtained by introducing iminodiacetic acid groups into a porous SiO₂ carrier coated with a chloromethyl styrene-divinylbenzene copolymer (SiO₂ based **I**mino**D**iacetic **A**cid **R**esin : SIDAR). In this work, Zr(IV) was used as a simulant for Pu(IV). We investigated the adsorption removal behavior of Zr(IV) from spent PUREX solvent by these adsorbents, and selected appropriate adsorbents based on these experimental results. Furthermore, it was examined the dynamic adsorption removal behavior of Zr(IV) from spent PUREX solvent using packed columns with the selected adsorbent.

2. Experimental

2.1. Preparation of the simulated spent PUREX solvent

The simulated spent PUREX solvent was prepared by varying the mixing ratio of DBP and TBP. In this work, spent PUREX solvent was prepared by changing the mixture ratio of TBP and DBP based on 30%TBP-70%*n*-dodecane. **Figure 1** shows structure of TBP and DBP. DBP content in the simulated spent PUREX solvent was prepared at 0 – 100 vol% versus TBP (samples denoted as

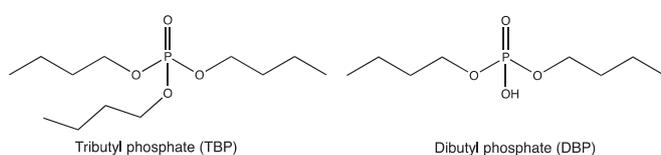


Figure 1. Structure of TBP and DBP

DSP-*n*, where *n* = 0 to 100). The extraction ability of DSP-*n* was investigated by batch extraction experiments. In this work, we used Zr(IV) as a simulant of Pu(IV) because it has the same valence, is extractable to TBP, and forms similar complexes with Pu(IV) and TBP [20,21]. In the batch extraction experiment, 5 cm³ of DSP-*n* and 5 cm³ of 0.001 - 3 M HNO₃ containing 20 mM Zr(IV) was put into a glass flask and mechanically shaken in the water bath at 298 K until equilibrium state. Zr(IV) solution was prepared using Zirconium (IV) nitrate (Wako Pure Chemical Industries, Ltd.) at analytical grade. Zr(IV) concentration in aqueous phase of before and after the batch wise experiment were measured by ICP-OES, it was determined extracted amount of Zr(IV) on DSP-*n*.

2.2. The method to perform quantitative analysis of Zr(IV) in organic phase

In this research, we have investigated a method for quantitatively analyzing Zr(IV) in the organic phase using fluorescence spectroscopy. DSP-*n* containing Zr(IV) used in the batch extraction experiments was diluted to 20-30 ppb using ethanol and 0.3 M HNO₃, and 3-hydroxyflavone as the fluorescent reagent. These diluted samples were measured in a spectrofluorometer with an excitation light wavelength of 391 nm and a fluorescence wavelength range of 300-450 nm. In order to prepare the calibration curve of Zr(IV) in DSP-*n*, Zr(IV) extracted DSP-*n* was prepared in advance by a batch extraction experiment. After the batch extraction experiment, quantitative analysis of Zr(IV) in the aqueous phase was carried out by ICP-OES, and Zr(IV) concentration in DSP-*n* was calculated based on the results. **Figure 2** shows the fluorescence spectra of Zr(IV) in DSP-10. From Figure 2, the fluorescence peak of Zr(IV) was detected at an excitation wavelength of 391 nm in DSP-10, and it was confirmed that the fluorescence intensity increased as Zr(IV) concentration increased. **Figure 3** shows calibration curve of Zr(IV) by the fluorescence spectra at 391 nm. From Figure 3, the correlation coefficient between Zr(IV) concentration and fluorescence intensity was about 0.995 in DSP-10. This result indicated that quantitative measurement of Zr(IV) in DSP-10 is available by fluorescence spectroscopy. On the other hand, a good correlation between Zr(IV) concentration and fluorescence intensity was not obtained when DBP was > 20% (> DSP-20). This is probably because the reaction between 3-hydroxyflavone and Zr(IV) was inhibited by the formation

