

Selective Separation of Sr by Potassium Titanates from Solution of Nitrate – 15248

Hitoshi Kanda *, Hitoshi Mimura *, Yuichi Niibori *, Mamoru Iwasaki **, Koichi Mori **
* Tohoku University
** Kurita Water Industries Ltd.

ABSTRACT

The radioactive waste treatment is planned in LWTF (Low-level radioactive Waste Treatment Facility, JAEA) for the low-level liquid wastes generated from Tokai-reprocessing facility [1]. The target liquid wastes mainly consist of highly concentrated sodium nitrate (4.7 M NaNO₃) containing low level radioactive ¹³⁷Cs and ⁹⁰Sr, while the conventional adsorbent (Titanic acid-PAN) has some problems in the adsorption performance and irradiation resistance. In this study, the adsorption properties of Sr²⁺ ions, leaching properties of Sr²⁺ and irradiation properties were clarified by using the novel adsorbent of potassium titanates (KT-1). Relatively large uptake percentage (99%) and maximum uptake capacity (0.37 mmol/g) were obtained for the KT-1 compared to that of Titanic acid-PAN. As for the breakthrough properties, KT-1 had the smoother breakthrough curve and larger 5% breakthrough capacity compared to Titanic acid-PAN. From the results of batch and column experiments, KT-1 was effective for the uptake of Sr²⁺ ions in the presence of highly concentrated Na⁺ ions. The leached percentages of Sr²⁺ ions from calcined products of Sr-KT-1 in pure water and 0.1 M NaOH were less than the detection limit of ICP-AES, and those in 0.1 M HCl tended to markedly decrease with calcining temperature; the formation of SrTiO₃ phase above 800°C was effective for the lowering of leachability. The irradiation stability of the adsorbent was examined by instrumental analyses and the evaluation for the uptake percentage of Sr²⁺ ions by batch method. The growth of surface crystal was observed by SEM, but no significant change in X-ray diffraction peak was observed, and Sr²⁺ uptake (%) was almost constant. The novel adsorbent of KT-1 had excellent characteristics for Sr selectivity, uptake capacity, leachability and irradiation resistance. KT-1 is thus effective for the treatment and disposal in LWTF.

INTRODUCTION

The radioactive waste treatment by co-precipitation, ultrafiltration and adsorption methods (**Fig. 1**) are planned in LWTF (Low-level radioactive Waste Treatment Facility, JAEA) for the low level liquid wastes generated from Tokai-reprocessing facility. The target liquid wastes mainly consist of highly concentrated sodium nitrate (4.7 M NaNO₃) containing low level radioactive ¹³⁷Cs and ⁹⁰Sr. In the operation process, the chemical durability and irradiation stability are important characteristics; conventional adsorbent “Titanic acid-PAN” has some problems in the maximum uptake capacity, irradiation resistance and cost efficiency.

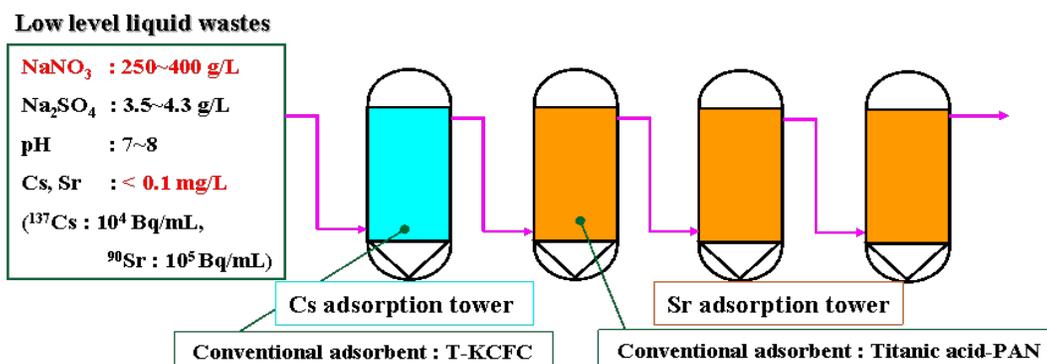


Fig. 1. Adsorption system in LWTF (Tokai-reprocessing facility).

