

Received November 7, 2017; reviewed; accepted March 23, 2018

Mass transfer process of leaching weathered crust elution-deposited rare earth ore with magnesium salts

Zhuo Chen ¹, Zhengyue Zhang ¹, Zhengyan He ¹, Ru-an Chi ¹

¹ Key Laboratory for Green Chemical Process of Ministry of Education, Hubei Novel Reactor and Green Chemical Technology Key Laboratory, Wuhan Institute of Technology, Wuhan, 430073, China

Corresponding author: rac@wit.edu.cn (Ru-an Chi)

Abstract: In order to optimize the leaching process of weathered crust elution-deposited rare earth ore with magnesium salts, the influence of different flow rate, concentration of magnesium ions, initial pH of magnesium salts solution and experimental temperature on the mass transfer process of rare earth and aluminum was investigated in the case of using magnesium salts as leaching agent. The relationship between the flow rate μ and the HETP (Height Equivalent of Theoretical Plate) is in accordance with the Van Deemter equation when magnesium salts were used as leaching agent. The optimum condition for rare earth and aluminum were 0.4 cm³/min of flow rate and 0.2 mol/dm³ of magnesium ion concentration of magnesium sulfate, magnesium chloride and magnesium nitrate respectively. Under this condition, the mass transfer efficiency of rare earth and aluminum with three kinds of magnesium salts follow the order of Mg(NO₃)₂>Mg(Cl)₂>MgSO₄. High temperature contributes to improving the mass transfer efficiency of rare earth and aluminum. Magnesium nitrate as the leaching agent can get the highest leaching mass transfer efficiency of rare earth, and magnesium sulfate as the leaching agent can make the impurity leaching and mass transfer efficiency of Al is the lowest.

Keywords: magnesium salts, mass transfer, theory plate, weathered crust elution-deposited rare earth ore

1. Introduction

Weathered crust elution-deposited rare earth ore enrich in heavy rare earth which was explored and used in the industry earliest in China (Yang et al., 2013; Lahiri and Jha, 2009). It is widely distributed in China's southern province, such as Jiangxi, Guangdong, Fujian, Guangxi, Yunnan, Hunan and Hainan provinces (Chi and Tian, 2012). Recently, the weathered crust elution-deposited rare earth ores had been found in Brazil, Chile, Madagascar, Myanmar and so on. The rare earth elements (REEs) are mainly adsorbed on the clay minerals as hydration or hydroxyl hydrate ions (Nesbitt, 1979) in the weathered crust elution-deposited rare earth ore. Chemical leaching technology is the unique way to extract rare earth from weathered crust elution-deposited rare earth ore (Kul et al., 2008). The major leaching agent in in-situ leaching is still ammonium salt and there are some problems existed in this process, such as pollution by amino-nitrogen. The large consumption of ammonium sulfate is easily to cause the enrichment of ammonia nitrogen in the underground water where easily lead to water eutrophication. It will affect the growth of vegetation in the mining area as well (Yong-Xiu et al., 2010).

Previous works were forced to use some other lixiviant to replace the ammonium salts for reducing the pollution by amino-nitrogen (Li et al., 2013). Xiao et al. concluded that magnesium sulfate could be appropriately proposed to be the leaching agent instead of ammonium salts (Yanfei et al., 2015; Yanfei et al., 2016; Xiao et al., 2015). The (Cs)₂SO₄/CsCl were used as lixiviant to exchange rare earth from weathered crust elution-deposited rare earth ores by Georgiana and the results had been shown that sulfates and chlorides showed the good extraction behaviour in the leaching process (Moldoveanu and Papangelakis, 2012). Li et al. used ammonium citrate to replace the ammonium sulfate and achieved

high leaching efficiency of rare earth (Qiong, 2015). According to the above research, some lixiviant had been used in industry under some special condition, such as: magnesium salts (Xiao et al., 2015). The study on the strengthen of mass transfer can not only increase the leaching efficiency of RE (Jun et al., 2010), but also reduce the consumption of leaching agents. He et al. has proved that the leaching efficiency of rare earth is largely determined by the efficiency of mass transfer which can enhance the recovery rate of rare earth (He et al., 2016).

In this paper, the leaching process is a typical mass transfer process (Levenspiel, 1962), which can be evaluated by chromatographic plate theory (Jun, Jingqun, Kaihong, et al., 2010). It is beneficial to investigate the leaching mass transfer (Bartlett, 1992) in order to know the mechanism of the rare earth leaching and to provide a scientific approach and a theoretical basis for leaching rare earths with magnesium salts. The chemical reaction equation is as follows (1)



Magnesium salt is used to replace the ammonium salt to reduce the ammonia leachate pollution in the traditional leaching process. Adding the proper amount of magnesium salt can also supply the magnesium in the tailings. Magnesium sulfate, magnesium chloride and magnesium nitrate were used as leaching agent and the effects of leaching flow rate, magnesium ions concentration, leaching agent initial pH and experimental temperature were discussed in the paper. The leaching process is optimized to improve the leaching efficiency of rare earth ore as well. It could be reducing the consumption of the lixiviant and improving the efficiency of rare earth extraction.

2. Materials and methods

2.1 Materials

The rare earth ore samples were collected from JiangXi province, China. Chemical composition of the rare earth ores was analysed by X-ray fluorescence and the results was shown in Table1. The partition of the rare earth was showed in the Fig. 1. All chemicals in this study were purchased from Sinopharm Chemical Reagent Co.,Ltd (Shanghai, China)with analytical grade and deionized water was used.

