

ON SORPTION OF THE RARE-EARTH ELEMENTS

Sultan Yulusov, Tatiana Y. Surkova, Leila U. Amanzholova, Madina B. Barmenshinova

Satbayev University
22 Satbayev str., Almaty, Republic of Kazakhstan
E-mail: s1981b@mail.ru

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ABSTRACT

The paper reports a kinetic study of the rare-earth elements' sorption from the pregnant and simulated solutions. The data obtained by IR spectroscopy analysis method is focused on the behavior of ion exchanger systems containing the individual rare-earth elements studied. It is suggested that the latter form hydrated complexes with the ion exchangers sulfonate group. Their size affects the sorption capacity of the resin towards rare-earth elements.

Keywords: rare earth elements, sorption, productive and model solutions, IR spectroscopy.

INTRODUCTION

Rare-earth elements (REE) have unique properties which provide their application in various spheres of modern industry, especially in science intensive ones. World demand for rare earth products in the last 20 years is developing in an increasing trend. In this regard, new non-traditional sources of REE are being sought. As it was shown in refs. [1, 2], uranium production solutions are one of these sources. Extraction is usually used to obtain REE from these solutions. Sorption is less common.

Sorption extraction is in fact preferable in this case because of REE low content in these solutions, which in turn results in significant extractant losses. In addition, as a rule, extractants are more toxic than sorbents.

The application of the IR spectroscopic analysis will provide to reveal the state of REE ions and impurity elements in the ion exchange system and hence make predictions about their behavior during sorption. This will lead to the development of new rational methods for their extraction accounting for the properties of the sorbents and the industrial solution.

EXPERIMENTAL

Subject of research

Industrial (pregnant) solutions from underground uranium leaching and simulated one were used in this investigation. The first one contained 7,8 mg/dm³ Y, 27,7

mg/dm³ Ce, 5,9 mg/dm³ Dy, 15,8 mg/dm³ La, 5,5 mg/dm³ Sm. The main elemental impurities referred to iron and aluminum, whose content was 0,45 g/dm³ and 0,81 g/dm³, correspondingly. The simulated solutions were prepared by introducing the individual REE studied in the form of sulfuric acid salts at a concentration of 0,3 g/dm³ to an aqueous H₂SO₄ solution of a concentration of 10 g/dm³.

Experimental technique

Sorption from the purified pregnant solutions was carried out in accordance with the generally accepted experimental technique [3]. The cation-exchange material KU-2-8n was used.

Methods of analysis

The REE concentration in the solution was determined using Perkin Elmer optical emission spectrometer with an inductively coupled plasma 'Optima 2000DV'.

The IR spectroscopic studies were carried out on "Avatar 370" FT-IR spectrometer in the spectral range of 4000 cm⁻¹ - 400 cm⁻¹ using tablets prepared by pressing 200 mg KBr with 2 mg of the sample. Prefix for the experiment: Transmission E.S.P.

RESULTS AND DISCUSSION

Fig. 1 illustrates the kinetics of REE sorption by KU-2-8n ionite from the PSV production solution. An ambiguous time dependence of REE degree of extraction is outlined. The decrease of the degree of sorption during

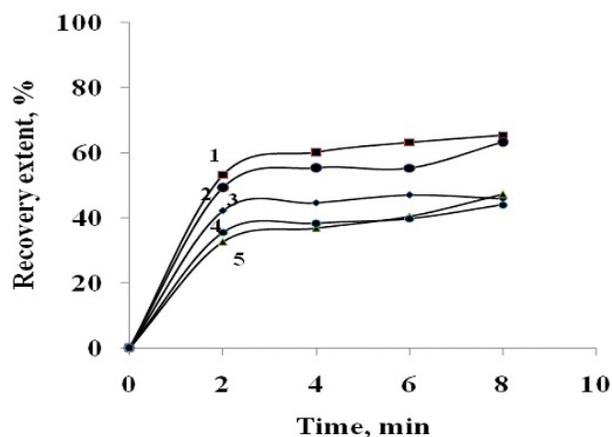


Fig. 1. Change of the sorption degree of REE from the productive solutions with the time (1 - Ce; 2 - La; 3 - Y; 4 - Dy; 5 - Sm).

