Institute of Research and Innovation

Separation of Actinoids from HLW by Thiacalix[4]arene Compound Impregnated Silica Ion-exchanger

Takahiro Kikuchi, Ichiro Goto, Kazunori Suzuki

Institute of Research and Innovation (IRI),
1201, Takada, Kashiwa, Chiba, 277-0861, Japan.

Introduction

Institute of Research and Innovation

- High level radioactive waste (HLW) generated from commercial reprocessing facilities contains two main element groups with heat generated nuclides

- One is Cs/Sr with half-life period of 30 years, and another is trivalent actinoids in which ^{241}Am has half-life period of 400 years

- The heat generation of Cs/Sr reduces to a few watts in the periods of 200-300 years

- The heat derived from ^{241}Am decreases only half of initial heat release even in 400 years

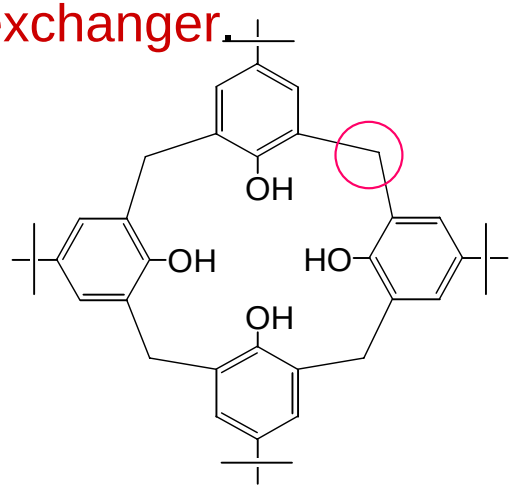
- It is reasonable to dispose only actinoids in the geological repository

- This study investigated the chelating ion-exchange treatment to separate from actinoids in high-level liquid waste (HLLW) by using CMPO and thiacalix[4]arene impregnated silica ion-exchanger (CMPO-CAPS Process).

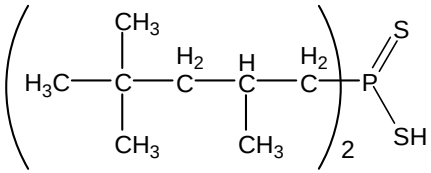
Thiacalix[4]arene compounds

Institute of Research and Innovation

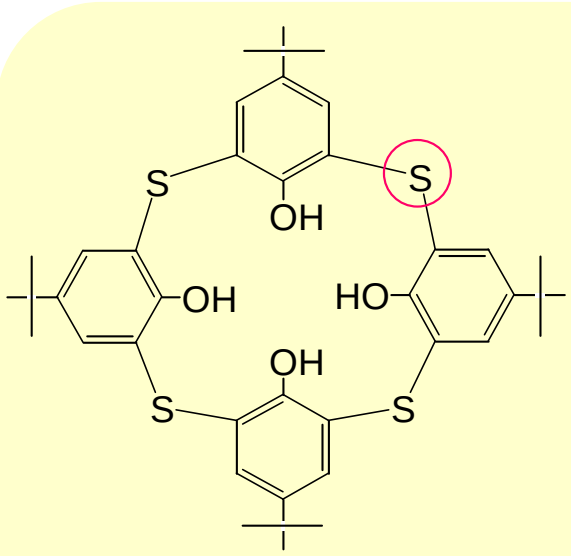
Thiacalix[4]arene compounds have four p-tert-butylphnol are linked by four sulfide groups instead of methylen groups. Thiacalix[4]arene compounds have high complexation ability toward transition metal ions. We prepared thiacalix[4]arene compounds impregnated silica exchangers for separation of Am from lanthanoids, and we found that sulfonyl type thiacalix[4]arene impregnated silica exchanger (CAPS-SO2-exchanger) have the excellent separation performance for Am in weak-acid solution. We investigate that adsorption ability of CAPS-SO2-exchanger is compared with that of Cyanex301-exchanger.



