

## Use of Layered Double Hydroxide (LDH) Sorbents to Remove Radioactive Iodine Species – 17178

Jaehyuk Kang \* and Wooyong Um \*, \*\*

\* Pohang University of Science and Technology (POSTECH), South Korea

\*\* Pacific Northwest National Laboratory, USA

### ABSTRACT

To more efficiently manage the radioactive iodine waste, layered double hydroxides (LDHs) were synthesized and characterized using XRD, FT-IR, SEM-EDS, and ICP-AES. Batch adsorption experiments to remove  $I^-$  and  $IO_3^-$  under DIW condition were conducted to check overall removal efficiencies with and without calcination using ICP-MS. Synthesized MgFe\_Cl\_C\_21 LDHs consisting of  $Mg^{2+}$  and  $Fe^{3+}$  in a 2:1 concentration ratio of the divalent ion to the trivalent ion after calcination showed the highest  $I^-$  removal efficiency, 89.2 % and synthesized CoCr\_Cl\_NC\_41 LDHs consisting of  $Co^{2+}$  and  $Cr^{3+}$  in a 4:1 concentration ratio of the divalent ion to the trivalent ion without calcination showed the highest  $IO_3^-$  removal efficiency, 97.0 %.

### INTRODUCTION

Electric power production by nuclear power plants (NPPs) for continuous energy can be beneficial without producing greenhouse gas ( $CO_2$ ). However, all radioactive wastes generated from NPPs operation should be managed securely and safely - especially the waste that includes radioactive iodine species such as I-125, I-129, and I-131 whose half-lives are  $t_{1/2} = 59.40$  d,  $t_{1/2} = 1.57 \times 10^7$  y, and  $t_{1/2} = 8.02$  d, respectively [1]. External exposure to these radioactive iodine species causes harmful effects on humans such as skin burns, and internal exposure can also affect the thyroid gland [2, 3]. In addition, due to high volatility iodide ( $I^-$ ) and iodate ( $IO_3^-$ ) can be released into the environment during severe NPPs accidents [4]. Because of the high mobility and toxicity of radioactive iodine species, methods for removing them should be developed to ensure secure operation of NPPs and protect the environment [5]. So far, various methods for removing radioactive iodine species in either the gas or solution phase have been conducted using adsorbents. Especially, Ag-zeolite [6] shows high performance for removal of iodine because it has high specific surface area (SSA), high affinity between iodine species and silver, and high thermal stability. However, there are problems such as high cost and toxicity of silver [7] for using Ag-zeolite.

In this study, LDHs were synthesized and used to remove iodine species from solution. LDHs, as a group of anionic clays, consist of a positive charge outer-layer of metal-O/OH and a negative charge inner-layer of anions that contain water molecules [8]. In this structure, outer-layers on the top and bottom hold a positive charge because of isomorphic substitution of  $M^{3+}$  (trivalent metal ion) for  $M^{2+}$  (divalent metal ion) due to their similar ionic sizes. This isomorphic substitution causes a negative charge

deficiency and leads to a permanently positive structural charge in the LDHs structure. Because of these properties, anions of inner-layer can be easily exchanged with anionic contaminants. In addition, LDHs have a memory effect which means that after calcination at high temperature, they can be reformed by easily taking some anionic contaminants from solution to recover their original structure [9].

The main purpose of this study was to evaluate synthesized LDHs for removal of  $I^-$  and  $IO_3^-$  under deionized water (DIW) condition; (1) various LDHs were synthesized and characterized, (2) effect of ratio of the  $M^{2+}$  concentration to  $M^{3+}$  concentration and calcination conditions which affect iodine adsorption were quantified, and (3)  $I^-$  and  $IO_3^-$  removal mechanisms were investigated and the overall efficiency was evaluated.