Table 1. Main chemical composition of the RE ores (wt.%)

component	REO	Al ₂ O ₃	MnO ₂	ZnO	CaO	MgO	K ₂ O	SiO ₂
content	0.14	15.23	0.01	0.01	0.02	0.62	3.54	66.48
component	SO ₃	TiO ₂	Fe ₂ O ₃	Rb ₂ O	SrO	ZrO ₂	BaO	Loss
content	0.04	1.40	4.07	0.01	0.01	0.02	0.04	8.36

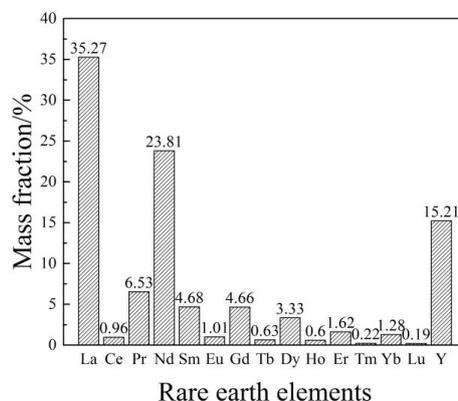


Fig 1. Rare earth elements of the ore sample

Rare earth exists as ion-exchangeable phase in the weathered crust elution-deposited rare earth ore. In this kind of mineral, aluminum, calcium, magnesium, manganese and zinc mainly in the rare-earth

ore with ion phase. Since Al is main impurity in rare earth ore, it is beneficial to prevent or reduce aluminum into leaching solution for improve the quality of leaching solution. In doing so, it is able to improve weathered crust rare earth products quality ultimately.

2.2 Column leaching experiments and analytical methods

In the column leaching experiments, the rare earth ores from JiangXi were dired at 353K for 8 hours, and then 250 g of the rare earth ores were packed into the column. Leaching agents was added from the top of the leaching column at a constant flow rate by a peristaltic pump. The leachate was collected with conical flask at the bottom of leaching column. The total content of RE in the leachate was determined using EDTA titration and the Al was determined by ICP-OES.

3 Results and discussion

3.1 Effects of the leach flow rate on mass transfer with magnesium salts

The flow rate of magnesium salts is a significant factor which influences the mass transfer efficiency of rare earth (Tian et al., 2013). In the leaching process, constant flow pumps were used to control the flow rate of magnesium salts. Fig. 3 shows the leaching behaviour of RE and Al.

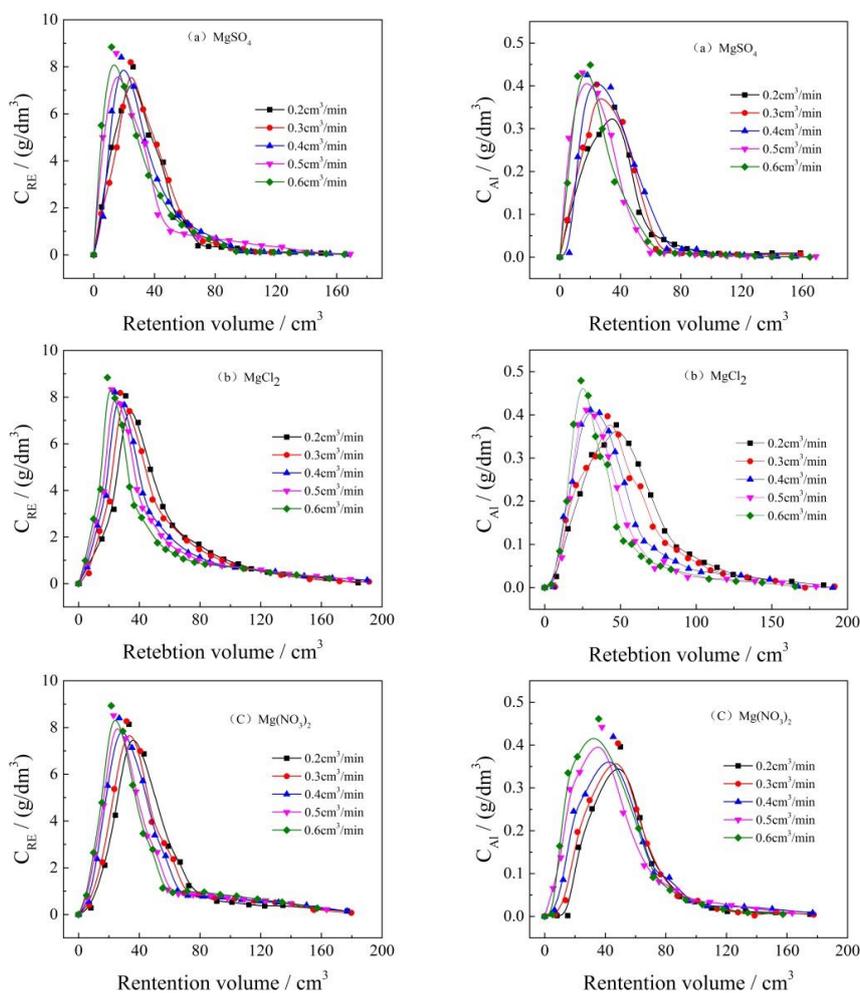


Fig. 2. Leaching behaviour of RE^{3+} and Al^{3+} (250 g of rare earth ore, $C_{Mg^{2+}} = 0.2 \text{ mol/dm}^3$, $T = 298\text{K}$); (a) $MgSO_4$, (b) $MgCl_2$, (c) $Mg(NO_3)_2$