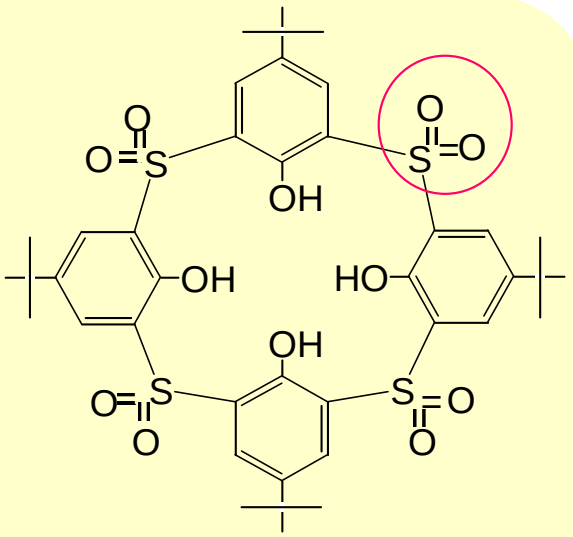
Calix[4]arene



Cyanex301



CAPS4



CAPS4-SO2

Concept of CMPO-CAPS Process

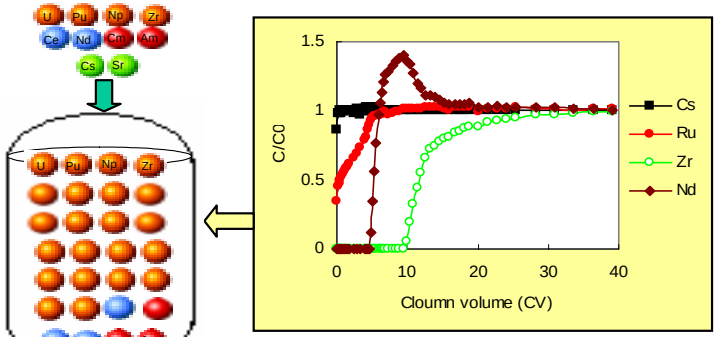
Institute of Research and Innovation

-CMPO-CAPS-process is composed of the three separation columns.
-Cs and Sr are passed through the CMPO-exchanger and separated from HLLW.
-Minor actinoids such as Am are separated from lanthanoids by thiacalix[4]arene compounds impregnated silica exchangers (CAPS-SO2-exchanger).
-In this study, we report the experiment results that were foundations of CMPO-CAPS-process flow.

Separation of Cs/Sr by CMPO impregnated silica exchanger

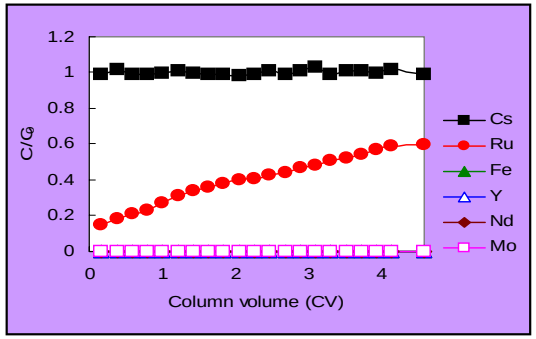
Separation of Am/Cm by CAPS-SO2 impregnated exchanger

CMPO -exchanger 1



Recovery of U(Pu)/Np/Zr
Elution of Zr with citric acid

CMPO -exchanger 2



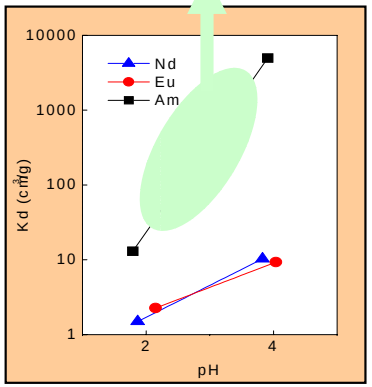
Cs, Sr and other FPs

MA/Lanthanoids is recovered by diluted HNO_3 (pH2)