As for the selective removal of radioactive Sr, titanate adsorbents are well known to have excellent adsorption ability for the high-level liquid wastes [2]-[4]. In particular, the potassium titanates with layer structure (**Fig. 2**) developed by Fujiki and Komatsu had excellent adsorption properties for Sr^{2+} ions in radioactive waste solutions [3][4]. These adsorbents are fine crystalline powder and cannot be used directly to the practical column separation process, however, the adsorbents were successfully granulated by the authors. The present study deals with adsorption properties of Sr^{2+} ions, leaching properties of Sr^{2+} ions from the calcined products and irradiation properties.

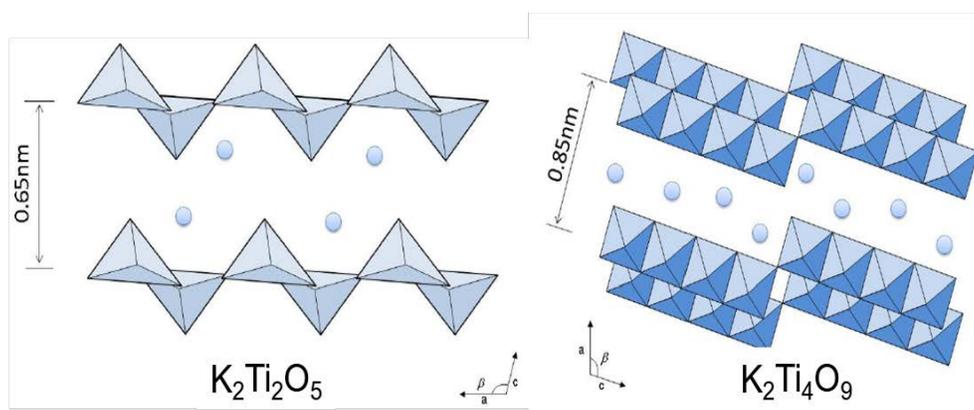


Fig. 2. Schematic view of potassium titanates.

EXPERIMENTAL

Materials

In this study, novel granulated adsorbent of potassium titanate (KT-1) (**Fig. 3**) was used. This granulated adsorbent was produced as follows; powdered titanates (Otsuka Chemical Co., Ltd.) were kneaded with clay binder and water-soluble polymer and then the granulated pellets were sieved and calcined in the temperature range from 700 to 800°C. Originally, this adsorbent was developed by Otsuka Chemical Co., Ltd. in order to remove radioactive Sr^{2+} ions from highly contaminated water generated in Fukushima NPP-1, and it has a highly adsorption performance of Sr^{2+} ions under high salt concentration[5].



Fig. 3. Digital microscope images of KT-1.

Uptake Experiment of Sr^{2+} Ions by Batch Methods

The uptake rate of Sr^{2+} ions for KT-1 was estimated by the batch method. An aqueous solution (5 cm^3) containing 0.1 ppm Cs^+ ions and Sr^{2+} ions spiked with ^{85}Sr ($10,000 \text{ cpm/cm}^3$), 400 g/L NaNO_3 and $4.3 \text{ g/L Na}_2\text{SO}_4$ was contacted with 50 mg of the sample at $25 \pm 1^\circ\text{C}$ up to 24 hours. The concentrations of Sr^{2+} ions were estimated by isotope tracer technique (NaI(Tl) scintillation counter). The uptake percentage (R , %) is defined as :

$$R = (C_i - C_f) / C_i \times 100 \quad (\%), \quad (\text{Eq. 1})$$

where C_i , C_f (cpm/cm^3) are the radioactivity counts of nuclides at initial and at equilibrium, respectively; m (g) the weight of solid sample; V (cm^3) the volume of aqueous phase.

