ISSN: 2350-0328
International Journal of AdvancedResearch in Science, Engineering and Technology
Vol. 7, Issue 7 , July 2020

Use of Hydrometallurgical Methods for Extracting Rare-Earth Elements from Ash and Slag

Tursunboy Kamolov, Hasan Sharipov, Fotima Akhmedova, Farxod Navrozov,Otabek Abdullayev

Doctoral student, candidate of technical sciences, SUE “Fan vatarakkiyot” Tashkent state technical university, Tashkent, Uzbekistan
Doctor of chemical sciences, professor, SUE “Fan vatarakkiyot” Tashkent state technical university, Tashkent, Uzbekistan
Doctoral student, SUE “Fan vatarakkiyot” Tashkent state technical university, Tashkent, Uzbekistan
Doctoral student, SUE “Fan vatarakkiyot” Tashkent state technical university, Tashkent, Uzbekistan
Doctoral student, SUE “Fan vatarakkiyot” Tashkent state technical university, Tashkent, Uzbekistan

ABSTRACT . It has been created many different ways to extract rare earth elements from ash and slag waste. Nevertheless, it is worth noting the high efficiency of hydrometallurgical extraction methods. The purpose of this article is to study the process of hydrometallurgical extraction of rare-earth elements from ash and slag waste observing lanthanum extraction using Purolite C100H cation exchanger, a modern analogue of KU-2 cation exchanger, as an example. During the research, the dependence of sorption on the pH of the initial solution on Purolite C100H cation exchanger, the dependence of lanthanum sorption on Purolite C100H cation exchanger, and the dependence of the degree of lanthanum desorption on the concentration of hydrochloric acid were studied. As the results of the study showed, this hydrometallurgical extraction method is highly effective both in terms of extraction rates and in terms of purification rates

KEYWORDS: Rare-earth elements, ash and slag waste, cation exchanger, polymer matrix, sorption, desorption, cation-exchange resin.

I. INTRODUCTION

There are various methods for the extraction of valuable elements, including rare earth elements (REE), from the mineral part of coal, which consist in the chemical treatment of ash and slag waste after burning coal with various chemical reagents. The main method for processing ash and slag waste (ASW) is a hydrometallurgical method of opening using acid reagents, which can be used as mineral acids or organic cation-exchanges in the H^+ form.

II. SIGNIFICANCE OF THE SYSTEM

It has been created many different ways to extract rare earth elements from ash and slag waste. Nevertheless, it is worth noting the high efficiency of hydrometallurgical extraction methods.The study of literature survey is presented in section III, methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and conclusion.

III. METHODOLOGY

In accordance with literature data, it is known that for the sorption of REE cation exchangers with strongly acidic groups are used. Such, for example, is domestic KU-2 cation exchanger, obtained on the basis of a sulfonated copolymer of styrene and divinylbenzene and containing sulfo groups. Many studies have been conducted on the sorption leaching of REE on KU-2 cation-exchange resin [1]. The modern analogue of KU-2 cation exchanger is Purolite C100H cation exchanger. Purolite C100H is a cation exchange resin in the H^+ form, in the form of spherical particles, obtained on the basis of a sulfonated copolymer of styrene and divinylbenzene, which has a high exchange capacity and is completely ready for use in both domestic and industrial water treatment systems. Cation exchange resin extracts cations such as calcium, magnesium, sodium, etc. from water, replacing them with hydrogen ions.

Recovery of the cation exchange capacity after exhaustion of the exchange capacity is carried out with acid solutions (in most cases, hydrochloric or sulfuric). The recovered capacity depends on the amount used in the regeneration of the acid. Purolite C100H is also able to remove dissolved iron and manganese ions by the above mechanism and retain suspended particles due to the filtering effect of the resin layer. Purolite C100H is insoluble in dilute and medium concentrated acids, alkalis and in all common organic solvents. However, the presence of significant amounts of free chlorine, hypochlorite ions, or other strong oxidizing agents over a long period of time leads to the decomposition of cross-links in the polymer matrix. This leads to an increase in the moisture content in the resin, to a decrease in the mechanical strength of the particles, and also to the appearance of small amounts of washed away organic matter of decay products. Like most common polystyrene sulfonated resins, Purolite C100H is thermally stable to a temperature of 120 °C in salt (for example, sodium, calcium or magnesium) form. Cation exchanger in the H^+ form is significantly prone to hydrolysis in water at temperatures above 120 °C, which ultimately leads to a decrease in the capacity of the resin due to the gradual replacement of functional groups with hydroxyl groups.

We investigated the possibility of extracting REE from acidic solutions on Purolite C100H cation exchanger using the example of one of REE - lanthanum.

The work uses the strongly acidic Purolite C100H cation exchanger, which is cation exchanger in the H^+ form, in the form of spherical particles, obtained on the basis of a sulfonated copolymer of styrene and divinylbenzene, which has a high exchange capacity and is completely ready for use in both domestic and industrial water treatment systems. As soon as the capacity of the resin layer is exhausted, the exchange capacity is restored with acid solutions (in most cases, hydrochloric or sulfuric). The recovered capacity is largely dependent on the amount used in the regeneration of the acid. The characteristics of the resin are shown in tables 1 and 2.