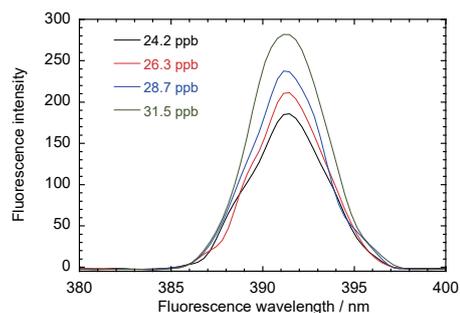


Figure 2. Fluorescence spectra of Zr(IV) in DSP-10

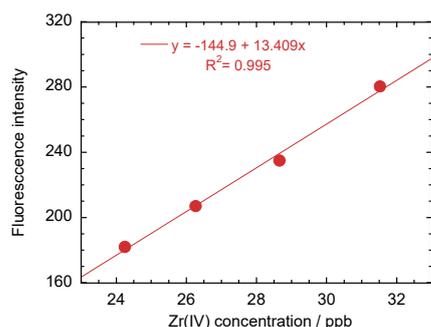


Figure 3. Calibration curve of Zr(IV) at 391 nm

of a strong complex between Zr(IV) and DBP with increasing DBP concentrations. These results show that Zr(IV) is quantifiable by fluorescence spectroscopy when the DBP is less than 10% (< DSP-10).

2.3. Preparation of adsorbents

Adsorption experiments of Zr(IV) in DSP-n were used various adsorbents; non-woven fabric graft-polymerized with a chelate functionality (iminodiacetic acid : IDA, amidoxime, phosphoric acid : PA) and particle iminodiacetic acid type chelate adsorbent. These non-woven fabric adsorbents were prepared by National Institutes for Quantum Science and Technology using the radiation graft polymerization method. Muro-chelate manufactured by Muromachi Chemical Co., Ltd. was used as the IDA adsorbent. In addition, the inorganic-organic hybrid chelate adsorbent (**SiO₂ based IminoDiacetic Acid Resin : SIDAR**) was synthesized and used for adsorption experiments. SIDAR was obtained by introducing iminodiacetic acid group using dimethyliminodiacetic acid into an inorganic-organic composite carrier (SiO₂-P) which is porous SiO₂ particles (average particle size 50 μm, average pore size 50 nm) coated with chloromethyl styrene-divinylbenzene copolymer (CMS-DVB). The cross-linking ratio in CMS-DVB copolymer was 10 %. Detail procedure of SiO₂-P can be found in Ref. [22]. **Figure 4** show the appearance and functional group

structure of non-woven fabric adsorbents, Muro-chelate and SIDAR.

2.4. Adsorption experiments of Zr(IV) in DSP-n

Prior to evaluation of adsorption performance on DSP-n, the adsorption performance of these adsorbents for Zr(IV) in nitric acid aqueous solution was evaluated. Adsorption performance was evaluated by calculating the amount of adsorption by the batch type adsorption experiment. **Table 1** shows the adsorption experiment conditions for Zr(IV) in nitric acid aqueous solution. In the batch adsorption experiment, predetermined amount of adsorbent and adsorption solution were put into a glass flask and shaken mechanically at 298 K in water bath for 3 hours. The adsorption amount of each adsorbent was calculated from the Zr(IV) concentrations before and after adsorption experiment.

