Adsorption of an uranyl ion onto a divinylbenzene amidoxime resin in sodium carbonate solutions

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탄산염 용액에서 아미드옥심 수지에 대한 우리닐 이온의 흡착거동

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Abstract: Distribution coefficients (Kd) of uranyl ion onto divinylbenzene amidoxime resins were measured in sodium carbonate solution and the Kd values were increased up to about 70 as the resin bead size was decreased. At a condition of 0.0044 M Na_2CO_3, the adsorption capacity for uranium was 3.4 μmole U/g-resin. The Kd values in the 0.5 M Na_2CO_3-$NaHCO_3$ solution, ranging from pH 9 to pH 11, revealed that they were increased as the pH increased and revealed lower values than those in the pure sodium carbonate solution. The amidoxime resins were characterized by FTIR-ATR showing the absorption bands of the amidoxime functional groups. A species of the uranyltricarbonate complex, $UO_2(CO_3)_3^{-4}$, was confirmed by UV-Vis spectroscopy, revealing four absorption peaks between 400 and 500 nm. Uranium was separated from some fission products by a column operation. However, most of the uranium and fission products were eluted before an adsorption and only a small amount of uranium was adsorbed onto the resin due to the low capacity of the resin.

요 약: Na_2CO_3 용액에서 DVB-amidoxime 수지에 대한 우리닐 이온의 분배계수를 측정하였다. 이때 분배계수 값은 수지의 입자크기가 작을수록 증가하였으며 최고 약 70 까지 나타났다. 0.0044 M Na_2CO_3 용액에서 우라늄의 흡착능은 3.4 μmole/g-resin 로 나타났다. pH 9 에서 pH 11 사이의 0.5 M Na_2CO_3-$NaHCO_3$ 용액에서 분배계수를 측정한 결과 pH 가 증가할 수록 분배계수 값이 증가하였으며, 또한 이 값은 순수한 Na_2CO_3 용액에서의 분배계수 값 보다 낮은 값을 보였다. FTIR 흡수분광법을 이용하여 amidoxime 수지의 성능을 확인하였다. UV-Vis 흡수분광법을 이용하여 $UO_2(CO_3)_3^{-4}$ 의 4개의 흡수피크(400~500 nm)를 확인하였다. Amidoxime 수지가 충진된 분리관을 이용하여 핵분열생성물질로 부터 우라늄을 분리하였다. 그러나, 대부분의 우라늄 및 핵분열생성물질이 용출되고 소량만이 흡착되었다. 이것은 amidoxime 수지의 낮은 흡착 능 때문으로 생각된다.

Key words : amidoxime resin, uranium, distribution coefficient, sodium carbonate solution

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1. Introduction

Uranium is a major element in the management of a spent nuclear fuel or radioactive wastes. Uranium is also present in a sea water as a trace level (~3 ppb).[1] Usually, an acid medium in a solvent extraction or an ion exchange system has been used for the separation of uranium from fission products in radioactive waste solutions including spent fuel solutions. In case of ion exchange system, generally, anion exchanger has been used for the separation of actinides from fission products. Recently, some adsorbents containing amidoxime functional groups selective for the uranyl ion have been developed for the recovery of uranium in sea water[1~4] and for an adsorption mechanism of lanthanides and transition metals in a neutral and acid medium.[5,6] Additionally, an amidoxime resin synthesized by using divinylbenzene copolymer and acrylonitrile was applied for the separation of uranium and plutonium from a simulated spent fuel solution in a carbonate medium.[7] In this system, the uranyl ion is adsorbed onto amidoxime resin by making an uranyltricarbonate complex, $UO_2(CO_3)_3^{-4}$, formed in an alkaline solution of a carbonate (pH>8).[8] A carbonate leaching of uranium from uranium contaminated soils has also been reported by using a sodium carbonate and a sodium bicarbonate solution.[9] Uranyl ion dissolves in carbonate solutions (pH>8) to form an uranyltricarbonate complex as mentioned above, so this system has been suggested to examine an applicability for a spent fuel treatment instead of a nitric acid system.

As mentioned above, most of the studies associated with amidoxime resins have been focused on resin charcaterizations after being synthesized and its application to the recovery of uranium in a sea water except for a few cases[8] dealing with a simulated spent fuel solution.