## **MATERIALS AND METHODS**

### **Materials**

The LDHs were synthesized by using two  $M^{2+}$  ( $Mg^{2+}$  and  $Co^{2+}$ ) and two  $M^{3+}$  ( $Fe^{3+}$  and  $Cr^{3+}$ ). 99 %  $MgCl_2 \cdot 6H_2O$  (Sigma-Aldrich Co. LLC), 97 %  $CoCl_2$  (Alfa Aesar), 98 %  $FeCl_3$  (Alfa Aesar) and 98 %  $CrCl_3 \cdot 6H_2O$  (Sigma-Aldrich Co. LLC) were used without pre-treatment. For iodine removal experiments, 0.1 M  $I^-$  standard solution (Thermo scientific) and 99.7 %  $NaIO_3$  (Samchun pure chemical Co., Ltd.) were used. Ag-zeolite (Ag, 35 % from Sigma-Aldrich Co. LLC) was also used to compare with performance of synthesized LDHs.

### **Synthesis of Layered Double Hydroxides**

LDHs were synthesized by the co-precipitation method. For  $M^{2+} : M^{3+}$  concentration ratio of 2:1, a mixed metal solution was obtained by dissolving 0.66 mol/L  $M^{2+}$  chloride ( $MgCl_2 \cdot 6H_2O$ ) and 0.33 mol/L  $M^{3+}$  chloride ( $FeCl_3$ ) in DIW. The mixed metal solution temperature was kept at room temperature. The pH was adjusted to 12 by adding 2.0 M NaOH solution. Subsequently, it was stored overnight at  $65 \pm 3$  °C. The solid product was obtained by centrifugation, then washed several times with DIW until the pH 8–9 of slurry. The final solid was dried at 110 °C for 12 h. For checking the calcination effect, dried final solid was heated at 500 °C for 2 h before use [10].

For  $M^{2+} : M^{3+}$  concentration ratio of 4:1, a mixed metal solution was obtained by dissolving 0.80 mol/L  $M^{2+}$  chloride ( $CoCl_2$ ) and 0.20 mol/L  $M^{3+}$  chloride ( $CrCl_3 \cdot 6H_2O$ ) in DIW. The subsequent processes were the same as above.

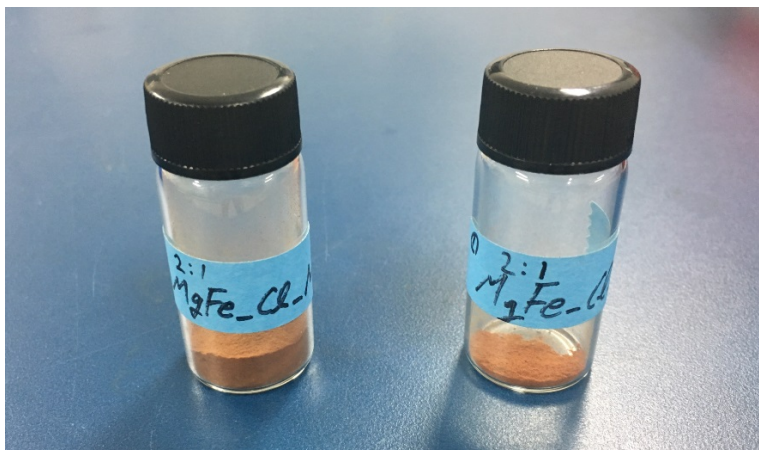


Fig. 1. Synthesized LDHs; left = before calcination, right = after calcination ( $M^{2+} = Mg^{2+}$ ;  $M^{3+} = Fe^{3+}$ ; anion =  $Cl^-$ ;  $M^{2+} : M^{3+}$  concentration ratio of 2:1)

### Characterizations of synthesized LDHs

After synthesis of LDHs, characterizations were carried out using X-ray diffractometer (XRD) patterns to check the mineral identification; Fourier transformed-infrared (FT-IR) spectrometer to determine the functional groups present; Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to observe morphology of surface and chemical elements; Inductively coupled plasma-atomic emission spectrometer (ICP-AES) to check the concentrations of  $M^{2+}$  and  $M^{3+}$  in LDHs after digestion.

### Iodine removal experiments

The batch experiments were conducted with I-127 solutions as surrogate for radioactive iodine. Individual 10 mL  $I^-$  and  $IO_3^-$  solutions as 4 ppm in DIW were prepared in vials and reacted with 0.01 g adsorbents. The samples unreacted with adsorbents were prepared as control samples to compare the data. The pH of final solution was 4.3–5.8. The vials mixed at 130 rpm in the dual action/platform shaker. Subsequently, the supernatants were separated using syringe filters and the iodine concentration was analyzed using inductively coupled plasma-mass spectrometer (ICP-MS).