As it showed in the Fig. 2, the concentration of RE and Al increased rapidly to a maximum value and then decreased slowly with the increased of the leaching solution volume when three kinds of magnesium salt were used as leaching agents. When the leaching flow rate of magnesium salt increased gradually, the maximum peak concentration of RE and Al increased, and the corresponding retention

volume decreased, and the leaching mass transfer efficiency increased. This is due to the enhancement in the flow rate of magnesium salt to speed up the flow of the solution in the ore body which can quickly bring rare earth out the ore body, to alleviate the rare earth anti-adsorption phenomenon (Sameni and Morshedi, 2000).

To better explain the result, the leaching curve of RE and Al under different flow rate with several kinds of magnesium salts were analyzed by the chromatographic plate theory (Lee et al., 1993):

$$\text{HETP} = \frac{L}{n} \quad (2)$$

$$n = 8 \ln 2 \times \left(\frac{V_R}{\Delta V_{1/2}^2} \right)^2 \quad (3)$$

where HETP (mm) is the height equivalent to a theoretical plate; L (mm) is the packed ore length; n is the true plate number; V_R (cm^3) is the retention volume, which represents the volume of the leachate collected from the bottom of the leaching column; $V_{1/2}$ (cm^3) is the peak width at half height. When the height of the assembly L is constant, the theoretical plate height HETP can be used to evaluate the leaching mass transfer efficiency of RE (Kim et al., 2009). The smaller the HETP, the larger the number of theoretical plates n and the higher the leaching mass transfer efficiency.

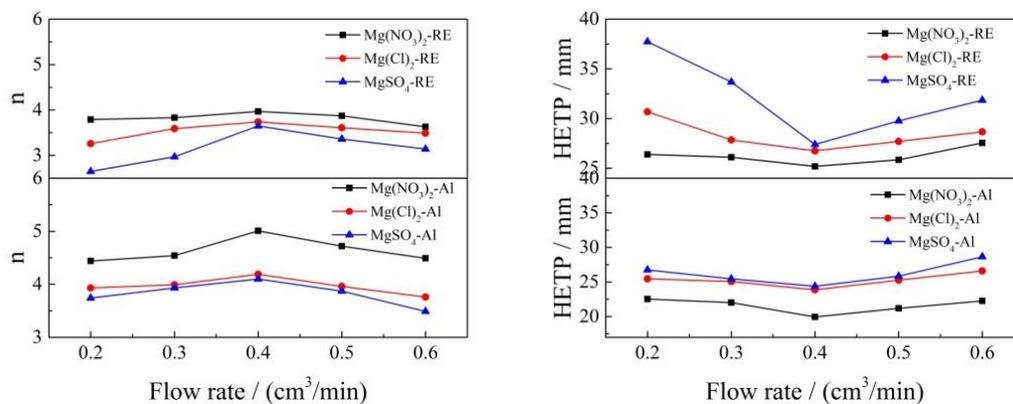


Fig. 3 Theory plate number curves of RE and Al; HETP of RE and Al under different flow rate

It can be seen from the Fig. 3 that the theoretical plate number of the three magnesium salts increased first and then decreased, reaching the peak at $0.4 \text{ cm}^3/\text{min}$ when the flow rate increased from $0.2 \text{ cm}^3/\text{min}$ to $0.6 \text{ cm}^3/\text{min}$. The theoretical plate height showed the opposite direction of the trend, the same at $0.4 \text{ cm}^3/\text{min}$ to reach the minimum. It can be illustrated that the flow rate of the magnesium ions between the mineral particles were greater than the diffusion rate of the magnesium ions in the mineral particles when the flow rate was too fast. The magnesium ions could not be sufficiently contacted with the mineral particles and was not conducive to the formation of multiple reaction balances. The flow of magnesium ions could not take away the rare earth timely because of the smaller flow velocity, it is easy to occur that rare earth ions are adsorbed on the surface of minerals again. It can be seen from the Fig. that theoretical plate number of magnesium nitrate is the largest, the theoretical plate height of magnesium nitrate is minimum, followed by magnesium chloride, and finally magnesium sulfate. It can be obtained magnesium nitrate leaching mass transfer efficiency is the best under the same flow rate.

3.2 Effects of magnesium concentration on mass transfer

The concentration of leaching agent plays a significant role in the leaching process, which influence the performance of ion exchange and diffusion. Fig. 4 shows the effect of different concentrations of MgSO_4 , $\text{Mg}(\text{Cl})_2$ and $\text{Mg}(\text{NO}_3)_2$ on mass transfer of RE and Al.

It is shown in the Fig. 4 that the peak value of RE concentration increased with the increase of magnesium ions concentration and the peak shape of leaching curve was also narrowed. It indicated that the total content of RE climbed up with the rise of magnesium ions concentration. On the one hand, the higher the concentration gradient of the magnesium ions formed. It increased the concentration

difference of magnesium ions between the flow center and the mineral surface. So that the diffusion ability of magnesium ion is strengthened with the concentration of magnesium ions increased. On the other hand, increasing the magnesium ion concentration can strengthen the intensity of exchange reaction during the leaching process, and the leaching efficiency of RE appeared a new level. However, the content of Al rose with the increase of magnesium ions making separating Al from RE more difficult.