CAPS-SO2 -exchanger

Lns waste

MA recovery with HNO_3



Adsorption and elution test for simulated HLLW on CMPO-exchanger

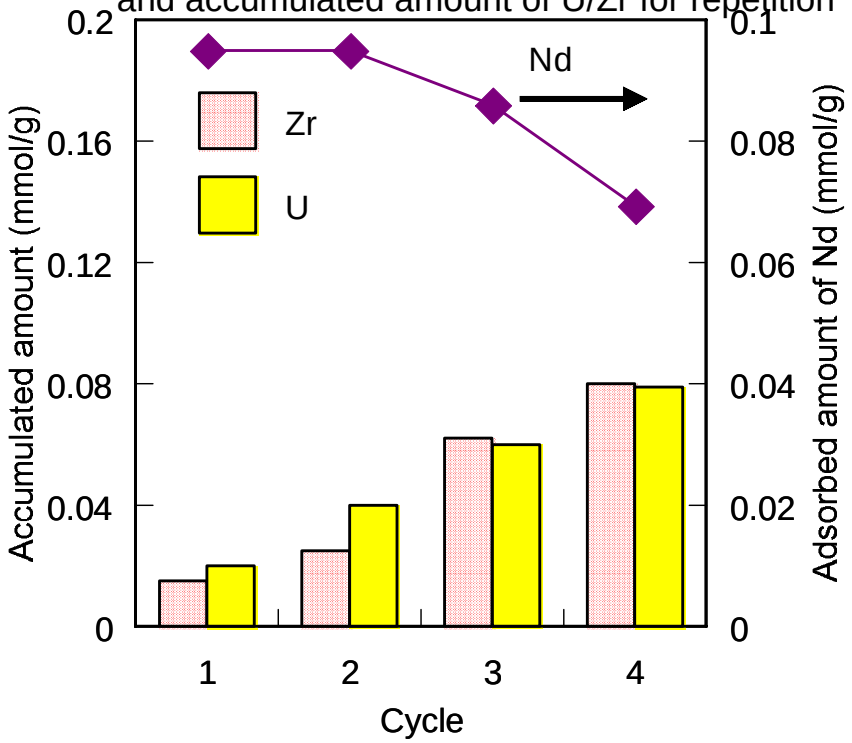
Institute of Research and Innovation

Chemical composition of simulated HLLW

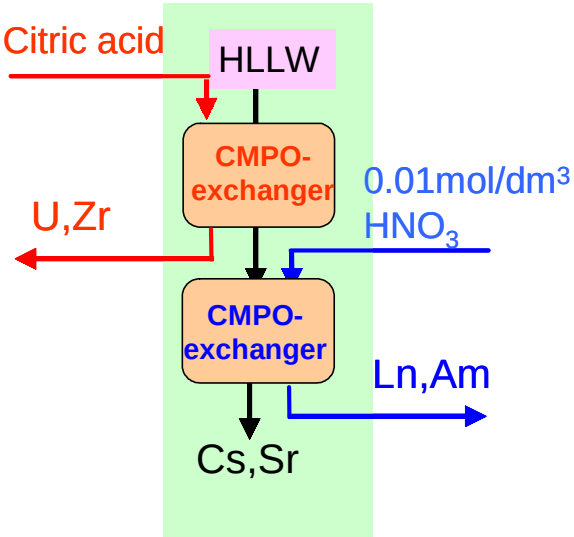
Element	Concentartion ($mmol/dm^3$)
Cs	3
Y	1
Nd	10
Ru	4
Zr	7
Mo	2
Fe	10
U	2
HNO_3	$3mol/dm^3$

Eluent: $0.01mol/m^3$ of HNO_3

Change in adsorbed amount of Nd, and accumulated amount of U/Zr for repetition



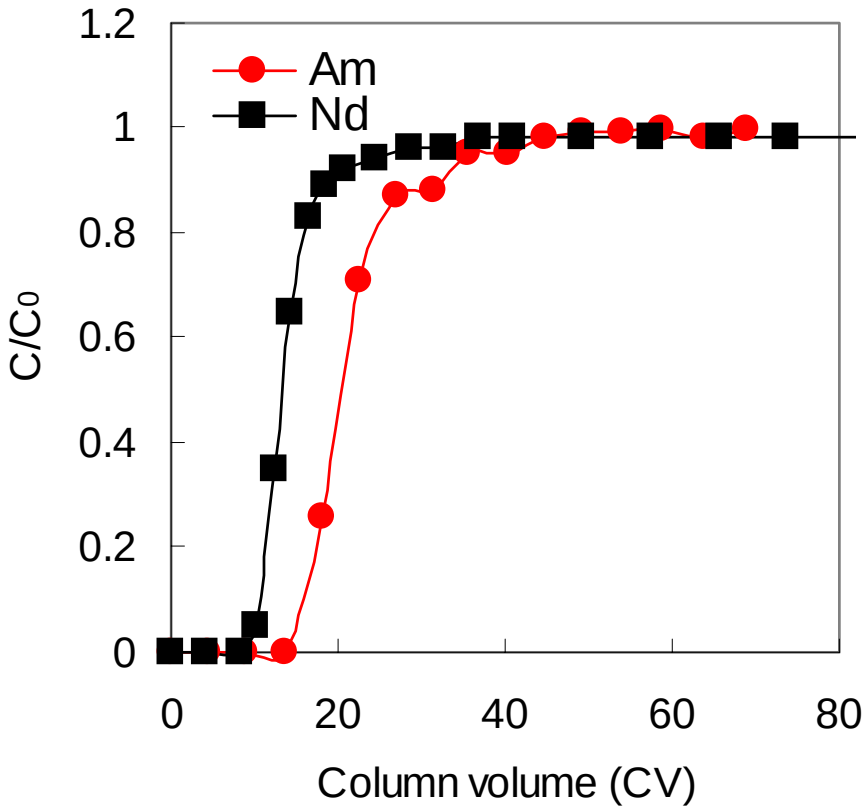
- Accumulated U and Zr on CMPO-exchanger inhibit the adsorption of Nd.
- Removal of U and Zr before separation between Cs/Sr and Am/lanthanoids is important.
- Even if the cycle times increases, the adsorbed amount of Nd on the 2nd column is attained a steady value.