Determination of Maximum Adsorption Amount of Sr^{2+} Ions

The maximum uptake amount (Q_{max} , mmol/g) of Sr^{2+} ions for KT-1 was estimated by batch method. An aqueous solution (5 cm^3) containing $0.1 \text{ mol/L Sr}^{2+}$ ions spiked with ^{85}Sr ($10,000 \text{ cpm/cm}^3$), 400 g/L NaNO_3 was contacted with 50 mg of the sample at $25 \pm 1^\circ\text{C}$ up to 24 h. The adsorption amount of Sr^{2+} ions were estimated by isotope tracer technique as follows.

$$Q_{\text{max}} = C_f / C_i \times C_s \times V / m \times 1000 \quad (\text{mmol/g}), \quad (\text{Eq. 2})$$

where C_i , C_f (cpm) are the radioactivity counts of solution at initial and adsorbent at equilibrium, respectively; C_s (mol/L) is the concentration of metal ions at initial; V (L) the volume of aqueous phase; m (g) is the weight of adsorbent.

Column Test

The adsorbent (2 g) were densely packed into a glass column ($5 \text{ mm}\Phi \times 200 \text{ mm}$ long). **Figure 4** shows the apparatus for the column experiments. A feed solution ($[\text{Cs}^+] = 200 \text{ ppm}$, $[\text{Sr}^{2+}] = 100 \text{ ppm}$, $[\text{Ca}^{2+}] = 100 \text{ ppm}$, $[\text{Mg}^{2+}] = 50 \text{ ppm}$, $[\text{RuNO}_3^{3+}] = 50 \text{ ppm}$, $[\text{NaNO}_3] = 400 \text{ g/L}$, $^{85}\text{Sr} = 2,500 \text{ cpm/cm}^3$) was passed through the column at a flow rate of $0.64 \text{ cm}^3/\text{min}$. Diverse metal cations such as Mg^{2+} , Ca^{2+} and RuNO_3^{3+} were added to the feed solution because the target liquid waste in LWTF contained these metal ions along with Sr^{2+} , Cs^+ and NaNO_3 . Every 5 cm^3 of the effluent was then taken by a fraction collector. A breakthrough curve was obtained by plotting the breakthrough ratio (C/C_0) against the effluent volume, where C_0 and C (ppm) are the concentrations of the initial solution and the effluent, respectively. The concentrations of Sr^{2+} were estimated by isotope tracer technique.

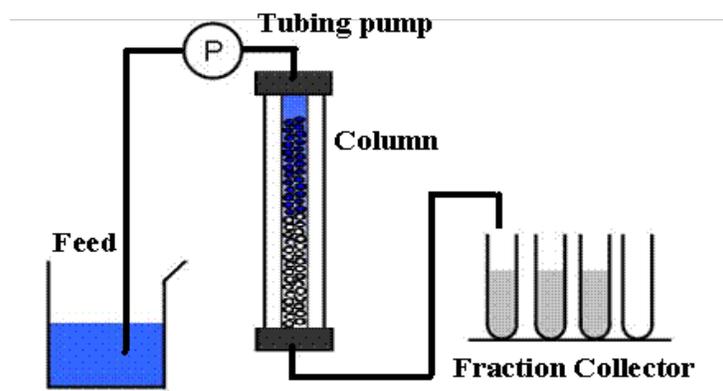


Fig. 4. Apparatus for the column experiments.

Stable Solidification by High Temperature Sintering and Leachability of Sr^{2+} ions

KT-1 adsorbents (10 g) were treated with 0.5 M SrCl_2 solution (200 cm^3). Sr^{2+} -saturated KT-1 adsorbents were then calcined at different temperatures from 500°C to $1,100^\circ\text{C}$. The Sr leachability test for the calcined specimens (50 mg) was carried out by batch method using pure water and 0.1 M HCl solution (5 cm^3) as leachant up to four weeks at 25°C and 90°C . The Sr^{2+} concentration in the leachant was measured by ICP-AES. The leached percentage was estimated as;

$$L = M_i/M_0 \times 100 (\%), \quad (\text{Eq.3})$$

Where M_i is the leached amount of Sr^{2+} and M_0 the initial amount of Sr^{2+} in the solid sample. After leaching, the pH of the leachant was measured and the leached specimens after four weeks were submitted to SEM observation and EDS analysis.