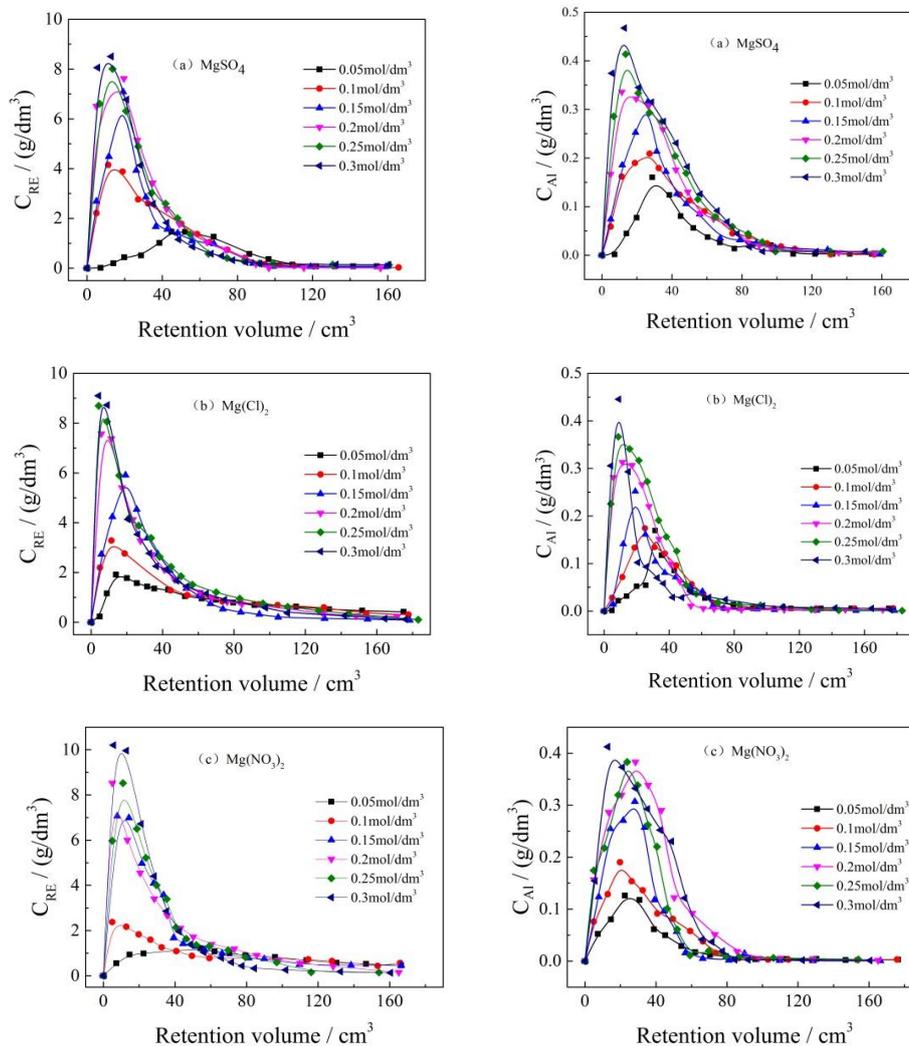


Fig. 4. Leaching behaviors of RE and Al (250 g of rare earth ore, $\mu=0.4\text{cm}^3/\text{min}$, $T = 298\text{K}$):
(a) MgSO_4 , (b) MgCl_2 , (c) $\text{Mg}(\text{NO}_3)_2$

HETP and theory plate of RE and Al under various concentration of magnesium ion are shown in the Fig. 5. It can be concluded that the HETP decreased and theory plate increased with the increase of magnesium ions concentration from 0.05 mol/dm^3 to 0.3 mol/dm^3 . However, HETP and theory plate had narrow gap when the concentration of magnesium ions exceeded 0.2 mol/dm^3 . It indicated that the increase of magnesium ions concentration has little effect on the mass transfer effect on leaching process. This is because when the magnesium ions concentration was high enough, the leaching velocity of rare earth ions move from the solid phase into the liquid phase is limited by the rare earth ion diffusion rate. The leaching kinetics of weathering crust elution-deposited rare earth ore are controlled by the solid film diffusion (Lasheen et al., 2009). The rise of magnesium ions concentration has little effect on the solid film diffusion.

Under the same concentration of magnesium ions, the mass transfer efficiency of RE and Al follow the order of $\text{Mg}(\text{NO}_3)_2 > \text{Mg}(\text{Cl})_2 > \text{MgSO}_4$. These results showed that excessive magnesium ions concentration would increase the production cost and environmental burden, and also enhanced the difficulty to separate RE and Al during the leaching process.