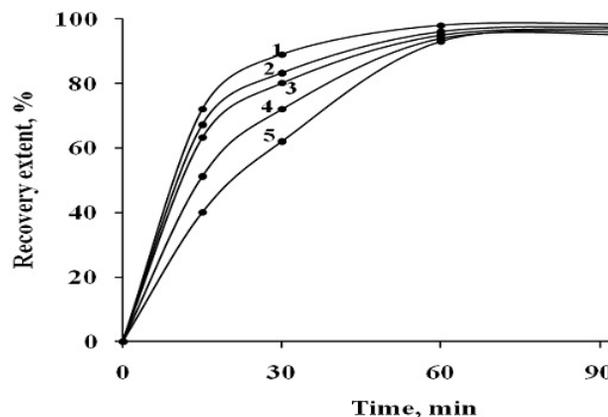


Fig. 2. Change of the sorption degree of REE from the model solutions with the time (1 - La; 2 - Ce; 3 - Y; 4 - Dy; 5 - Sm).

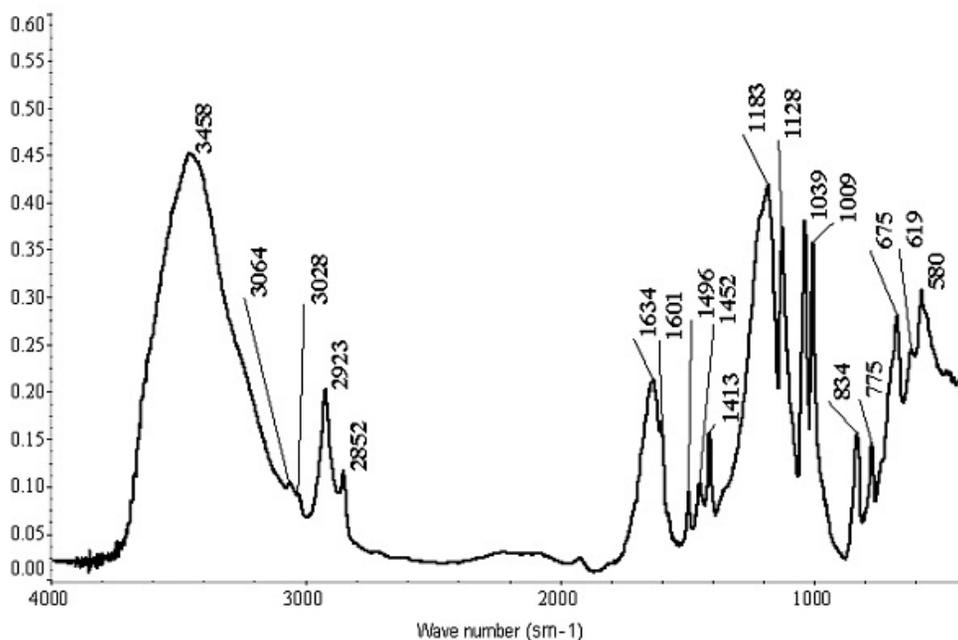


Fig. 3. IR-spectrum of the initial ion exchanger.

the first two hours leads to the line: Ce-La-Y-Sm-Dy. The REE nature, their concentration and that of the impurities present are among the factors affecting the process.

The effect of REE nature was followed using a model solution prepared by the procedure described above. The results obtained are shown in Fig. 2. It is evident that the line of the REE studied determined on the ground of decrease of their maximum degree of sorption

during the first hour is as follows: La - Ce - Y - Sm - Dy.

IR spectroscopic studies of the ionite saturated with REE is conducted to identify the causes of the regularity obtained in view of the information provided on the state of REE in the ion exchange system. The results obtained are presented in Figs. 3 - 5.