However, in this work, amidoxime resins were checked with carbonate solutions (a pure and mixed solution) and some variables to observe the uranium adsorption behavior before being placed in a spent fuel treatment. The distribution coefficients of uranyl ions onto amidoxime resins were measured with a variation of the carbonate concentration and pH of the solutions as a preliminary work for a spent fuel treatment with a strong alkaline carbonate solution because this system has an advantage to dissolve uranium alone from spent fuels, and its adsorption selectively onto amidoxime resin. In this work, this alkaline system using amicdoxime resin was also evaluated for the elution behaviors of uranium and some inactive fission products by a column operation to elucidate the degree of separation between these elements.

2. Experimental

2.1. Reagent and apparatus

The used divinylbenzene amidoxime resin [acrylonitrile (AN) : divinylbenzene (DVB)=5:5] was classified into three different types according to the bead sizes : R-101 (~2.4 mm, dia) synthesized by reacting AN-DVB copolymer (coarse grain) with hydroxylamine, R-102 (200-400 mesh size) by AN-DVB copolymer (ground fine powder) with hydroxylamine, R-103 (10-20 mesh size) by AN-DVB copolymer (fine powder) with hydroxylamine. The resin bead sizes were in the order of R-102<R-103<R-101. A carbonate solution was prepared by dissolving Na_2CO_3 (Merck Co, GR). U stock solution (2.1145 mg U/mL) was prepared by a dissolution of uranylnitrate hexahydrate $[UO_2(NO_3)_2 \cdot 6H_2O]$ (GR, Merck Co, Germany) in a Na_2CO_3 solution.

A FTIR-ATR (Travel IR, SENS IR Co) was used for a characterization of the amidoxime resins and a temperature controlled shaker (SI-900R, Shaking Incubater, JEIO Co) was used for mixing the solutions and maintaining a constant temperature. An inductively coupled plasma-atomic emission spectrometer (HORIBA, ULTIMA 2C, Jobin Yvon) was used for the measurement of uranium and other metal elements.

2.2. Measurement of the distribution coefficients (Kd)

The distribution coefficients of the uranyl ions were measured by a batch method as follows; Take 25 mL of 0.0044 M Na_2CO_3 solution (pH 10.9) and

add 0.5 mL of U stock solution (~1 mg U). Weigh the resins (1~1.5 g) and put it into the solutions. Total volume was 25.5 mL and the initial concentration of U was ~ 40 μg/mL. Control the temperature (30°C) in the shaking oven (120 rpm). Take 1 mL of a sample solution every one hour using a syringe filter and dilute it by about 10 times. Measured the U concentration by ICP-AES. For the effect of the pH on an adsorption of uranium onto the amidoxime resin, the distribution coefficients were measured using the 0.5 M Na_2CO_3-$NaHCO_3$ solution in a shaking oven (25°C, 150 rpm).

3. Results and Discussion

3.1. Characterization of the amidoxime resins

Amidoxime resins [R-C(-NH_2)(=NOH)] synthesized by a reaction of AN-DVB copolymer with hydroxylamine were obtained from a resin synthesizer.[10] In *Fig.* 1, the photographs of three amidoxime resins with their bead sizes and a SEM of a cross section of the R-102 resin are shown. As shown in *Fig.* 1, R-102 resin shows the finest powder shape and no pores were observed inside the resin (SEM). This means that a low sorption capacity for the uranyl ion is expected to be because the uranyl ion interacts with only the surface of the resin. The amidoxime resin was characterized by infrared spectra. *Fig.* 2
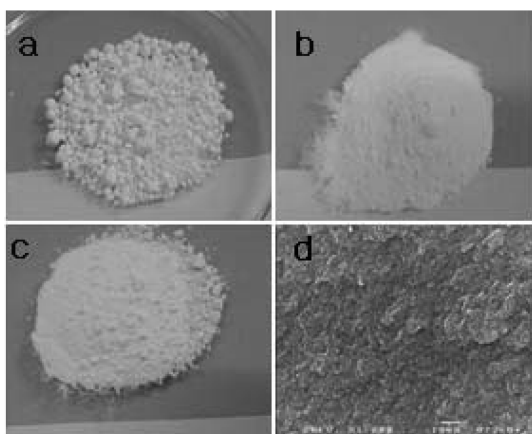

Fig. 1. Photographs and SEM of amidoxime resins. a: R-101, b: R-102, c: R-103, d: cross-section (1/1000) (R-102).
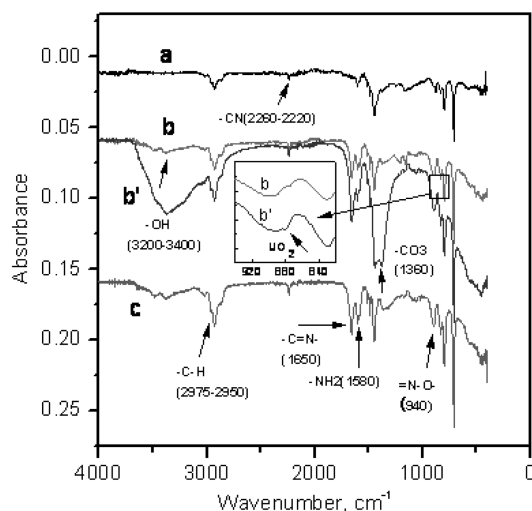