Table 1
Typical physical, chemical and technological properties

Structure of a polymer matrix	**Polystyrenecrosslinkedwith divinylbenzene**
Appearance	Translucent spherical amber or dark brown particles
The number of whole particles,%, not less	90
Functional groups	Sulfo groups
Ionic form (in a commercial product)	H^+
Bulk weight, g / l	800
Particle spread, mm	+1,2<5%,—0,3<1%
Uniformity coefficient	1,7 max
Moisture content, form H^+,%	51—55
Reversible swelling during the transition Na^+ -> H^+,%	5
Specific gravity, wet Na + form, g/ml	1,29
Full exchange capacity, N^+ - form:	
Wet cation exchanger, by volume g-equiv / l, not less	1,8
Dry cation exchange resin, by weight g-eq / l, not less	4,9
Maximum working temperature, Na^+ form, ° C, no more	120
PH range:	no

Table 2
Standard operating conditions (desalination, once-through regeneration)

Technological operation	Consumption	Incoming stream	Time, min	Total amount
The process of work (filtering)	8-40 OC*/h	Source water	—	—
Loosening flushing	7-12 m/h	Source water (5-20°C)	5-20	1,5-3,5 OC
Regeneration	1,6-6,5 OC/h	0,5-5% H_2SO_4 or 4-10% HCl	30	64-160 g of acid per 1 liter of resin
Flushing (Slow)	1,6-6,5 OC/h	fully or partially demineralized water	60 (approximately)	2-4 OC
Washing (fast)	8-40 OC/h	fully or partially demineralized water	60 (approximately)	3-10 OC

Like most common polystyrene sulfonated resins, Purolite C100H is thermally stable to a temperature of 150 °C in salt form.

IV. EXPERIMENTAL RESULTS

The dependence of lanthanum sorption on the pH of the initial solution was studied under static conditions. The initial solutions contained 1 g/l of lanthanum, the pH of the environment was varied in the range from 1 to 5 units, the ionite was weighed 0,100 g, the contact time was 24 hours. The concentration of lanthanum in the initial and equilibrium solution was determined photometrically. The sorption of lanthanum at different pH was calculated on the basis of the obtained data; the process is illustrated in Figure 1.

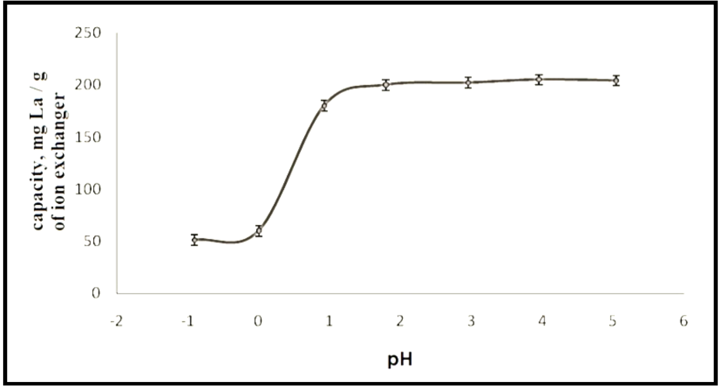

Figure 1. The dependence of the sorption of lanthanum on the pH of the initial solution oncation exchanger PuroliteC100H

The study of the dependence of the sorption of lanthanum from hydrochloric acid solutions, which are on Purolite C100H cation exchanger, on the pH of the initial solution showed that in the range of pH from 2 to 5 units the ion exchange static capacity practically does not change and the sorption value averages 200 mg/g.

The construction of the sorption isotherm of lanthanum was carried out from hydrochloric acid solutions, in the range of initial concentrations from 0,25 to 3,2 g/l, the pH of the solution is 2. Sorption was carried out for 24 hours. Lanthanum sorption was calculated by the difference in concentrations in the initial and equilibrium solutions.

According to the data obtained, the sorption of lanthanum on Purolite C100H was calculated. The data are shown in Figure 2.

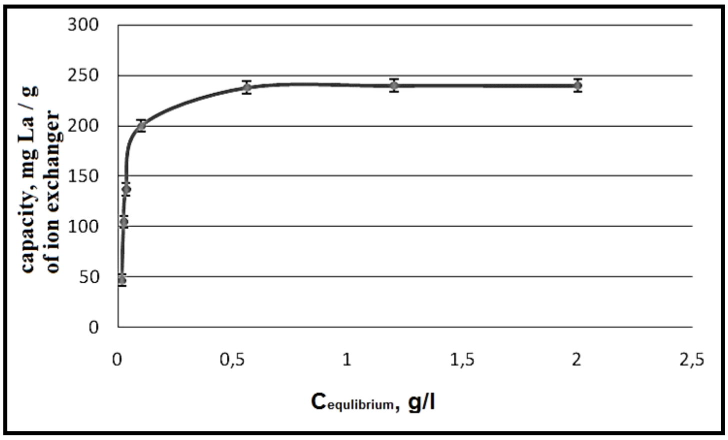

Figure 2. The dependence of the sorption of lanthanum on cation exchanger Purolite C100H on the concentration of the equilibrium solution

The sorption isotherm of lanthanum on Purolite C100H cation exchanger is a convex curve smoothly extending to a plateau. The maximum static exchange capacity (SEC) of PuroliteC100H ion exchanger is achieved at a concentration of lanthanum in an equilibrium solution of 0,51 g/l and amounted to 240 mg/g or 5,1 mg × equiv/g (C_d = 120).