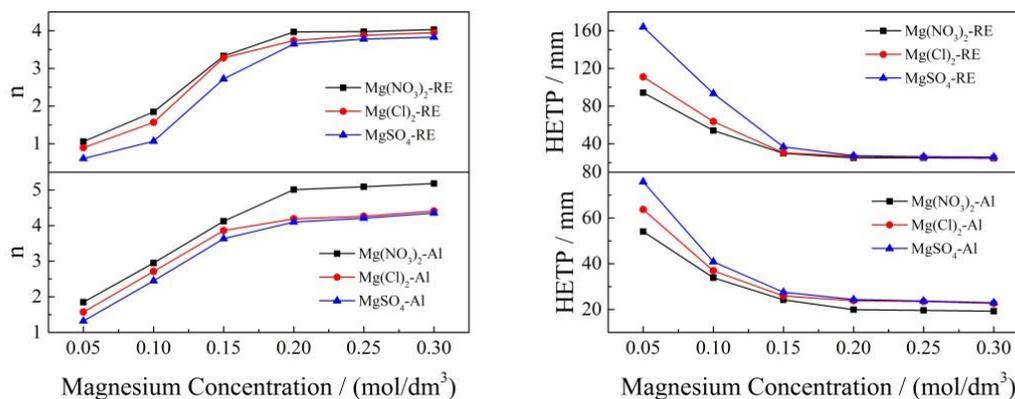


Fig. 5. Theory plate number curves of RE and Al; HETP of RE and Al under different magnesium concentration

3.3 Effect of pH on mass transfer with magnesium salts

In order to investigate the effect of pH on the mass transfer in different magnesium salts, magnesium nitrate, magnesium chloride and magnesium sulfate were used to leaching rare earth and the results were shown in Fig. 6. Sulfuric acid, hydrochloric acid, nitric acid and ammonia were used to adjust the pH of the leach solution.

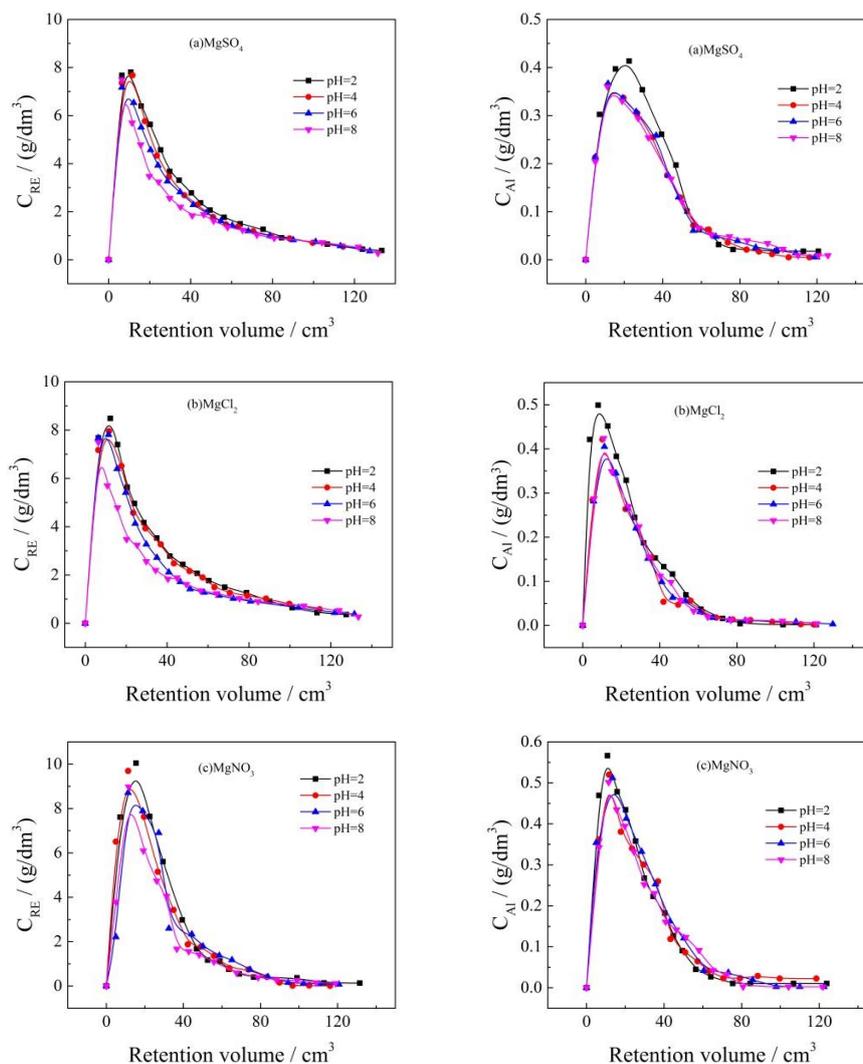


Fig. 6. Leaching behaviors of RE^{3+} and Al^{3+} (250 g of rare earth ore, $C_{Mg^{2+}} = 0.2 \text{ mol/dm}^3$, $\mu = 0.4 \text{ cm}^3/\text{min}$, $T=298\text{K}$): (a) $MgSO_4$, (b) $MgCl_2$, (c) $Mg(NO_3)_2$

According to Fig. 6, leaching curve of RE^{3+} showed a trend of first rise and then decline when the pH was changed from 2 to 8 and three kinds of magnesium salts were used as leaching agent. In the single magnesium salt leaching, the peak concentration of rare earth increases with the increase of pH, but the change of the whole shape is not obvious. This is because the clay minerals of the rare earth ores has a certain ability to buffer the acid and alkali which showed the mass transfer of rare earth was not influenced by the initial pH of magnesium salt obviously (Tertre et al., 2006). When a single magnesium salt was used as leaching agent, the peak concentration of Al increased with increasing of initial pH. There was a significant increase in content of Al when pH=2, because in the strong acid environment, there are other phase of the aluminum leaching into the leachate.