Irradiation Stability

The irradiation stability experiments for the KT-1 adsorbents were carried out at ^{60}Co γ -ray irradiation facility in Takasaki Advanced Radiation Research Institute, JAEA. The irradiation conditions were as follows; absorption dose rate: 2.8 kGy/h, irradiation time: 5h, 7d and 60d, absorption dose: 14 kGy, 470 kGy and 4.2 MGy. **Figure 5** shows the outline of the irradiation laboratory in the ^{60}Co irradiation facility. The irradiation stability of the irradiated adsorbent was examined by instrumental analyses (SEM, XRD) and the evaluation of uptake percentage of ^{85}Sr ions by batch method.

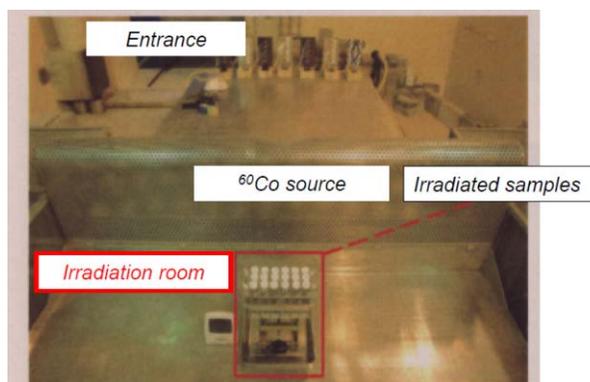


Fig. 5. Outline of irradiation laboratory in ^{60}Co irradiation facility.

RESULTS AND DISCUSSION

Uptake Rate and Maximum Adsorption Capacity of Sr^{2+} Ions

Relatively large uptake percentage (99%) was obtained for the KT-1 compared to that of Titanic acid-PAN (69%) [6] (Fig. 6), indicating that KT-1 has an excellent selectivity for Sr^{2+} ions even in the presence of highly concentrated Na^+ ions. Furthermore, Fig. 7 shows the comparison of maximum uptake capacity of Sr^{2+} ions for KT-1 and Titanic acid-PAN. The maximum uptake capacity of Sr^{2+} ions for KT-1 was estimated to be 0.37 mmol/g which is larger than that of Titanic acid-PAN (0.12 mmol/g) [6]. Thus, KT-1 adsorbent has relatively large uptake capacity for the practical treatment of Sr^{2+} ions in LWTF.

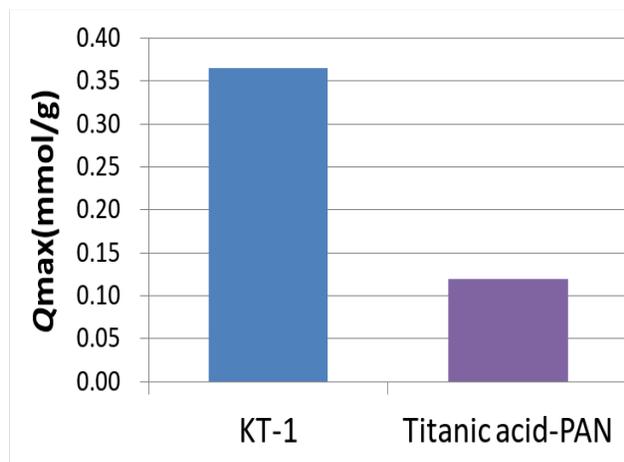


Fig. 6. Uptake rate of Sr^{2+} ions.
 $[\text{Cs}^+]$: 0.1 ppm, $[\text{Sr}^{2+}]$: 0.1 ppm,
 $[\text{NaNO}_3]$: 400 g/L, $[\text{Na}_2\text{SO}_4]$: 4.4 g/L,
 V/m : $100\text{cm}^3/\text{g}$, shaking time: 24 h, 25°C .