Table 1. Adsorption experiment conditions for Zr(IV) in nitric acid aqueous solution

Zr(IV) concentration [mM]	20	
Nitric acid concentration [M]	0.001-3	
Quantity of solution and adsorbent	Non-woven fabric adsorbents	Muro-chelate and SIDAR
	Solution : 2.0 cm ³ , Adsorbent : 1.0 cm ³	Solution : 4.0 cm ³ , Adsorbent : 0.2 g
Contact time [min]	180	
Temperature [K]	298	
Shaking conditions	Speed : 160 min ⁻¹ , Width : 40 mm	

The adsorption behavior of Zr (IV) in DSP-n for each adsorbent was evaluated by batch adsorption experiment as in the case of nitric acid solution. In the batch adsorption experiments, the amounts of each adsorbent and Zr(IV) extracted DSP-1 and DSP-10 shown in Table 1

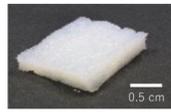
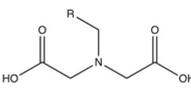
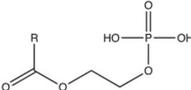
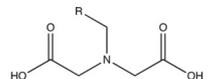
Adsorbent	Appearance	Functional group structure		
Non-woven fabric		Iminodiacetic acid (IDA)	Amidoxime	Phosphoric acid (PA)
				
Muro-chelate		Iminodiacetic acid (IDA)		
SIDAR		Iminodiacetic acid (IDA)		
				

Figure 4. Appearance and functional group structure of non-woven fabric adsorbents, Muro-chelate and SIDAR

were each placed in a glass flask and shaken mechanically in a water bath at 298 K for 3 hours. The adsorption amount of Zr(IV) on the adsorbents were calculated from the mass balance of Zr(IV) in the solvent.

2.5. Column experiments of Zr(IV) in DSP-10 using IDA resins

Column adsorption experiments were conducted to select adsorbents applicable to the column method and to evaluate their dynamic adsorption properties. Based on the adsorption behavior of Zr(IV) in DSP-10, the adsorbents were determined to Muro-chelate and SIDAR. In the column adsorption experiment, a glass column of *Dia.* 10 × *h* 50 mm was packed with each adsorbent to give 30 mm of bed height. Based on the conditions in **Table 2**, the simulated spent solvent was continuously passed through the top of the column, and the effluent from the bottom of the column was fractionated every 2.0 cm³ using a fraction collector. The dynamic adsorption performance of each adsorbent was evaluated by analyzing the concentration of Zr(IV) in the effluent collected by the fraction collector.

Table 2. Column adsorption experiment conditions

Column [mm]	<i>Dia.</i> 10 × <i>h</i> 100
Absorbent volume [cm ³]	2.36
Feed solution	[Zr(IV)] = 21.2 mM in DSP-10
Flow rate [cm ³ · min ⁻¹]	0.2
Temperature [K]	298

3. Results and discussion

3.1. Investigation for extraction performance of DBP

At first, it was investigated the effect of changing the DBP content in the PUREX solvent on the extraction behavior of Zr(IV). **Figure 5** shows the Zr(IV) extraction rate with DBP content change at each nitric acid concentration. From **Figure 5**, Zr(IV) extraction rate showed a constant values at any nitric acid concentration. In addition, the extraction rate was 100% when the DBP content was more than 10%, i.e., *n* was more than 10. From this result, it is considered that the affinity between DBP and Zr(IV) is high and forms a complex. It was reported that Zr-DBP forms a complex polymer which shows different types of bonding depending on the Zr-DBP ratio [23]. From these results, it is expected that several fission products as well as Pu(IV) are extracted and remain in spent PUREX solvent that produced DBP. In addition, it has been reported that the formation of DBP complexes with nuclides assumed to be dissolved in spent PUREX solvent is $Zr^{4+} > Pu^{4+} > UO_2^{2+} > (RuNO)^{3+} > Nb^{5+}$ [24]. Based on the experimental results and these findings, it is considered that these nuclides are difficult to remove from spent PURX solvent by the usual back-extraction operation using the difference in distribution because of their strong affinity to DBP.