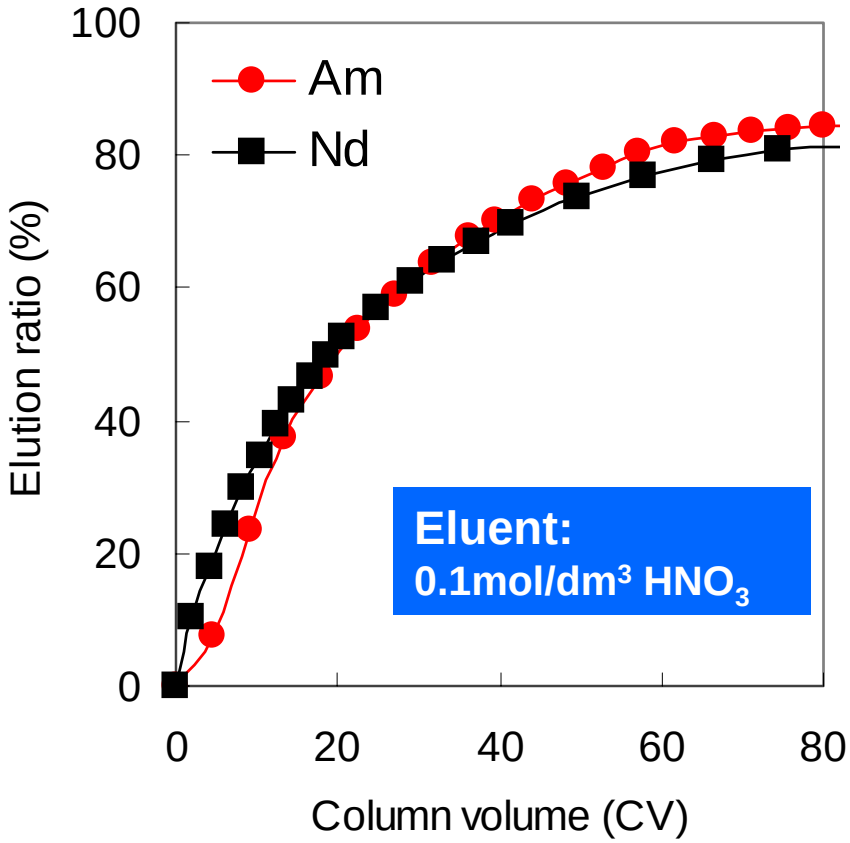
Adsorption and elution behavior of Nd and ^{241}Am on CMPO-exchanger