## RESULTS AND DISCUSSIONS

### Characterizations of synthesized LDHs

The XRD patterns of synthesized LDHs are shown in Fig. 2. The peak at  $10-15^\circ$  (2-theta) as d-spacing points in most LDHs was observed. This peak intensity indicates the distance of the inner-layer [11]. With increase of that point, the distance of the inner-layer also shows to increase. After calcination process, the peak intensity as shown for the inner-layer distance decreased; it assumed that water and anions in inner-layer were evaporated or volatilized because of high temperature.

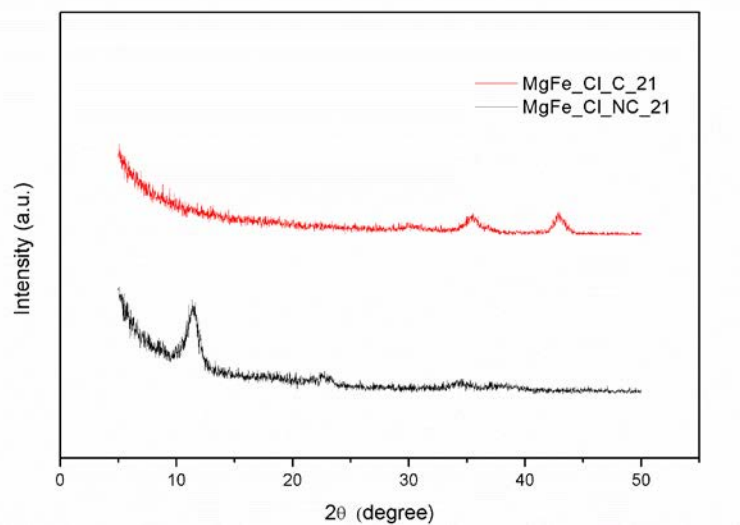


Fig. 2. X-ray diffraction patterns of synthesized LDHs ( $M^{2+} = Mg^{2+}$ ;  $M^{3+} = Fe^{3+}$ ; anion =  $Cl^-$ ;  $M^{2+} : M^{3+}$  concentration ratio of 2:1)

The FT-IR spectra of synthesized LDHs are shown in Fig. 3. Most LDHs indicate that the peaks at  $3,000\text{--}3,700\text{ cm}^{-1}$  result from  $OH^-$  groups in water molecules; the peaks at  $750\text{--}1,500\text{ cm}^{-1}$  and  $500\text{--}700\text{ cm}^{-1}$  indicate vibration of anion and metal oxide/hydroxide groups [12]. After calcination process, the FT-IR spectra of synthesized LDHs was changed; the peaks at  $3,000\text{--}3,700\text{ cm}^{-1}$  and  $750\text{--}1,500\text{ cm}^{-1}$  were disappeared. It assumed that high temperature affected the structure of synthesized LDHs;  $OH^-$  groups in water molecules and anion were evaporated and volatilized.

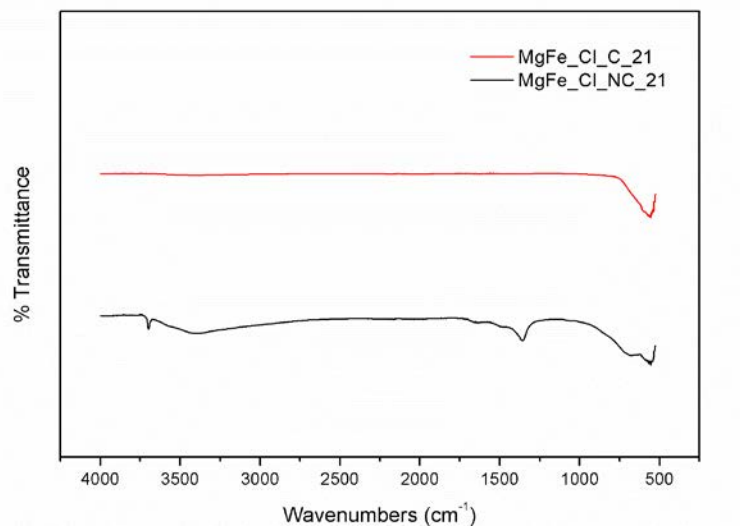


Fig. 3. FT-IR spectra of synthesized LDHs ( $M^{2+} = Mg^{2+}$ ;  $M^{3+} = Fe^{3+}$ ; anion =  $Cl^-$ ;  $M^{2+} : M^{3+}$  concentration ratio of 2:1)