The spectrum of the initial sorbent KY-2-8H in H-form (Fig. 3) shows bands referring to the styrene-

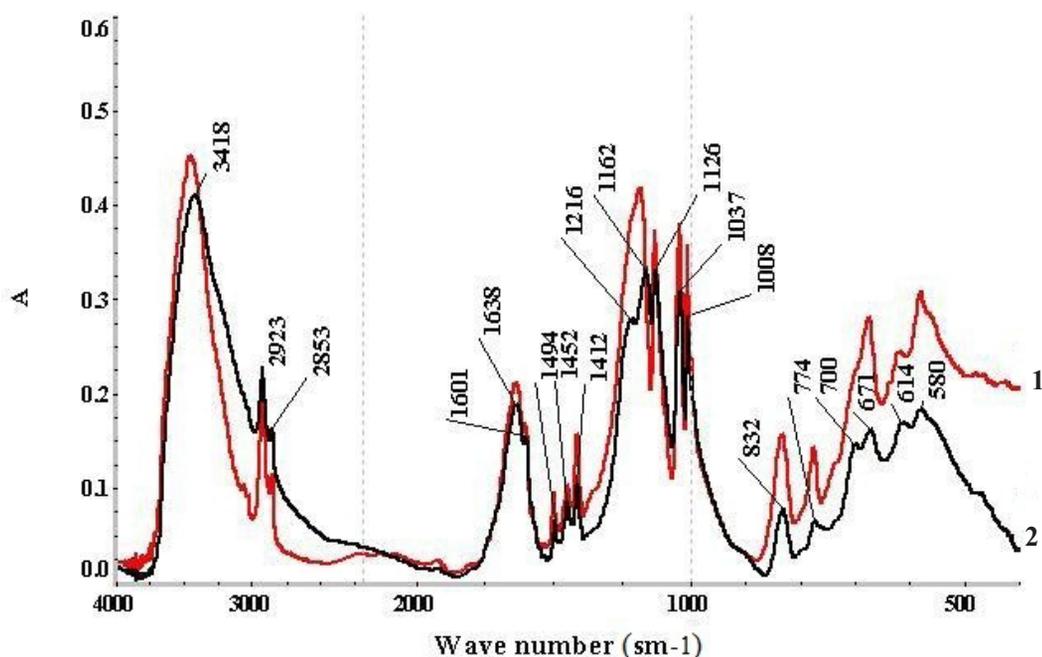


Fig. 4. IR-spectra: 1 - the initial ion exchanger; 2 - lanthanum saturated ion exchanger.

divinylbenzene matrix of the ion exchanger: 3064 cm^{-1} , 3028 cm^{-1} , 2923 cm^{-1} , 2852 cm^{-1} , 1601 cm^{-1} , 1496 cm^{-1} , 1452 cm^{-1} , 1413 cm^{-1} , 1183 cm^{-1} , 834 cm^{-1} , 775 cm^{-1} , 675 cm^{-1} [4 - 8]. The intensive absorption bands of maxima at 1183 cm^{-1} , 1128 cm^{-1} , 1039 cm^{-1} , 1009 cm^{-1} correspond to the stretching vibrations of the sulfo groups in the sulphocathionites [4 - 6], while the bands at 619 cm^{-1} and 580 cm^{-1} correspond to the vibrations of sulphocathionites C-S sulfo groups [4, 5].

Fig. 4 shows the spectrum of the ion exchanger saturated with lanthanum. It is seen that the absorption band of the stretching vibrations ν (OH) is broadened and shifted by 40 cm^{-1} to the long-wave region. Splitting (maxima at 1162 cm^{-1} and 1216 cm^{-1}) of the absorption band of asymmetric stretching vibrations of the S = O bond is noted in Fig. 3. It indicates a transition of the sulfate groups to a polarized state induced by the lanthanum ions present. A decrease in the intensities of the ionite absorption bands, and appearance of a band in the region of extra-plane deformation vibrations of benzene ring C-H bonds at 700 cm^{-1} in the spectral profile [8] are also observed.