Fig. 2. FTIR-ATR spectrum of amidoxime resin (AN : DVB = 5 : 5). a: R-101, b: R-102, b': R-102 adsorbed with $UO_2(CO_3)_x^{(2-2x)}$, c: R-103.

shows the infrared spectra of the three amidoxime resins. Three IR spectra show the same absorption peak patterns except for R-101 which shows a slightly lower peak shape than the other two. The main absorptions at 2975~2950, 1650 and 940 cm^{-1} indicate the vibrations due to -C-H of the aliphatic alkyl chain, and -C=N- and =N-O- of the amidoxime group, respectively. The absorption at 1580 cm^{-1} is due to the bending vibration of -NH_2 of the amidoxime group. The IR spectrum of the uranyl carbonate adsorbed onto the amidoxime resin (R-102) (b') was measured and compared with that of the pure amidoxime resin (b). In *Fig.* 2(b'), the broad absorption at 3200~3400 cm^{-1} is due to the -OH group of amidoxime or the water content which was not evaporated. As shown in *Fig.* 2 (b'), a new band was observed at 1360 cm^{-1}. This peak was assigned as CO_3, which was confirmed by matching it with that of $CaCO_3$, and the small peak observed at 890 cm^{-1} seems to be the stretching and deformation vibration of UO_2. This peak also agreed with the literature.[11]

3.2. Measurement of the distribution coefficients
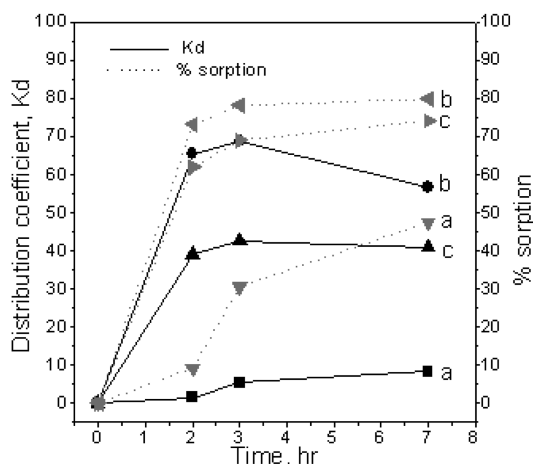
The sodium carbonate solutions were prepared by

Fig. 3. Distribution coefficient and % sorption of UO_2^{2+} onto amidoxime resin in Na_2CO_3 solution. a: R-101, b: R-102, c: R-103, Na_2CO_3; 0.0044 M (pH 10.9), 25 mL, U; 1 mg, Temp.; 30°C, Shaking; 120 rpm.

Fig. 4. Distribution coefficient (Kd) and % sorption of UO_2^{2+} onto amidoxime resin in $Na_2CO_3.NaHCO_3$ solution. Resin; R-102 (0.75 gr), 0.5 M Na_2CO_3-$NaHCO_3$, 30 mL, U; 1.05725 mg, Temp.; 25°C, Shaking; 150 rpm, Contact time; 3 hrs.

referring to an equation for predicting the pH related to the carbonate concentration and the dissociation constants of carbonic acid, the partial pressure of carbon dioxide in air and so on.[12]