Institute of Research and Innovation

Break through curve



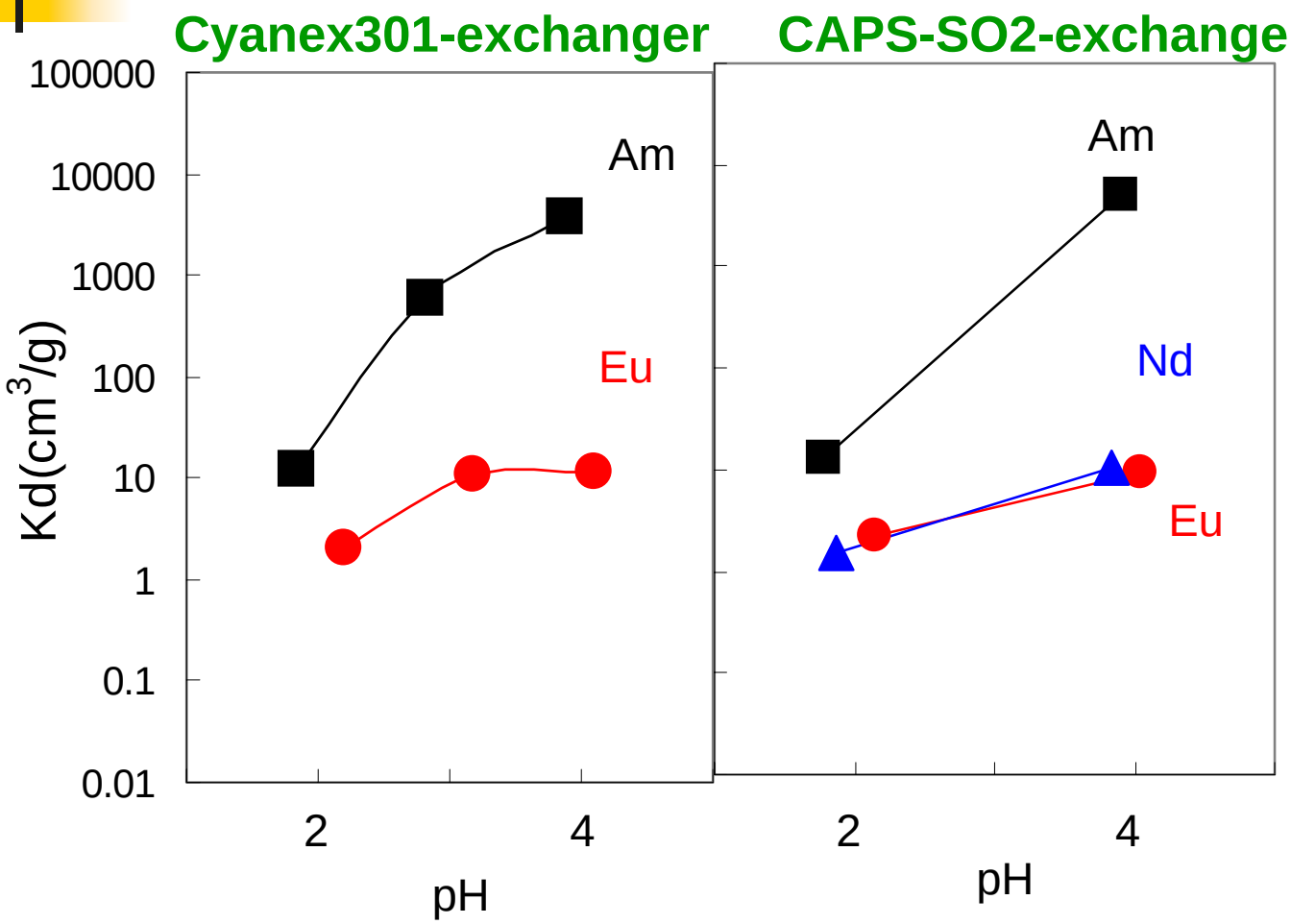
Elution curve



1. Adsorption/elution behavior of Am is same as that of Nd.
2. Separation of Am from lanthanoids is difficult.

Adsorption abilities of Cyanex301- and CAPS-SO2-exchanger

Institute of Research and Innovation



Distribution coefficients (Kd)

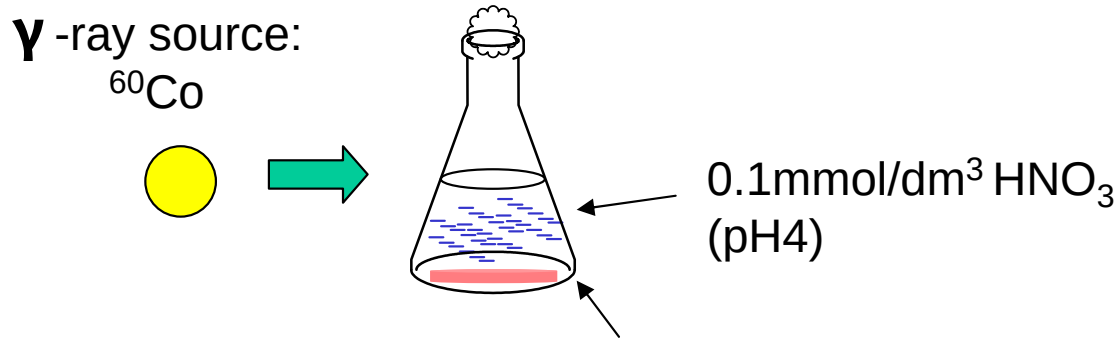
$$Kd = \frac{C_i - C_e}{C_e} \cdot \frac{V_s}{W_e} \quad (cm^3/g)$$

1. The adsorption ability for Am of CAPS-SO2-exchanger indicates the same as that of Cyanex301-exchanger.
2. The adsorption capability of those exchangers remarkably decrease at pH 2, then Am is possible to be recovered by acidic eluent such as nitric acid.

Gamma ray irradiation

Institute of Research and Innovation

CMPO-exchanger could be reused for several hundred cycles up to a dose of 2MGy.
We investigated chemical stability of CAPS-SO2- and Cyanex301-exchanger for gamma-ray irradiation.