### Iodine removal experiments

To check the iodine removal efficiencies, batch experiments were carried out using synthesized LDHs. The removal efficiencies (%) of  $I^-$  and  $IO_3^-$  are shown in TABLE I. After calcination process, the structure of synthesized LDHs become compact because  $OH^-$  groups and water molecules of inner-layer were evaporated and volatilized; it means decrease of inner-layer distance. Also, through memory effect, LDHs could attract more anions to reform original structure when it was immersed in solution including anions. Therefore, ionic size could be considered as important factor for anions to enter the inner-layer of compacted LDHs. Ionic size of  $I^-$  (206 pm) is smaller than that of  $IO_3^-$  (~270 pm). Commonly, synthesized LDHs with calcination showed higher  $I^-$  removal efficiency under the same background conditions. However, synthesized LDHs without calcination showed higher  $IO_3^-$  removal efficiency (TABLE I). So, it was suggested that inner-layer distance of synthesized LDHs with calcination be smaller than ionic size of  $IO_3^-$ .

Synthesized MgFe\_Cl\_C\_21 LDHs showed highest performance as 89.2 % for  $I^-$  removal and synthesized CoCr\_Cl\_NC\_41 LDHs showed highest performance as 97.0 % for  $IO_3^-$  removal.

TABLE I. The removal efficiencies of  $I^-$  and  $IO_3^-$  using synthesized LDHs

Iodine species	Adsorbent <sup>a</sup>	Reaction time (day)	Removal efficiency (%)
$I^-$	MgFe_Cl_C_21	3	89.2
	MgFe_Cl_NC_21		6.20
	CoCr_Cl_C_41		55.6
	CoCr_Cl_NC_41		31.6
$IO_3^-$	MgFe_Cl_C_21	1	21.2
	MgFe_Cl_NC_21		22.1
	CoCr_Cl_C_41		15.0
	CoCr_Cl_NC_41		97.0

<sup>a</sup>  $M^{2+}$  =  $Mg^{2+}$  or  $Co^{2+}$ ;  $M^{3+}$  =  $Fe^{3+}$  or  $Cr^{3+}$ ; anion = Cl<sup>-</sup>; C = with calcination; NC = without calcination;  $M^{2+}$  :  $M^{3+}$  concentration ratio of x : 1 (= x1 : 21, 41)

To compare the iodine removal efficiencies between Ag-zeolite and synthesized LDHs, batch experiments were also conducted. The results are shown in TABLE II. For  $I^-$  removal, both Ag-zeolite and synthesized MgFe\_Cl\_C\_21 LDHs showed quite high performance as 98.9 % and 91.1 %, respectively. However, for  $IO_3^-$  removal, Ag-zeolite showed low performance as 5.70 %, whereas synthesized CoCr\_Cl\_NC\_41 LDHs showed high performance as 96.8 %. It was assumed that  $Ag^+$  was easily reacted with  $I^-$  to form AgI in structure of Ag-zeolite although surface charge of Ag-

zeolite was negative, however, reaction between  $\text{Ag}^+$  and  $\text{IO}_3^-$  to form  $\text{AgIO}_3$  was difficult under the same conditions.

TABLE II. The comparison data of iodine removal efficiencies between Ag-zeolite and synthesized LDHs that achieved highest performance

Iodine species	Adsorbent <sup>a</sup>	Reaction time (day)	Removal efficiency (%)
$\text{I}^-$	Ag-zeolite	7	98.9
	MgFe_Cl_C_21		91.1
$\text{IO}_3^-$	Ag-zeolite		5.70
	CoCr_Cl_NC_41		96.8

<sup>a</sup>  $\text{M}^{2+}$  =  $\text{Mg}^{2+}$  or  $\text{Co}^{2+}$ ;  $\text{M}^{3+}$  =  $\text{Fe}^{3+}$  or  $\text{Cr}^{3+}$ ; anion =  $\text{Cl}^-$ ; C = with calcination; NC = without calcination;  $\text{M}^{2+}$  :  $\text{M}^{3+}$  concentration ratio of x : 1 (= x1 : 21, 41)