The distribution coefficient was calculated by the formula: $C_d = \overline{X}/X$,

where $\overline{X}$ – equivalent fraction of ions in ion exchanger, X - in solution.

Under similar conditions, the maximum static exchange capacity of KU-2 cation exchanger at an equilibrium metal concentration of 1,6 g/l is 3,3 mg×equiv/g (C_d = 50). So, Purolite C100H has higher capacitive characteristics than KU-2 cation exchanger.

It was found that the balance of the exchange is achieved at 5 hours of contact of the ion exchanger with the solution on a Purolite C100H sorbent. Thus, we can say that Purolite C100H cation exchanger has high kinetic characteristics with respect to lanthanum in hydrochloric acid solutions.

In ion-exchange processes, ion exchangers gradually transfer from one ionic form to another, losing the ability to participate in this reaction. However, due to the reversibility of the exchange, the ion exchanger can be regenerated: it can be returned to the original working form.

Cation exchangers are preferably regenerated with hydrochloric acid, which is easily purified from impurities by distillation of the azeotropic mixture with water, although in specific cases it is possible to take dilute solutions of sulfuric or nitric acid, choosing such concentrations of these reagents and such temperatures at which the occurrence of redox reactions is excluded [2].

We have investigated the possibility of desorption of lanthanum under static conditions with hydrochloric acid solutions (2,0; 3,0; 4,0; 5,0 mol/l). In accordance with literature data, it is known that the desorption of ions of rare-earth elements from KU-2 cation-exchange resin is carried out 3-4 n. hydrochloric acid [3]. Desorption from a resin containing 207 mg of La^{3+}/g_{ionite} was studied (this amount of lanthanum was sorbed under the following conditions: m_{ionite} = 0,100 g, $R_{initial}$ = 1,2 g/l, pH = 2).

Desorption conditions: m_{ionite} = 0,100 g, the volume of the eluting solution is 20,0 ml, the contact time is 24 hours, the concentration of hydrochloric acid is 2,0; 3,0; 4,0; 5,0 mol/l.

The desorption results are presented in table 3.

Table 3

The dependence of the degree of desorption of lanthanum on the concentration of hydrochloric acid

№	**C_{HCl}, mol/l**	**$\overline{m}_{La^{3+}}$, contained in 20,0 ml of solution after desorption, g**	**$X_{cp} \pm \frac{tS}{\sqrt{n}}$**
1	2,0	16,3	79±4
2	3,0	16,9	82±4
3	4,0	17,2	83±5
4	5,0	17,4	84±5

As can be seen from table 3, the degree of desorption of lanthanum is practically independent of the concentration of hydrochloric acid in this concentration range. For further studies, a concentration of hydrochloric acid of 3mol/l was chosen.

The possibility of desorption of lanthanum under static conditions with a 3,0 M hydrochloric acid solution, depending on the contact time, was investigated. Desorption from a resin containing 207 mg of La^{3+}/g_{ionite} was studied (this amount of lanthanum was sorbed under the following conditions: m_{ionite} = 0,100 g, $R_{initial}$ = 1,2 g/l, pH = 2).

Desorption conditions: m_{ionite} = 0,100 g, the volume of the eluting solution is 20,0 ml, the contact time is 1, 2, 3, 4, 5, 24 hours, the concentration of hydrochloric acid is 3,0 mol/l.

The maximum degree of desorption of 80% is achieved already at 4 hours of contact of the ion exchanger with the solution on a Purolite C100H sorbent. The desorption results from Purolite C100H cation-exchange show the possibility of reusing the ion exchange resin for sorption of metal from solution.

V. CONCLUSION AND FUTURE WORK

Thus, the proposed method allows to extract rare earth metals from coal or ASW and allocate them in a concentrate with high rates of extraction and purification.

REFERENCES

[1]. Kamolov T.O., Sharipov H.T., TuresebekovA.Kh., Khamidova G.S., Borbat V.F. Elemental and mineralogical composition of inorganic components of Angren coals, and ash and slag waste. Materialsofascientificandpracticalconference, Cheboksary, April 22, 2011

[2]. Kamolov T.O. Ash and slag waste of thermal power plants - an unconventional type of raw materials of rare metals // Materials of the Russian scientific-practical conference "Modern problems of natural science research." Cheboksary, May 12-14, 2011

[3]. SharipovKh.T.,TuresebekovA.Kh., Guro V.P., Kamolov T.O. Non-traditional types of raw materials of rare-earth metals // Collection of materials of the International scientific and technical conference "Actual issues of obtaining and application of REM-2015". Moscow, 2015