Filtration → filtrate → The dissolved amount of sulfur was measured by ICP-AES

Exchanger

Washing with deionized water

Vacuum drying at R.T. for 24h

Adsorption experiments

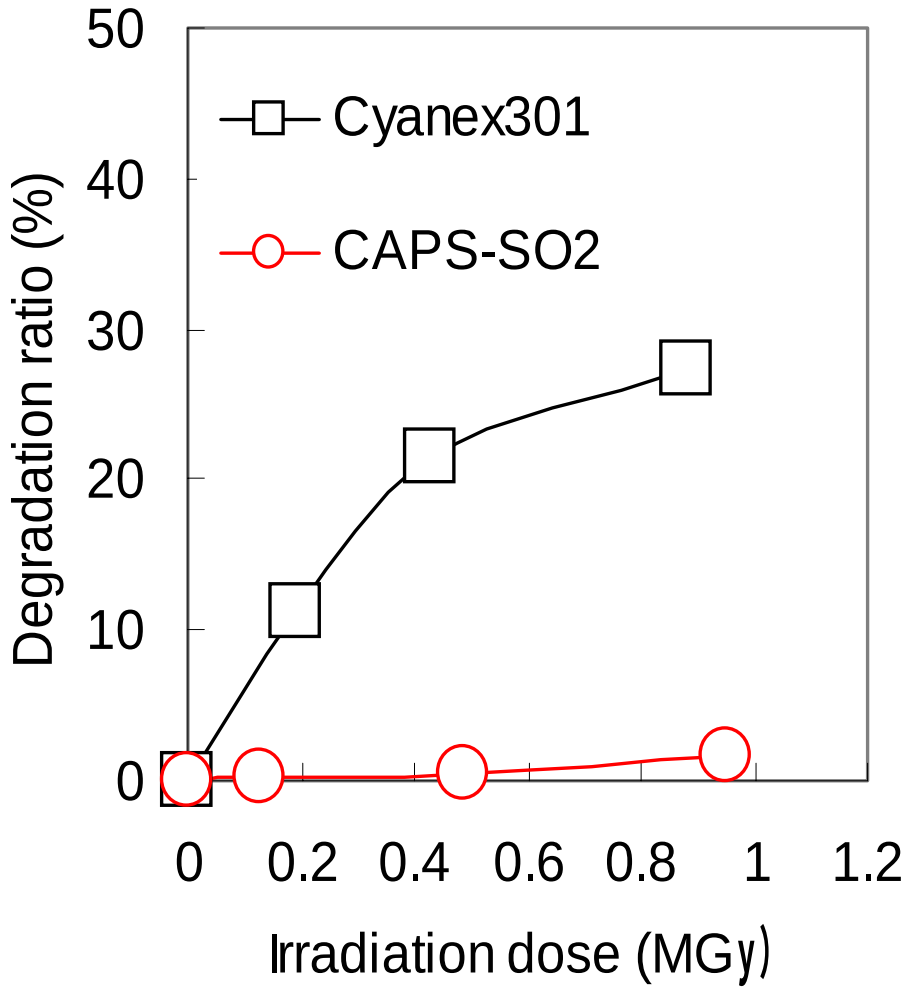
The degradation ratio (Dr) of the exchanger was calculated from sulfur concentration in the solution.

$$Dr = \frac{S_d}{S_e} \times 100(\%)$$

S_d: Amount of dissolved sulfur after irradiation.
S_e: Initial amount of sulfur in the adsorbent.

