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Sorption of rare earth metals under static conditions from solutions after leaching of phosphogypsum

Abstract: Processing of apatite raw materials is associated with the formation of multi-tonnage waste - phosphogypsum. The content of rare-earth metals in such waste reaches 1 %, which allows us to consider it a man-made source of rare-earth metals and their compounds. Until now there are neither processing enterprises nor effective technological processes for phosphogypsum processing. It is rational to use a method involving the extraction of valuable components and the overall reduction of phosphogypsum volumes. One such method can be the sorption extraction of REM after leaching of phosphogypsum with hydrochloric acid. In this work the results of sorption by sulphocationites are presented: Purosorb SAC 140 (in H- and Na-forms); Purolite C150 (in H- and Na-forms) and Puromet MTC 1600 (in H- and Na-forms).

Keywords: Rare earth metals (REM), sorption, hydrochloric acid, phosphogypsum, sorbent.

Introduction

Rare earth metals (REM) are one of the most important raw materials that ensure the development of modern knowledge-intensive industries. REMs are essential for such high-tech industries as space, aviation nuclear, and radioelectronics. In connection with the increasing demand for rare earths in various industrial fields and with the growth of REM prices on the world market, the problem of developing new raw material sources is now becoming increasingly necessary. One of the most promising sources of technogenic raw materials for REM extraction is phosphogypsum - the main by-product of phosphoric acid production by sulphuric acid decomposition of phosphate raw materials. Being a product of the chemical process, phosphogypsum, unlike natural gypsum, contains several residual components such as phosphorus, fluorine, and REM. The direct use of phosphogypsum in industrial production, in agriculture can negatively affect its consumption due to the presence of harmful components. In addition, valuable components present in phosphogypsum are lost. Depending on the process conditions, about 70-85 % of the rare earth elements (REE) initially present in the phosphate rock are transferred to the phosphogypsum (Najmanbaev et al., 2015; Koopman & Witkamp, 2000; Kenzhaliyev, 2019; Litvinova & Oleynik, 2021; Kulczycka, et al., 2021).

The process of sorption on organic ions is one of the most promising ways to concentrate REM from highly dilute solutions. This method has several advantages: simplicity of apparatus design, economy and environmental friendliness.

The work aims to study the process of sorption of rare-earth metals from the prepared solution after hydrochloric acid leaching of phosphogypsum under static conditions with the use of the above-mentioned sorbents at different ratios of the amount of sorbent to a given volume of solution.

Research Methods

Cation exchange resins are produced by industry in sodium form. Cationic resins in sodium and hydrogen forms were used for research. Ionites were purified from synthesis products and converted to H-form by hydrochloric acid solution (GOST, 1964). A certain volume of each ionite pre-swollen in distilled water was loaded into glass columns. Then 5% hydrochloric acid solution was passed through each column at a rate of 3 wpm until the acid concentration was equalised at the inlet and outlet. Ionites from acid were washed with distilled water to pH = 6 - 7. The prepared ionites were dried at 50 °C to constant weight.

To investigate the process of sorption of rare earth metals, solutions containing REM were preliminarily produced by leaching of phosphogypsum, a waste product of sulfuric acid processing of apatite concentrate. 20 litres of solution containing, g/dm³: 0,04475 ΣREM; 3,12 Ca; 0,486 Al; 0,45 Fe; 0,13 Mg. The elemental content of rare earth metals in solution is, mg/dm³: 9.87 Ce; 0.86 Dy; 6.21 Er; 0.25 Eu; 1.5 Gd; 0.14 Ho; 8.68 La; 0.05 Lu; 5.23 Nd; 1.54 Pr; 0.06 Sc; 0.89 Sm; 0 Tb; 0.3 Tm; 8.97 Y; 0.2 Yb.

The following macroporous sulphocationites were used as sorbents for REM sorption: Purosorb SAC 140 (in H- and Na-forms); Purolite C150 (in H- and Na-forms) and Puromet MTC 1600 (in H- and Na-forms).

The quantitative content of basic elements in solutions was determined on an atomic emission spectrometer with inductively coupled plasma Optima 8300DV, on an atomic absorption spectrometer SHIMADZU type AA-7000 (Japan).

Research Results

Sorption was carried out under static conditions at a temperature of 25 ± 5 °C on an orbital shaker with a rotation speed of 160 rpm. To perform sorption, a certain amount of cationites in H- and/or Na-form was placed in dry flasks of 0.25 dm³ volume, poured a given volume of solution containing REM, and set on a stirring device. Contact of cationites with the solution was carried out for 5 days with stirring on three working days, then the solution was separated from the ionite by filtration.

The stock solution and sorption filtrates were analysed for the content of rare earth metals and associated impurity components.

As shown in Figure 1, that at 0.1 g of sorbent per 100 ml of solution the best performance on recovery of 45.2 % of REM has sorbent Puromet MTC 1600 in Na-form, when increasing the amount of sorbent from 0.1 to 0.4 g per 100 ml of solution sorbent Purosorb SAC 140 in Na-form showed almost the same recovery of 43.7 % of REM. Purolite C150 sorbent showed lower recovery of REM. Further increasing the amount of sorbent to 0.6 g per 100 ml of solution did not show higher REM recovery results on the sorbents. Compared to H-form, Na-form is more effective for all studied sorbents.