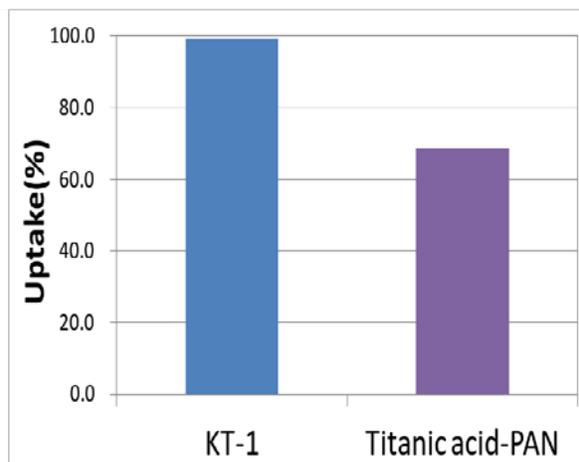


Fig. 7. Maximum uptake capacity of Sr^{2+} ions.
 $[\text{Sr}^{2+}]$: 0.1 M, $[\text{NaNO}_3]$: 400 g/L,
 V/m : $100\text{cm}^3/\text{g}$, shaking time: 24 h, 25°C .

Breakthrough Properties

For the practical treatment of Sr^{2+} ions in LWTF, the evaluation of column adsorption properties is essential in the presence of highly concentrated Na^+ ions and diverse metal cations (Cs^+ , Sr^{2+} , Ca^{2+} , Mg^{2+} and RuNO_3^+). Figures 8 and 9 show the breakthrough curves of Sr^{2+} ions for KT-1 and Titanic acid-PAN and estimated 5% breakthrough capacities, respectively. The breakthrough curve of Sr^{2+} ions for Titanic acid-PAN shows a concentration phenomenon of Sr^{2+} ; in the breakthrough curve, C/C_0 value over 1.0 was

observed due to the release of adsorbed Sr^{2+} ions by the coexisting metal ions such as Ca^{2+} and Mg^{2+} ions. In contrast, the breakthrough curve of Sr^{2+} ions for KT-1 had a profile with gentle rising and the 5% breakthrough capacity was estimated to be $20 \mu\text{mol/g}$ which was larger than that of Titanic acid-PAN.

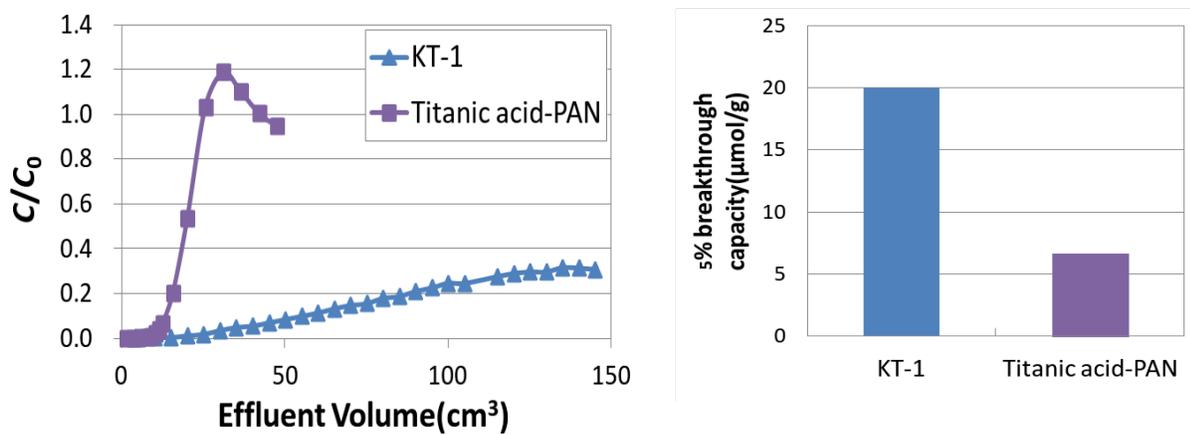


Fig. 9. 5 % Breakthrough capacities of Sr^{2+} .
Fig. 8. Breakthrough curve of Sr^{2+} ions.