Chemical stability for radiolytic degradation

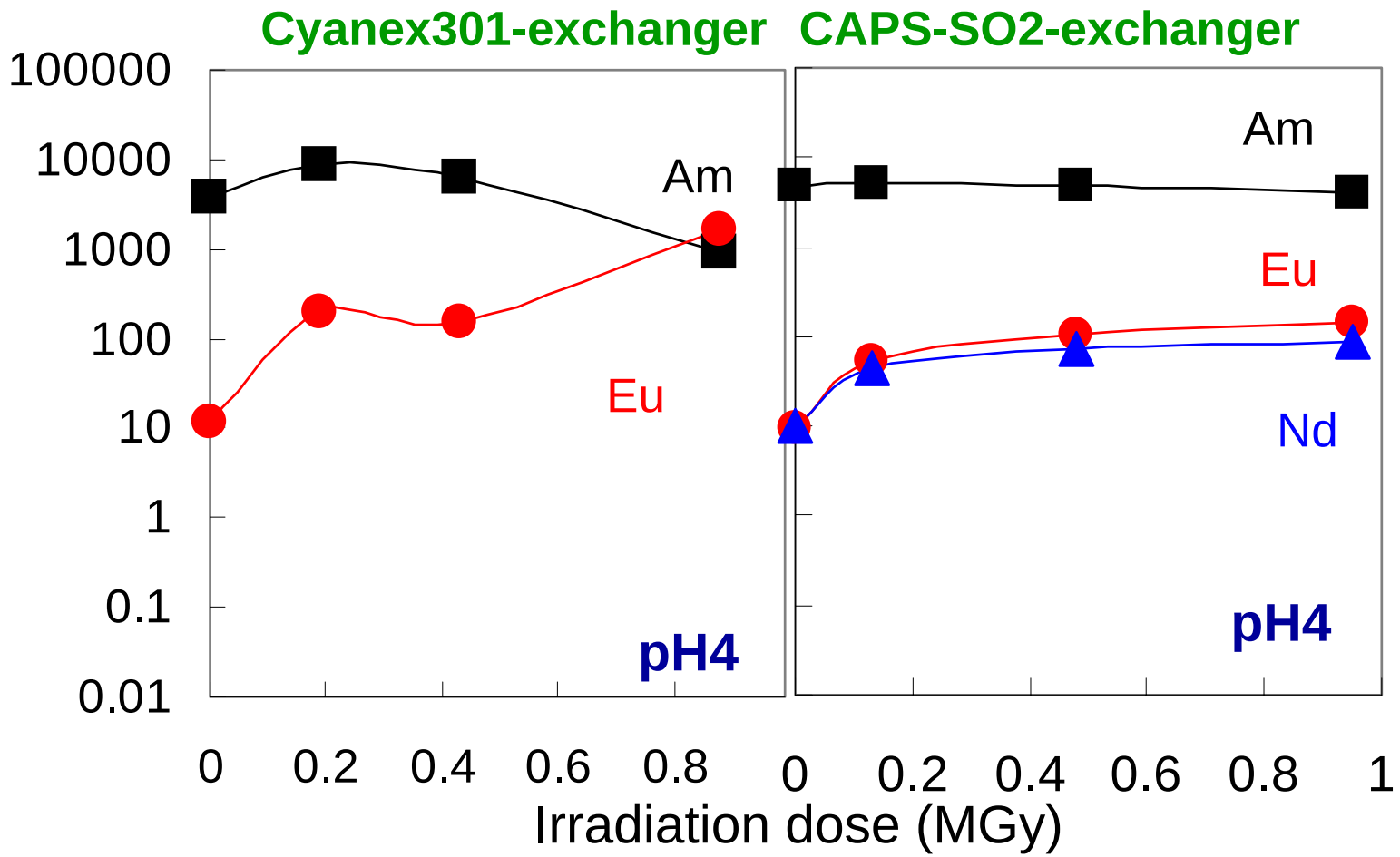
Institute of Research and Innovation



CAPS-SO2-exchanger is more stable than Cyanex301-exchanger

Change in adsorption ability after gamma-ray irradiation

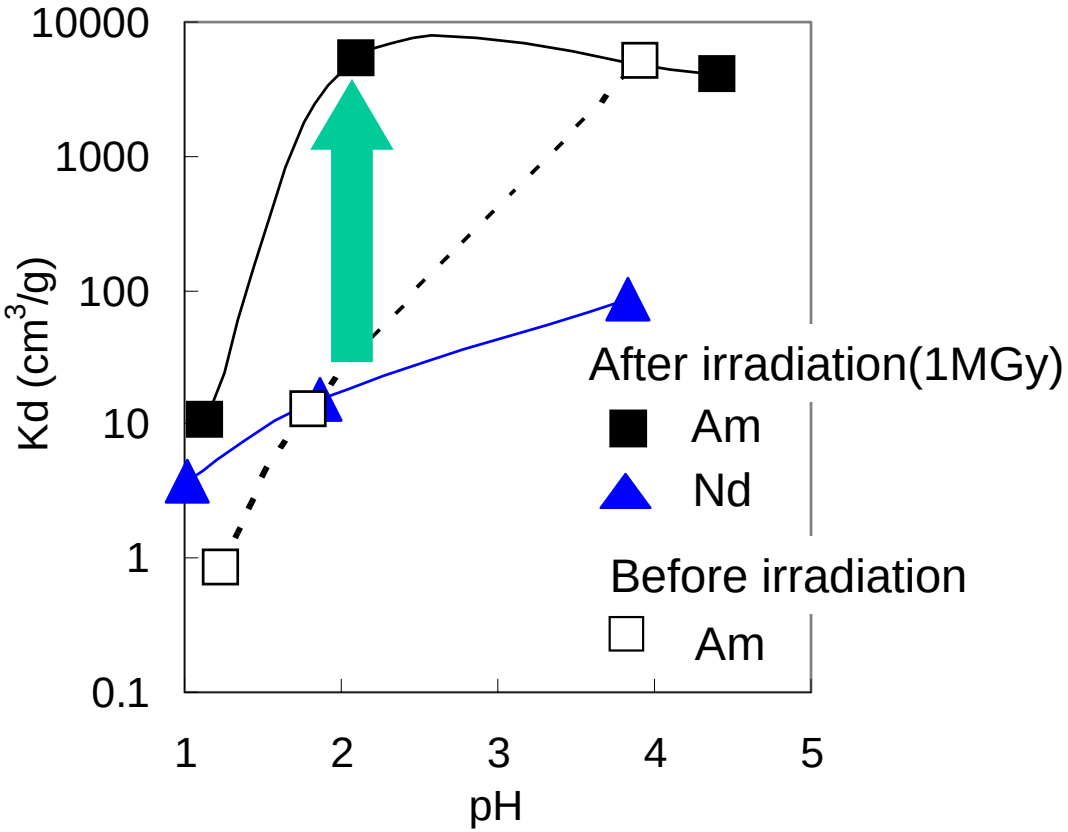
Institute of Research and Innovation

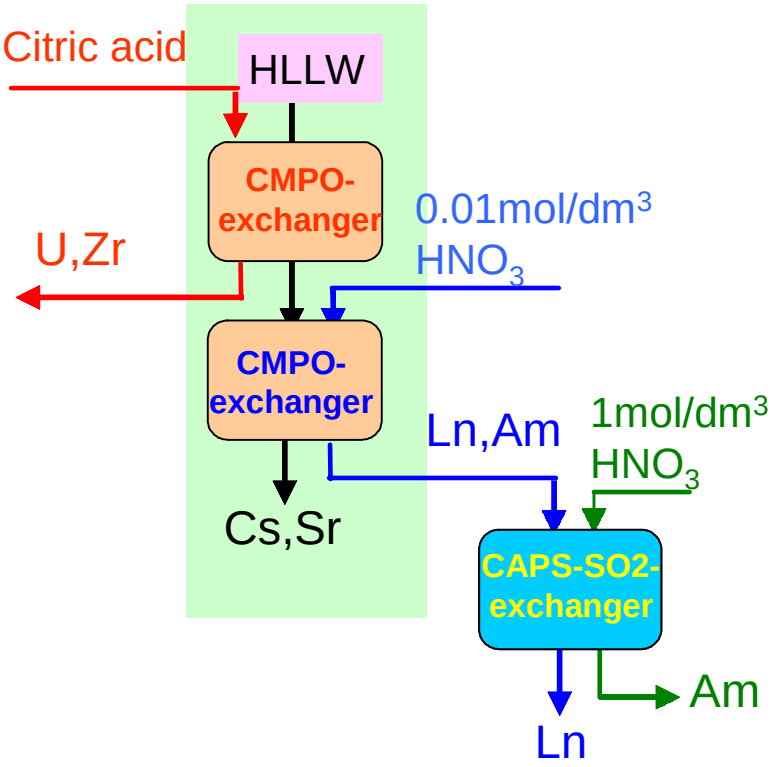


1. The value of Kd_{Eu} on Cyanex301-exchanger increases with increasing irradiation dose. The value of Kd_{Am} slightly decreases.
2. The value of Kd_{Am} is constant on CAPS-SO2-exchanger .

Adsorption behavior of CAPS-SO2-exchanger after irradiation (1MGy)

Institute of Research and Innovation





1. The value of Kd_{Am} at pH 2 increases to almost 5000 cm^3/g by irradiation
2. Am and lanthanoids are recovered from CMPO-exchanger by using 0.01mol/dm^3 HNO_3, then pH value of the eluent is nearly 2. Irradiated CAPS-SO2-exchanger can separate Am from lanthanoids without any pH control by neutralization or dilution.

Conclusion

Institute of Research and Innovation

1. Basic process concept of ion-exchange treatment which we call CMPO-CAPS process is proposed.

2. Removing of U and Zr in HLLW is important to carry out the effective adsorption and elution for Am and lanthanoids on CMPO-exchanger. And, separation of Cs/Sr can be achieved.

3. Recovered lanthanoids and actinoids from CMPO-exchanger are treated by CAPS-SO2-exchanger.

4. CAPS-SO2-exchanger has the excellent separation performance for actinoids, and it has the excellent chemical durability for gamma-ray irradiation.