In order to better analyze the mass transfer effect of RE and Al with magnesium salts, the leaching curve in Fig. 6 was analyzed by chromatography and the results were shown in Fig. 7. The theory plate number of RE and Al decreased with the rise in pH, while the HETP showed the opposite trend. The theory plate number and HETP of magnesium nitrate are significantly larger than magnesium chloride and magnesium sulfate, because chelating ability of NO_3^- with RE^{3+} and Al^{3+} is greater than Cl^- and SO_4^{2-} , mass transfer efficiency of magnesium nitrate is the best in three magnesium salts.

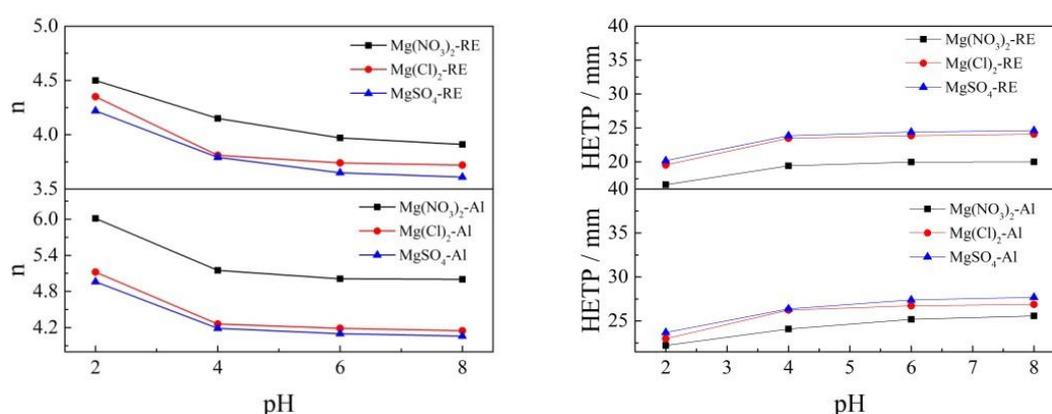


Fig. 7. Theory plate number curves of RE and Al; HETP of RE and Al under different pH

3.4 Effects of temperature on mass transfer with magnesium salts

In order to investigate the effect of temperature on the mass transfer, the magnesium sulfate, magnesium chloride and magnesium nitrate were used as leaching agents and the results were shown in Fig. 8. The glass columns were replaced by a special column which can recycle water to keep the whole chemical reaction under the constant temperature.

Fig. 8 described the effects of temperature on the process of mass transfer in different magnesium salts. It can be seen from the Fig. 8 that with the increase of leaching temperature, the peak concentration of RE and Al increased gradually when single magnesium salt was used as leaching agent, and the collected volume which related to the highest concentration decreased. It was indicated that the mass transfer process of RE and Al in magnesium salts were contributed by the temperature increased. The enhancement of temperature increased the thermal motion of ions, which increases the diffusivity and exchangeability of the magnesium salts solution. The ion exchange reaction rate of RE ions and magnesium ions speed up, and the leaching rate of RE and Al improved. In addition, the higher of the leaching temperature, the faster the permeation rate of the magnesium salts, the shorter the time required for leaching.

The leaching curves in the Fig. 8 were analyzed by the chromatographic plate theory. The number of theory plate and height of theory plate were calculated and result was shown in the Fig. 9. There was a slight rise in the theory plate of RE and Al. With the rising of temperature, HETP showed a descending trend in the graph. The theory plate number of magnesium nitrate and magnesium chloride was affected by the temperature more obviously than the magnesium sulfate. When the temperature increases, magnesium sulfate as leaching agent resulted in less impurities and magnesium nitrate can recover more rare earth in the leaching.