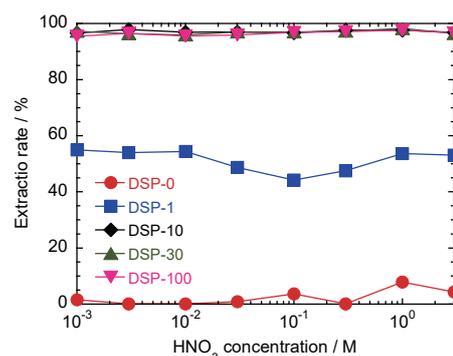


Figure 5. Nitric acid concentration dependence on Zr(IV) extraction rate by DSP-*n*

3.2. Adsorption behavior of Zr(IV) in DSP-*n* by adsorbents

Prior to evaluating adsorption behavior of Zr(IV) in DSP-*n*, adsorption behavior of Zr(IV) in nitric acid solution was evaluated by various adsorbents. **Figure 6** shows dependence of the change in Zr(IV) adsorption amount on nitric acid concentration for each adsorbent. As shown in **Figure 6**, it was confirmed that both non-woven fabric adsorbents decreased Zr(IV) adsorption amount with increasing nitric acid concentration. It is reported that the amidoxime type exhibits excellent adsorption in the neutral to alkaline range, the IDA type in the neutral range, and the phosphate type in the wide range of alkaline to acidic range [25]. This is due to the chelating reaction of metal ions being inhibited by the increase in H⁺ content of the aqueous solution with increasing acidity, and it is assumed that a similar adsorption behavior occurred with Zr(IV). In addition, it was confirmed that Zr(IV) adsorption amount decreased with increasing nitric acid concentration for Muro-chelate as well. This was considered the decrease Zr(IV) adsorption amount on Muro-chelate with increasing nitric acid concentration as in the case of non-woven fabric adsorbents.

Table 3 shows Zr(IV) adsorption amount and removal ratio in DSP-1 and DSP-10 for each adsorbent. From **Table 3**, it was confirmed that adsorption amount of Zr(IV) per gram of non-woven fabric adsorbents in DSP-1 and 10 was in the order of PA type > IDA type > Amidoxime type. On the other hand, the removal ratio was

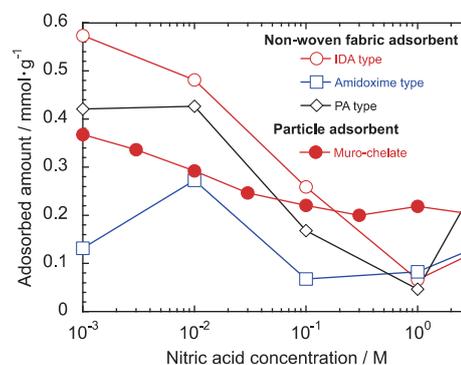


Figure 6. Dependence of the change in Zr(IV) adsorption amount on nitric acid concentration for each adsorbent

Table 3. Adsorption amount of Zr(IV) in DSP-1 and DSP-10 for each adsorbent.

Kinds and types of adsorbents		DSP-1 (Zr(IV) content : 9.9 mM)		DSP-10 (Zr(IV) content : 17.3 mM)	
		Adsorption amount [mmol·g ⁻¹]	Removal ratio [%]	Adsorption amount [mmol·g ⁻¹]	Removal ratio [%]
Non-woven fabric adsorbents	IDA	0.29	14.6	0.72	22.9
	Amidoxime	0.027	14.9	0.12	33.3
	PA	0.35	14.1	0.85	31.9
Particle adsorbent	Muro-chelate	0.024	12.1	0.067	19.4

similar for DSP-1, and the order for DSP-10 was Amidoxime type > PA type > IDA type. In addition, it was confirmed that Zr(IV) adsorption amount and removal ratio increased with increasing DBP concentration in both non-woven fabric adsorbents. From these results, it is suggested that any of the non-woven adsorbents of amidoxime, PA, and IDA types can be applied for Zr(IV) removal from spent PUREX solvents. In particular, IDA-type adsorbents, which are easy to synthesize and consist only of C, H, O, and N, are considered suitable as nuclide removal materials from spent PUREX solvents from the viewpoints of economy, safety, and disposal.