The spectra of the ion exchanger saturated with Ce, Y, Dy, Sm do not differ significantly from that of sample containing lanthanum. Based on IR spectroscopic stud-

ies, it can be assumed that REE form hydrated complexes with the sulfonate group of the ion exchanger. Having smaller dimensions than the anion of the complex, REE cations polarize it. The more the anion is polarized, the more it is hydrated, which ultimately increases the size of the polarized particle. Due to the different polarizing effect of the cations on the anion of the complex determined by the different structure of their electron shells, the hydrate shell of the polarized particles has a different size. Hence, the dimensions of the particle as a whole are different, which is reflected in IR spectra by the different intensities observed (Table 1). The particle size affects the degree of sorption of individual REE.

A mathematical processing of cation exchange spectra in the range of 1400 cm^{-1} - 900 cm^{-1} (Fig. 5) is carried out. It is found that the intensity of the band at 1220 cm^{-1} referring to the stretching vibrations of the sulfo groups coordinated by REE decreases following the line: La (0.138), Ce (0.128), Y (0.126), Sm (0.125), Dy (0.103). A correlation with the dependence of REE atomic radii on the coordination number [9] is observed as the line in this case is as follows: La (1,877Å), Ce (1,825Å), Y (1,801Å), Sm (1,802Å), Dy (1,773Å). Thus, it can be assumed that the REE cation interacts with the sulphonic groups of the ion exchanger forming a com-

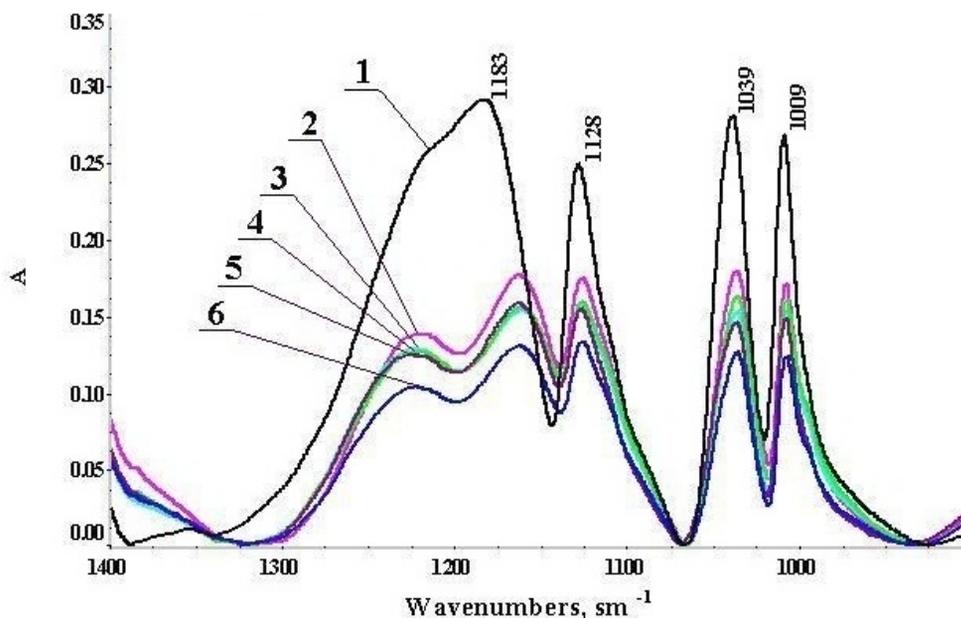


Fig. 5. IR-spectra: 1 - the initial ion exchanger; 2 - La; 3 - Ce; 4 - Y; 5 - Sm; 6 - Dy.

plex surrounded by water molecules. The latter enter the near sphere of the hydrate shell. The size of the formed complex affects in turn the degree of sorption of the individual REE on the ion exchanger used.

Thus, the IR spectroscopic data referring to the value of the maximum degree of sorption provides to show that its decrease with REE nature leads to the following line: La-Ce-Y-Sm-Dy. This is in accord with the dependences described above.

CONCLUSIONS

The investigation carried out shows that one can estimate the effect of the nature of rare-earth elements on the degree of their sorption extraction on the ground of IR spectroscopic data obtained.

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