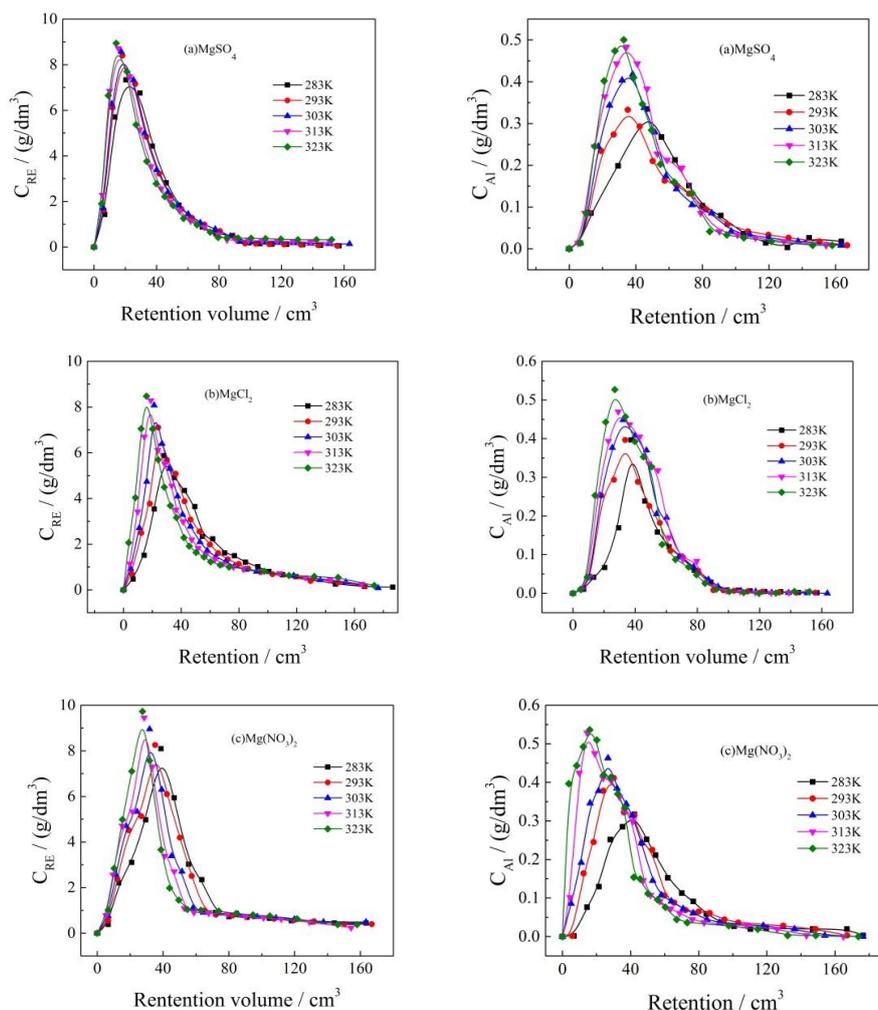


Fig. 8. Leaching behaviors of RE³⁺ and Al³⁺ (250 g of rare earth ore, C_{Mg2+} = 0.2 mol/dm³, μ = 0.4 cm³/min): (a) MgSO₄, (b) MgCl₂, (c) Mg(NO₃)₂

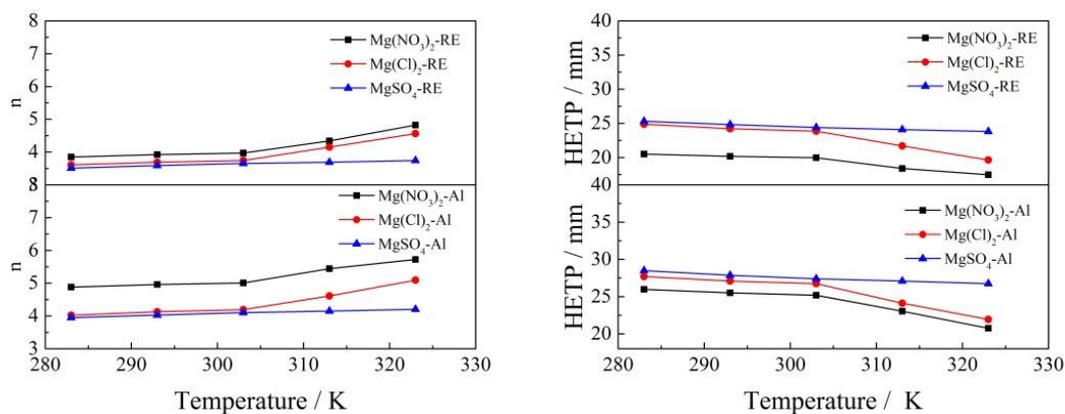


Fig. 9. Theory plate number curves of RE and Al; HETP of RE and Al under different temperature

4 Conclusions

The effects of flow rate, magnesium ion concentration, initial pH of magnesium salts and experimental temperature on the mass transfer with magnesium salts were studied during the leaching process. The following conclusions were gained: The relationship between the flow rate μ and the HETP is in accordance with the Van Deemter equation when magnesium salts were used for leaching, and there is

an optimum flow rate ($0.4 \text{ cm}^3/\text{min}$) to minimize the leaching of RE and Al by HETP. With the rising of magnesium ion concentration, HETP gradually goes down, it has certain effect on the leaching mass transfer efficiency and increases the difficulty of the leaching solution purity when the concentration of magnesium ions enhanced too much. The initial pH of the magnesium salts has almost no effect on the mass transfer efficiency of RE, but the strong acidity ($\text{pH} < 4$) of magnesium salts can greatly enhance the leaching mass transfer efficiency of dissolution of adsorbed hydroxyl aluminum and the separation of RE and Al. High temperature contributes to the decrease of HETP and the improvement of leaching mass transfer efficiency of rare earth and aluminum. The leaching efficiency of Al is stronger than that of RE, but its leaching lags behind RE. It is possible to split the time to collect leachate to improve the purity of rare earth in the solution. The mass transfer efficiency of rare earth and aluminum with three kinds of magnesium salts follow the order of $\text{Mg}(\text{NO}_3)_2 > \text{Mg}(\text{Cl})_2 > \text{MgSO}_4$. Magnesium nitrate as the leaching agent can get the highest leaching mass transfer efficiency of rare earth, and magnesium sulfate as the leaching agent can make the impurity leaching and mass transfer efficiency of Al is the lowest.

Acknowledgments

The work is financially supported by the grants from the National Natural Science Foundation of China (NO. 41472071 and No. 51734001).