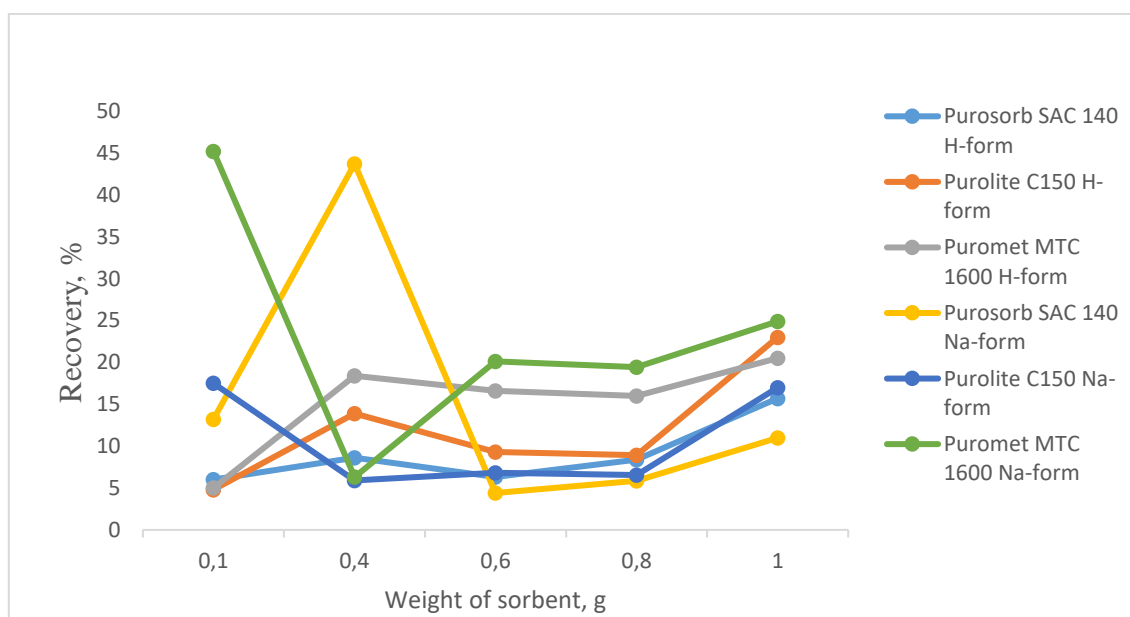


Figure 1. Sorption of REM from solution after phosphogypsum leaching on strongly acidic cationites

We were also interested in the behaviour of calcium, magnesium, aluminium and iron impurities during the sorption of rare-earth metals from hydrochloric acid solutions on the studied macroporous sulphocationites. Tables 1-4 present data on the behaviour of the listed impurity components during sorption of rare-earth metals from solution.

Table 1 - Calcium sorption from solution after phosphogypsum leaching on strongly acidic cationites

Quantity of sorbent per 100 ml of solution, g,	Calcium recovery per sorbent, %					
	H-form			Na-form		
	Purosorb SAC 140	Purolite C150	Puromet MTC 1600	Purosorb SAC 140	Purolite C150	Puromet MTC 1600
0.1	0	0	0	13.1	0	45.8
0.4	-	-	6.29	4.0	-	37.1
0.6	0.18	0.8	5.3	2.4	19.2	3.4

The most interfering impurity in sorption, taking into account its content in solution, is calcium.

Table 2 - Magnesium sorption from solution after phosphogypsum leaching on strongly acidic cationites

Quantity of sorbent per 100 ml of solution, g,	Magnesium recovery per sorbent, %					
	H-form			Na-form		
	Purosorb SAC 140	Purolite C150	Puromet MTC 1600	Purosorb SAC 140	Purolite C150	Puromet MTC 1600
0.1	0	1.5	0	0	3.1	0
0.4	2.3	0	0	0	0	0

Table 3 - Sorption of aluminium from solution after phosphogypsum leaching on strongly acidic cationites

Quantity of sorbent per 100 ml of solution, g,	Aluminium recovery per sorbent, %					
	H-form			Na-form		
	Purosorb SAC 140	Purolite C150	Puromet MTC 1600	Purosorb SAC 140	Purolite C150	Puromet MTC 1600
0.1	0	7.2	7.4	17.0	19.0	9.0
0.4	11.1	14.5	19.2	22.3	23.2	14.0
0.6	2.3	0.8	1.7	1.0	4.8	5.4

Table 4 - Sorption of iron from solution after phosphogypsum leaching on strongly acidic cationites

Quantity of sorbent per 100 ml of solution, g,	Iron recovery per sorbent, %					
	H-form			Na-form		
	Purosorb SAC 140	Purolite C150	Puromet MTC 1600	Purosorb SAC 140	Purolite C150	Puromet MTC 1600
0.1	0	7.3	8.7	14.5	15.3	5.9
0.4	13.1	10.0	22.8	20.1	23.4	15.0
0.6	7.9	5.5	11.1	16.8	17.6	5.2

According to the analysis of sorption filtrates calcium is sorbed by sorbents Purosorb SAC 140 and Puromet MTC 1600 in Na-forms at all ratios of sorbent mass to solution volume. When the amount of sorbent is increased to 0.6 g per 10 ml of solution, calcium is sorbed by all resins in hydrogen and sodium forms. At further processing of saturated resins, it is necessary to take into account the presence of calcium impurity in them.

As the results of analyses of sorption filtrates at all studied cationites from the considered impurities magnesium is practically not sorbed on sorbents, except for single cases.

Aluminium and iron impurities are sorbed with an average degree, practically in all cases. At the same time in studies at sorption of rare-earth metals on sulfocationite KU-2, it was found that aluminium and iron are weakly retained by the resin and do not interfere with the extraction of REM concentrate (Lokhova et al., 2018; Mihajlichenk et al., 2015; Papkova et al., 2016).

Conclusions

Thus, the obtained results of REM sorption studies on different sulfocationites showed that the most acceptable for further studies on sorption under dynamic conditions to extract REM from hydrochloric acid solutions after phosphogypsum leaching are Purosorb SAC 140 and Puromet MTC 1600 in Na-forms, which showed the best REM recovery rates, 43.7 and 45.2 %, respectively.

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