From these experimental results, it was shown that any of the non-woven fabric adsorbents evaluated in this work are suitable for the removal of Zr(IV) from spent PUREX solvents. However, although the non-woven fabric adsorbents are suitable for batch processing, they are not suitable for continuous processing such as the column method. Batch processing has issues such as long treatment time, increase in secondary wastes such as spent adsorbent, and processing volume is small. Therefore, in this work, we evaluated particulate IDA adsorbents applicable to the column method with the aim of developing a system capable of continuously removing nuclides from spent PUREX solvents. As shown in Table 3, Muro-chelate, which is an IDA-type resin, adsorbed about 1/10th the amount of Zr(IV) per unit weight of the IDA-type non-woven fabric adsorbent. However, Zr(IV) removal ratio from DSP-1, 10 was almost the same as that of IDA-type non-woven fabric adsorbent. In general, adsorbents with a copolymer matrix such as Muro-chelate have a small pore size, which makes it difficult for large adsorbed species such as Zr-DBP complexes to diffuse through the pores, limiting the adsorption site and adsorption rate [26]. In this work, in order to solve these problems of conventional IDA-type adsorbents, we have developed SIDAR, the organic-inorganic hybrid IDA-type adsorbent using porous SiO₂ particles as a carrier.

3.3. Adsorption behavior of Zr(IV) in DSP-10 by SIDAR

Figure 7 shows time course of Zr(IV) adsorption amount on SIDAR and Muro-chelate in 3 M nitric acid solution. From Figure 7, it was confirmed that Muro-chelate was not reached adsorption equilibrium even at 1440 minutes. On the other hand, SIDAR reached adsorption equilibrium in approximately 200 minutes. Furthermore, it was indicated that SIDAR have approximately twice Zr(IV) adsorption amount as Muro-

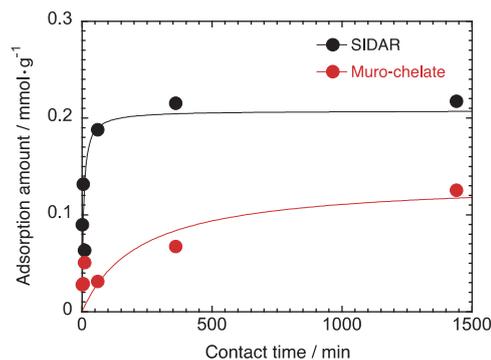


Figure 7. Time course of Zr(IV) adsorption amount on SIDAR and Muro-chelate in 3 M nitric acid solution

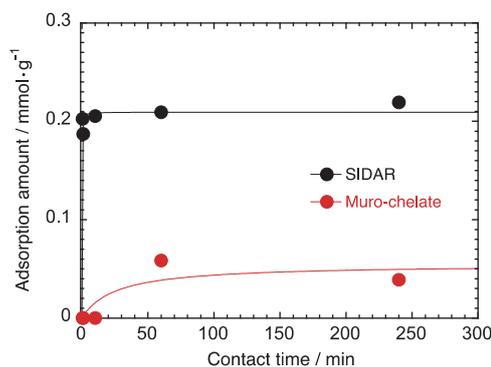


Figure 8. Time course of Zr(IV) adsorption amount on SIDAR and Muro-chelate in DSP-10

chelate. From these experimental results, it was found that SIDAR has excellent Zr(IV) adsorption speed and adsorption capacity in 3 M nitric acid solution.