References

- BARTLETT, R. W. 1992. *Simulation of ore heap leaching using deterministic models*. Hydrometallurgy, 29(1), 231-260.
- CHI, R., and TIAN, J. 2012. *Weathered crust elution-deposited rare earth ores*. Nonferrous Metals Science and Engineering(2).
- HE, Z., ZHANG, Z., YU, J., XU, Z., and CHI, R. A. 2016. *Process optimization of rare earth and aluminum leaching from weathered crust elution-deposited rare earth ore with compound ammonium salts*. Journal of Rare Earths, 34(4), 413-419.
- JUN, T., JINGQUN, Y., KAIHONG, C., GUOHUA, R., MINTAO, J., and RUAN, C. 2010. *Optimisation of mass transfer in column elution of rare earths from low grade weathered crust elution-deposited rare earth ore*. Hydrometallurgy, 103(1-4), 211-214.
- JUN, T., JINGQUN, Y., RUAN, C., GUOHUA, R., MINTAO, J., and KEXIAN, O. 2010. *Kinetics on leaching rare earth from the weathered crust elution-deposited rare earth ores with ammonium sulfate solution*. Hydrometallurgy, 101(3-4), 166-170.
- KIM, S. E., THAI, H. T., and LEE, J. 2009. *Buckling analysis of plates using the two variable refined plate theory*. Thin-Walled Structures, 47(4), 455-462.
- KUL, M., TOPKAYA, Y., and KARAKAYA, İ. 2008. *Rare earth double sulfates from pre-concentrated bastnasite*. Hydrometallurgy, 93(3), 129-135.
- LAHIRI, A., and JHA, A. 2009. *Selective separation of rare earths and impurities from ilmenite ore by addition of K^+ and Al^{3+} ions*. Hydrometallurgy, 95(3-4), 254-261.
- LASHEEN, T. A., HAZEK, M. N. E., and HELAL, A. S. 2009. *Kinetics of reductive leaching of manganese oxide ore with molasses in nitric acid solution*. Hydrometallurgy, 98(3-4), 314-317.
- LEE, W. C., TSAI, G. J., and TSAO, G. T. 1993. *Analysis of chromatography by plate theory*. Separations Technology, 3(4), 178-197.
- LEVENSPIEL, O. 1962. *Chemical Reaction Engineering*. Industrial and Engineering Chemistry Research, 38(11), 1055-1076.
- LI, M., ZHANG, X., LIU, Z., HU, Y., WANG, M., LIU, J., and YANG, J. 2013. *Kinetics of leaching fluoride from mixed rare earth concentrate with hydrochloric acid*. Hydrometallurgy, 2013, 140(11):71-76.
- MOLDOVEANU, G. A., and PAPANGELAKIS, V. G. 2012. *Recovery of rare earth elements adsorbed on clay minerals: I. Desorption mechanism*. Hydrometallurgy, 117-118, 71-78.
- NESBITT, H. W. 1979. *Mobility and fractionation of rare earth elements during weathering of a granodiorite*. Nature, 279(5710), 206-210.
- QIONG, L. 2015. *Studies on Coordination Leaching of Weathered Crust Elution-deposited Rare Earth Ore with Citrate*. Chinese Rare Earths.

- SAMENI, A. M., and MORSHEDI, A. 2000. *Hydraulic conductivity of calcareous soils as affected by salinity and sodicity. II. Effect of gypsum application and flow rate of leaching solution*. Communications in Soil Science and Plant Analysis, 31(1-2), 69-80.
- TERTRE, E., BERGER, G., SIMONI, E., CASTET, S., GIFFAUT, E., LOUBET, M., and CATALETTE, H. 2006. *Europium retention onto clay minerals from 25 to 150 °C: Experimental measurements, spectroscopic features and sorption modelling*. Geochimica Et Cosmochimica Acta, 70(18), 4563-4578.
- TIAN, J., TANG, X., YIN, J., CHEN, J., LUO, X., and RAO, G. 2013. *Enhanced Leachability of a Lean Weathered Crust Elution-Deposited Rare-Earth Ore: Effects of Sesbania Gum Filter-Aid Reagent*. Metallurgical and Materials Transactions B, 44(5), 1070-1077.
- XIAO, Y. F., FENG, Z. Y., HU, G. H., HUANG, L., HUANG, X. W., CHEN, Y. Y., and LI, M. L. 2015. *Leaching and mass transfer characteristics of elements from ion-adsorption type rare earth ore*. Rare Metals, 34(5), 357-365.
- XIAO, Y. F., FENG, Z. Y., HU, G. H., HUANG, L., HUANG, X. W., CHEN, Y. Y., and LI, M. L. 2015. *Leaching and mass transfer characteristics of elements from ion-adsorption type rare earth ore*. Rare Metals, 34(5), 357-365.
- YANFEI, X., ZONGYU, F., XIAOWEI, H., LI, H., YINGYING, C., LIANGSHI, W., and ZHIQI, L. 2015. *Recovery of rare earths from weathered crust elution-deposited rare earth ore without ammonia-nitrogen pollution: I. leaching with magnesium sulfate*. Hydrometallurgy, 153, 58-65.
- YANFEI, X., ZONGYU, F., XIAOWEI, H., LI, H., YINGYING, C., XIANGSHENG, L., ZHIQI, L. 2016. *Recovery of rare earth from the ion-adsorption type rare earths ore: II. Compound leaching*. Hydrometallurgy, 163, 83-90.
- YANG, X. J., LIN, A., LI, X. L., WU, Y., ZHOU, W., and CHEN, Z. 2013. *China's ion-adsorption rare earth resources, mining consequences and preservation*. Environmental Development, 8(1), 131-136.
- YONG-XIU, L. I., ZHANG, L., and ZHOU, X. M. 2010. *Resource and Environment Protected Exploitation Model for Ion-type Rare Earth Deposit in Southern of China*. Chinese Rare Earths, 31(2), 80-85.