Weight of adsorbents: 2 g, Column diameter: 5 mm Φ , Flow rate: 0.67 cm^3/min (KT-1), 0.17 cm^3/min (Titanic acid-PAN), Feed: 200 ppm Cs^+ , 100 ppm Sr^{2+} , 100 ppm Ca^{2+} , 50 ppm Mg^{2+} , 50 ppm RuNO_3^+ , 400 g/L NaNO_3 .

Leachability of Sr

The stable solidification of Sr-saturated KT-1 was examined by high temperature sintering. The leached amounts of Sr^{2+} ions from the sintered products in pure water and 0.1 M NaOH were less than the detection limit (0.1 $\mu\text{g}/\text{ml}$) of ICP-AES, and the leached percentage was estimated to be less than 0.0033% even after 4 weeks-leaching. In either case, the final pH of the leachant was around 12. As for the 4 weeks-leaching at 25 and 90 $^\circ\text{C}$ in acid solution (0.1 M HCl), the leached percentage tended to markedly decrease with calcining temperature (Figs. 10 and 11); the formation of SrTiO_3 phase above 800 $^\circ\text{C}$ was effective for the lowering of leachability. Figure 12 shows SEM images of 1,100 $^\circ\text{C}$ sintered Sr-saturated KT-1 and after leaching specimens. No significant change on the surface of sintered products after leaching was observed, indicating the excellent stability.

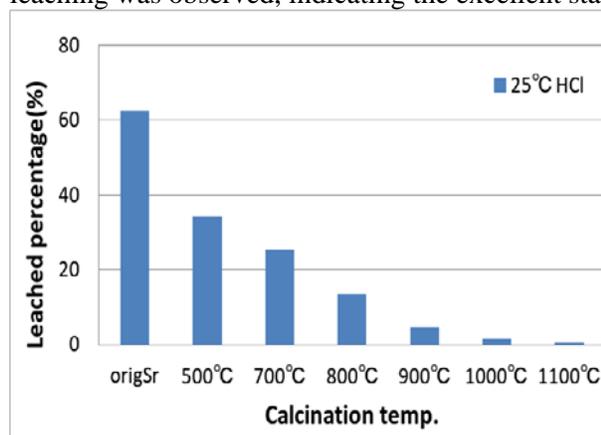
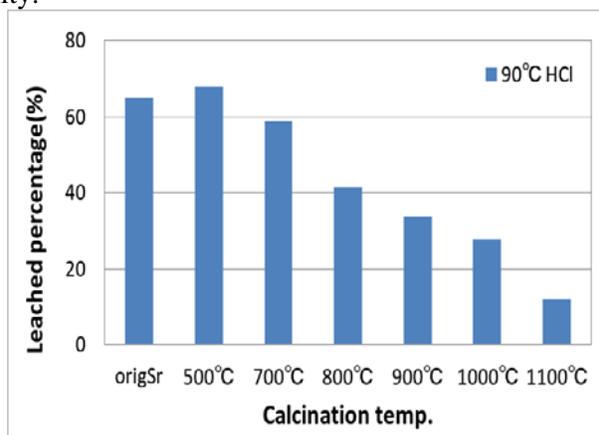


Fig. 10. Leached percentage (%) of Sr. 4 weeks-leaching, V/m: 100 cm^3/g , 0.1 M HCl, 25 $^\circ\text{C}$