Figure 8 shows time course of Zr(IV) adsorption amount on SIDAR and Muro-chelate in DSP-10. As shown Figure 8, Muro-chelate took more than 100 minutes to reach adsorption equilibrium, while SIDAR reached adsorption equilibrium within 30 minutes. Furthermore, it was indicated that Zr(IV) adsorption amount of SIDAR in DSP-10 was about four times larger than that of Muro-chelate. The removal ratio of Zr(IV) from DSP-10 was 17.0% for Muro-chelate and 63.3% for SIDAR. The fast adsorption speed of SIDAR is attributed to the small particle size of the porous silica support and the short diffusion range of adsorbed species due to the retention of polymeric resin within the approximately 50

nm pores. In addition, the specific surface areas calculated by the BET method were $63.8 \text{ m}^2 \cdot \text{g}^{-1}$ for SIDAR and $4.99 \text{ m}^2 \cdot \text{g}^{-1}$ for Muro-chelate. Furthermore, the total pore volume was $0.121 \text{ cm}^3 \cdot \text{g}^{-1}$ for SIDAR and $1.61 \times 10^{-2} \text{ cm}^3 \cdot \text{g}^{-1}$ for Muro-chelate. This suggests that SIDAR has superior performance to Muro-chelate in terms of adsorption speed and adsorption capacity.

3.4. Dynamic adsorption behavior of Zr(IV) in DSP-10 using SIDAR packed column

Figure 9 shows the breakthrough curve of Zr(IV) in DSP-10 using Muro-chelate and SIDAR packed columns. From Figure 9, it was found that the breakthrough point of Zr(IV) in SIDAR is around 6.3 bed volumes (BV), and that of Muro-chelate is around 1.5 BV. From the column experiment results, dynamic adsorption amount of Zr(IV) in DSP-10 was estimated to be $0.115 \text{ mmol} \cdot \text{cm}^{-3}$ for SIDAR and $3.38 \times 10^{-2} \text{ mmol} \cdot \text{cm}^{-3}$ for Muro-chelate. These results indicated that SIDAR has excellent dynamic adsorption properties. Furthermore, it has been reported that inorganic-organic hybrid adsorbents such as SIDAR have a very low pressure drop compared to conventional copolymer-based adsorbents because the copolymer with functional groups is embedded in hard porous silica particles, which suppresses swelling and shrinkage caused by changes in liquid properties [27]. These results suggested that it is possible to continuously remove nuclides from spent PUREX solvent by using SIDAR packed column.

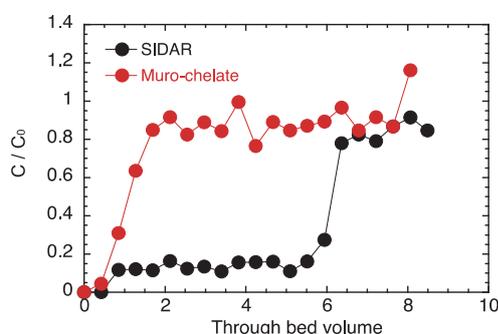


Figure 9. Breakthrough curves of Zr(IV) in DSP-10 using Muro-chelate and SIDAR packed column

4. Conclusions

In this work, we investigated adsorbents suitable for the adsorption and removal of Zr(IV) extracted in the TBP-DBP mixed phase. All of the chelating non-woven adsorbents used in this research are applicable to the removal of Zr(IV) from spent PUREX solvent, and especially IDA-type adsorbent was considered suitable from the viewpoints of economy, safety, and disposal. In addition, it was found that the removal rate of Zr(IV) from DSP-1 and DSP-10 using Muro-chelate, which is an IDA-type adsorbent, was almost the same as that using IDA-type non-woven fabric adsorbent. SIDAR significantly improved the adsorption speed and adsorption amount, which had been issues with Muro-chelate, reaching

adsorption equilibrium in about 30 minutes, and the adsorption amount was four times greater than that of Muro-chelate. In addition, removal ratio of Zr(IV) from DSP-10 was 17.0% for Muro-chelate and 63.3% for SIDAR. Furthermore, it was found that dynamic adsorption amount of Zr(IV) in DSP-10 was about 3.4 times higher than that on Muro-chelate. From this research results, it is suggested that SIDAR is the most optimal adsorbent for the removal of nuclides from spent PUREX solvent and that nuclides can be effectively removed from spent PUREX solvent using SIDAR-packed columns.

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