## CONCLUSIONS

The synthesis of various LDHs and iodine removal experiments were conducted under DIW condition. The highest performance for iodine removal was found in MgFe\_Cl\_C\_21 LDHs (89.2 % as  $\text{I}^-$  removal efficiency) and CoCr\_Cl\_NC\_41 LDHs (97.0 % as  $\text{IO}_3^-$  removal efficiency). This is expected to show positive iodine removal treatment method, because it is simple and cheap method compared with Ag-zeolite, especially for  $\text{IO}_3^-$  removal. This results could be used to improve understanding of radioactive iodine waste management from waste streams of NPPs.

## REFERENCES

1. Y. Watanabe, T. Ikoma, H. Yamada, Y. Suetsugu, Y. Komatsu, G. W. Stevens, et al., "Novel long-term immobilization method for radioactive iodine-129 using a zeolite/apatite composite sintered body," ACS applied materials & interfaces, vol. 1, pp. 1579-1584, 2009.
2. J. Robbins and A. B. Schneider, "Thyroid cancer following exposure to radioactive iodine," Reviews in Endocrine and Metabolic Disorders, vol. 1, pp. 197-203, 2000.
3. A. Ilin and A. Nersesyan, "Toxicology of iodine: A mini review," Archive of Oncology, vol. 21, pp. 65-71, 2013.
4. C.-C. Lin and J.-H. Chao, "Reassessment of Reactor Coolant and Iodine Chemistry under Accident Conditions," Journal of nuclear science and technology, vol. 46, pp. 1023-1031, 2009.
5. Q. Cheng, W. Yang, Z. Li, Q. Zhu, T. Chu, D. He, et al., "Adsorption of gaseous radioactive iodine by Ag/13X zeolite at high temperatures," Journal of Radioanalytical and Nuclear Chemistry, vol. 303, pp. 1883-1889, 2015.
6. B. S. Choi, G. I. Park, J. W. Lee, H. Y. Yang, and S. K. Ryu, "Performance test of silver ion-exchanged zeolite for the removal of gaseous radioactive methyl iodide at high temperature condition," Journal of Radioanalytical and Nuclear Chemistry,

- vol. 256, pp. 19-26, 2003.
7. U.S. EPA, "40 CFR 261 - Identification and Listing of Hazardous Waste", Environmental Protection Agency, Washington, D.C., 2012
  8. V. Rives and M. a. A. Ulibarri, "Layered double hydroxides (LDH) intercalated with metal coordination compounds and oxometalates," *Coordination Chemistry Reviews*, vol. 181, pp. 61-120, 1999.
  9. F. L. Theiss, M. J. Sear-Hall, S. J. Palmer, and R. L. Frost, "Zinc aluminium layered double hydroxides for the removal of iodine and iodide from aqueous solutions," *Desalination and Water Treatment*, vol. 39, pp. 166-175, 2012.
  10. T.-H. Kim, I. Heo, S.-M. Paek, C.-B. Park, A.-J. Choi, S.-H. Lee, et al., "Layered metal hydroxides containing calcium and their structural analysis," *Bulletin of the Korean Chemical Society*, vol. 33, pp. 1845-1850, 2012.
  11. S. J. Palmer, A. Soisonard, and R. L. Frost, "Determination of the mechanism (s) for the inclusion of arsenate, vanadate, or molybdate anions into hydrotalcites with variable cationic ratio," *Journal of colloid and interface science*, vol. 329, pp. 404-409, 2009.
  12. N. Oladoja, R. Adelagun, I. Ololade, E. Anthony, and M. Alfred, "Synthesis of nano-sized hydrocalumite from a Gastropod shell for aqua system phosphate removal," *Separation and Purification Technology*, vol. 124, pp. 186-194, 2014.

## **ACKNOWLEDGEMENTS**

This work was supported by the National Research Foundation of Korea (NRF) grants funded by the Korean government (MSIP : Ministry of Science, ICT and Future Planning), (No. NRF-2016R1D1A1B02013310 and NRF-2015M2A7A1000191)