6 Fig. 11. Leached percentage (%) of Sr. 4 weeks-leaching, V/m: 100 cm^3/g , 0.1 M HCl, 90 $^\circ\text{C}$

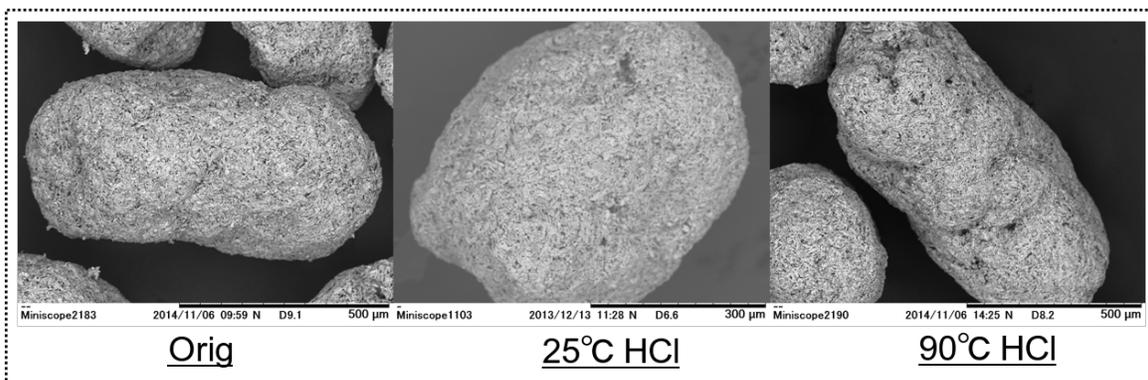


Fig.12. SEM images of sintered products of Sr-saturated KT-1(1,100°C) (left) and specimens after leaching (middle, right).

Irradiation Stability

The evaluation of irradiation stability for KT-1 is one of the most important issues for the practical use in LWTF. **Figure 13** shows the SEM images of KT-1 and irradiated specimens up to 4.2 MGy. In the case of irradiation less than 470 kGy, the surface morphology of KT-1 was not changed, however, at 4.2 MGy irradiation, the growth of surface crystal was observed. This crystal consists of 61.3 % (at.) O, 21.2% (at.) C, 15.7% (at.) K and other elements (Ti, Mg, Si, Al) measured by EDS. **Figure 14** shows X-ray diffraction (XRD) patterns of original KT-1 and irradiated specimens. No significant change in the diffraction peaks was observed, and the uptake rate of Sr^{2+} ions for the irradiated specimens up to 4.2 MGy irradiation show similar tendency (**Fig. 15**).

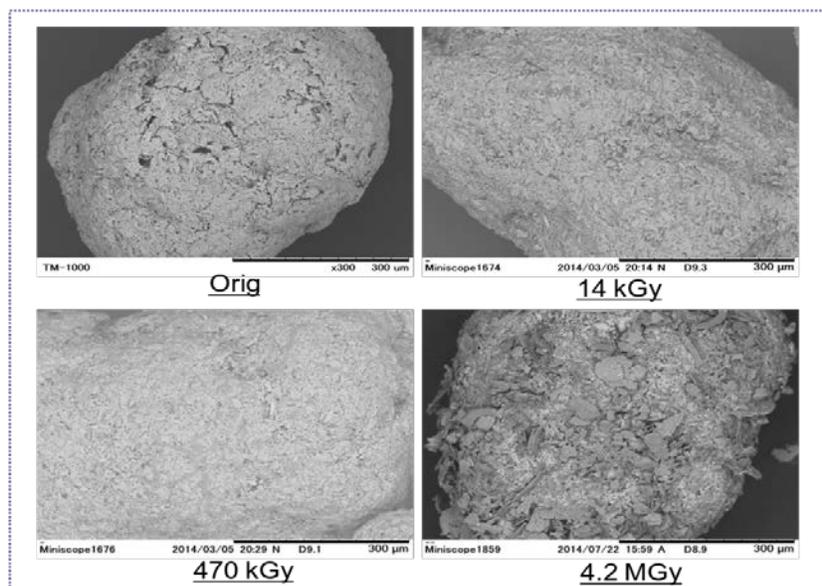


Fig.13. SEM images of original KT-1 and irradiated specimens.