A sodium carbonate solution of 0.0044 M (pH 10.9) was prepared and the pH of the solutions was controlled by using nitric acid or sodium hydroxide solution. The distribution coefficients (Kd) and adsorption of the uranyl ions onto the amidoxime resins (% sorption) were measured in a sodium carbonate solution and shown in *Fig*. 3. As shown in *Fig*. 3, the ion exchange reaction between the uranyl ion and amidoxime resin reached an equilibrium within about 2 hr and the decrease of the Kd value for the R-102 resin after 3 hr seems to be due to a volume reduction of the solution caused by a sampling for the measurement of uranium by ICP-AES. The distribution coefficients of uranium for the three types of resins were increased as the resin bead size was decreased and the maximum Kd value was about 70. Increase of the Kd value seems to be due to an increase of the surface area as the resin bead size was decreased. In this condition, about 80% (~0.8 mg) of the uranyl ion was adsorbed onto the resin (R-102) and the capacity of the uranium adsorption onto the resin was 3.4 μmole U/g-resin which is much lower than that of other commercial
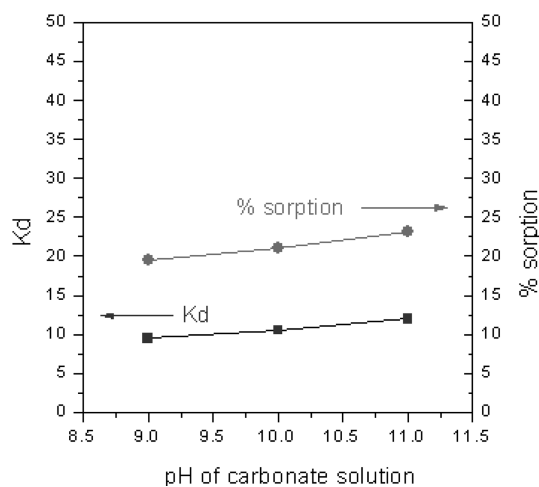
resins. These Kd values were also much lower than those reported in other works[5] (Kd ~130). This lower Kd value seems to be due to the lower capacity of the resins as mentioned above and the low mass transfer between the uranyl ion and the surface of the resin due to the hydrophobic character of the resin (AN/DVB = 5/5). Especially, for R-101 and R-103, the resins were not sufficiently wetted by the carbonate solution and floated because of their low specific weights due to their large bead sizes, and the hydrophobic effect as well. The distribution coefficients of the uranyl ions were measured in a 0.5 M Na_2CO_3-$NaHCO_3$ solution to elucidate the effect of the pH on the adsorption because this carbonate solution is generally recommended for the dissolution of uranium alone from spent fuels[7]. As shown in *Fig*. 4, the distribution coefficients are slightly increased as the pH is increased and the distribution coefficients are also much lower (~10). This low value of Kd means that the formation of the uranyltricarbonate complex would be hindered by the HCO_3^-. The higher Kd value with the higher pH is due to the fact that more carbonate is produced as the pH is increased. The adsorption mechanism of the uranyl ion onto the resin is a chelation of $UO_2(CO_3)_2^{-2}$ or
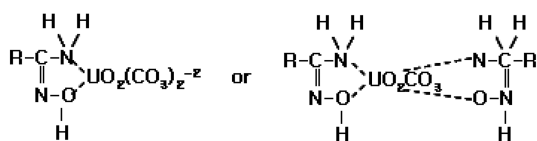
Fig. 5. Adsorption mechanism of uranyl carbonate onto amidoxime resin.

UO_2CO_3 with $-NH_2$ and $-OH$ of the amidoxime resin after a dissociation of the uranyltricarbonate complex[4,11] as shown in *Fig.* 5. That is, one or two carbonate group of uranyltricarbonate complex, $UO_2(CO_3)_3^{-4}$, are substituted with two or four sites of the amidoxime resin for an adsorption. But the exact mechanism is not clear. The Kd and % sorption were calculated using equations (1) and (2).

$$Kd = \frac{[UO_2^{2+}]resin}{[UO_2^{2+}]sol} = \frac{(Co-C)V}{CW}(cm^3/g) \quad (1)$$

$$\% \ sorption = \frac{(Co-C)100}{Co} = \frac{100Kd}{Kd+V/W} \quad (2)$$

Where, Co and C are the concentrations of uanium at an initial and equilibrium state, respectively. V is the volume of the solution and W is the weight of the resin.

3.3. Speciation of the uranyltricarbonate complex

Uranyl ion is presented as an uranyltricarbonate complex in a carbonate solution only over pH 9 and this complex reveals four absorption peaks between 400 nm and 500 nm[6]. In this work, the UV-Vis spectra of the uranyl ions were measured for different carbonate solutions. *Fig.* 6 shows the UV-Vis spectra measured for the carbonate solutions such as 0.0044 M Na_2CO_3 (pH 10.9), 0.072 M Na_2CO_3 (pH 11.36), and 0.5 M Na_2CO_3-$NaHCO_3$ (pH 9, 10 and 11), respectively. As shown in *Fig.* 6, four absorption peaks were clearly resolved which agreed well with the literatures[7]. This confirms that the uranyltricarbonate complexes were formed in this system. However, the peak heights in the pure carbonate solutions (a, b) were higher than those in the carbonate-bicarbonate solutions (c, d, e). This means that the uranyltricarbonate complex is formed
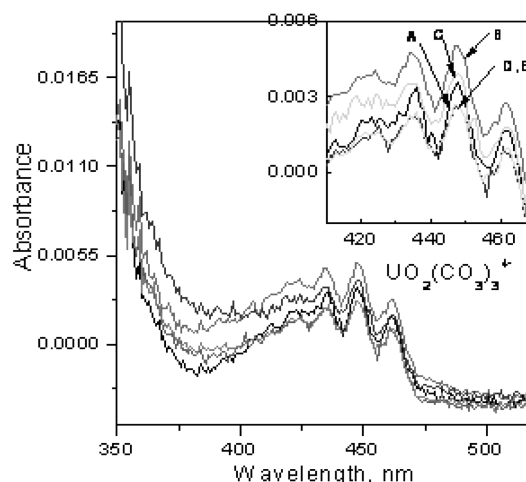