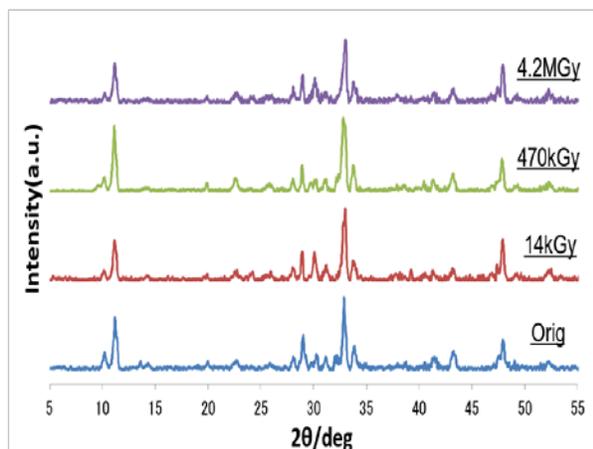


Fig. 14. XRD patterns of original KT-1 and irradiated specimens.

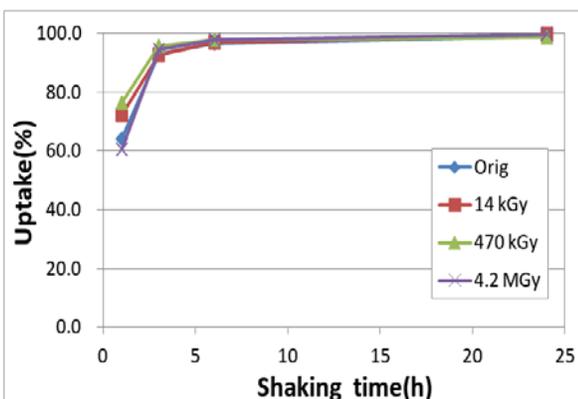


Fig. 15. Uptake rate of Sr for original KT-1 and irradiated specimens.

[Cs⁺]: 0.1 ppm, [Sr²⁺]: 0.1 ppm,
[NaNO₃]: 400 g/L, [Na₂SO₄]: 4.4 g/L,
V/m: 100cm³/g, shaking time: 1 d, 25°C.

CONCLUSIONS

The adsorption properties of Sr²⁺ ions for novel granular potassium titanates of “KT-1” were examined by batch method. Compared to the conventional adsorbent of “Titanic acid-PAN”, relatively large uptake percentage (99%) and maximum uptake capacity (0.37 mmol/g) were obtained for KT-1 in the presence of 400 g/L NaNO₃. Breakthrough properties of Sr²⁺ ions were examined by passing simulated solution through the column packed with KT-1. The breakthrough profile of Sr²⁺ ions for KT-1 showed a gentle rising, and 5% breakthrough capacity was larger than that of Titanic acid-PAN. The leached amounts of Sr²⁺ ions in pure water and 0.1 M NaOH were less than the detection limit of ICP-AES; the leached percentage was estimated to be less than 0.0033%. The leachability of Sr²⁺ ions in 0.1 M HCl tended to decrease markedly with calcining temperature; the formation of SrTiO₃ phase above 800°C was effective for the lowering of leachability. The irradiation stability of KT-1 was evaluated by instrumental analyses and batch adsorption method using the irradiated specimens of KT-1 up to 4.2 MGy. The growth of surface crystal was observed for the irradiated specimen at 4.2 MGy, while no significant change in XRD patterns was observed, and the uptake percentage of Sr²⁺ ions was almost constant. Thus, the novel adsorbent of KT-1 had excellent properties in terms of Sr selectivity, uptake capacity, leachability and irradiation resistance for the treatment of Sr²⁺ ions in the presence of highly concentrated Na⁺ ions.

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