Fig. 6. UV-Vis spectrum of uranyl carbonate complexes. U; 0.2586 mM, A; 0.0044M Na_2CO_3 (pH 10.9), B; 0.072 M Na_2CO_3 (pH 11.36), C; 0.5 M Na_2CO_3-$NaHCO_3$ (pH 9.01), D ; 0.5 M Na_2CO_3-$NaHCO_3$ (pH 10.00), E; 0.5 M Na_2CO_3-$NaHCO_3$ (pH 10.99).

more easily in the Na_2CO_3 solution when compared to the Na_2CO_3-$NaHCO_3$ solution. Accordingly, a pure carbonate solution is recommended for the adsorption of uranium onto amidoxime resin in spent fuel solutions.

3.4. Elution behavior of uranium and some fission products

Fig. 7 shows the elution behaviors of the uranyl ion and some inactive fission products such as Mo, Pd, Re, Ru and Zr. The reason why these fission products were taken is that these elements are known to be dissolved together with uranium in a sodium carbonate solution or accompanied with uranium in the separation system of a nitric acid medium, and Re was taken because of its analogue to Tc. As shown in *Fig.* 7. Most of the fission products were separated from uranium even though Re was eluted late and revealed a tailing which was slightly overlapped with U. However, most of the U and fission products were eluted at the loading and washing steps and only a small amount of uranium was adsorbed onto the resin and eluted by the 0.5 M HNO_3 eluent. Moreover, the flow rate was so low that the eluent was fed into the column by a
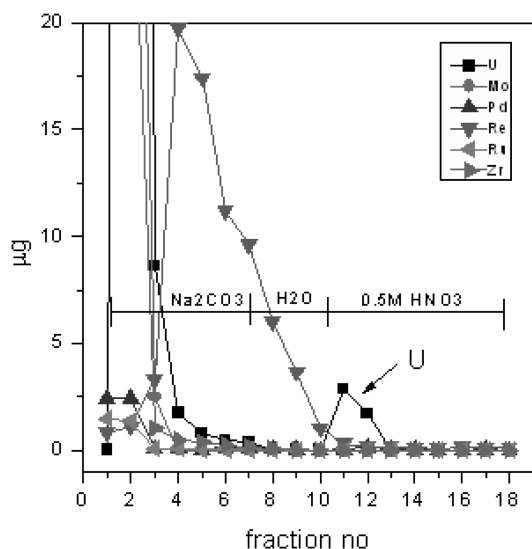
Fig. 7. Chromatogram of uranyl ion eluted from amidoxime resin column using sodiun carbonate solution as an eluent. Resin; R-103 1.0 g, Column; 1(dia)×3 cm (h), U; 300 μg, FPs; Mo, Pd, Re, Ru, Zr 100 μg each, loading (1) and washing (2~6); 0.072 M Na$_2$CO$_3$ (pH 11.43), washing (7~10); H$_2$O, U elution (11~18); 0.5 M HNO$_3$, flow rate; 0.2 mL/min, 1 fraction; 3 mL.

peristaltic pump. This low flow rate seems to be caused by the hydrophobicity of the resin as mentioned above. The result of this phenomenon in which the uranium is eluted early prior to an adsorption is due to the low capacity of the resin onto which the elements were overloaded.

4. Conclusion

The distribution coefficients of uranyl ions, onto an amidoxime resin, measured in this work, showed lower values when compared to other works. However, the ion exchange mechanism and the species of the uranyltricarbonate complex were confirmed and an applicability of this system to spent fuel treatments is expected to a certain extent. In the future, another higher capacity and more hydrophylic amidoxime resin will be synthesized by increasing the content of the acrylonitrile(AN) content in the resin and this work will also be continued.

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