17TH EUROPEAN MEETING ON SUPERCRITICAL FLUIDS

7TH EUROPEAN MEETING HIGH PRESSURE TECHNOLOGY

Institute of Chemical and Environmental Technology (ITQUIMA)

APRIL 8 - 11, 2019

PROGRAMME

UCLM Universidad de Castilla-La Mancha
CAMPUS DE EXCELENCIA INTERNACIONAL

itquima UCLM

A model for supercritical-fluid extraction of rare earth elements from phosphogypsum leaching solutions

Tokpayev R.R*., Khavaza T.N., Atchabarova A.A., Beknazarov K.I., Nefedov A.N., Nauryzbayev M.K.

Center of Physical Chemical Methods of Research and Analysis of Al-Farabi Kazakh National University, 050012, Almaty, Republic of Kazakhstan

**Corresponding author: rustamtokpaev@mail.ru*

1. Introduction

Progress in the rare earth industry over the last 5-7 years is associated with a decrease in the quota for the export of rare earth elements (REEs) by China, as a result of which most countries rely on their own strategic resources, as a result they have activated the development and implementation of programs for the development of this industry[1]. Kazakhstan has a significant amount of mineral raw materials of rare and REEs, but unfortunately, the development of rare earth deposits does not occur, which is due to several factors: the loss of the market during the economic reform period, the lack of processing industries in the country using rare metal and rare earth products. One of the promising sources of rare-earth metals is the waste of the phosphorus industry in Kazakhstan, in particular phosphogypsum, which is formed during the processing of phosphate rock at the "Kazphosphate" LLP. To date, the volume of waste phosphogypsum has more than 15 million tons, the total content of REEs in which is ~ 3 kg/t. The process of extracting rare-earth metals from phosphogypsum is very long and laborious, and as a result, the method of mathematical modeling was applied to optimize the decomposition of phosphogypsum and supercritical fluid extraction of rare-earth metals from leaching solutions.

2. Results and discussion

To determine the parameters of the maximum yield of REEs from phosphogypsum, a mathematical model was developed for the process of leaching and supercritical extraction of REM from phosphogypsum with a mixture containing sc-CO_2, TBP, HNO_3, H_2O. The model is based on the equilibrium reactions of the components present in the mixture. In the case of phosphogypsum decomposition in the presence of nitric acid, Ca^{2+}, Fe^{2+}, Al^{3+}, Mg^{2+}, La^{2+}, Ce^{2+}, Nd^{3+}, Y^{3+}, H_2O, H^+, Cl^-, SO_4^{2-}, PO_4^{3-}, sc-CO_2, TBF were chosen as independent components of the mixture. The systems of chemical reactions with their participation were recorded in the form of a matrix, where the processes of sedimentation with the participation of anions SO_4^{2-}, PO_4^{3-}, OH^- and complexation with sc-CO_2-TBP were taken into account. The effect of temperature on the equilibrium involving components of the mixture was taken into account through the Arrhenius form of representing the equilibrium constant:

$$K_f = A^f \left(T/T_{ref}\right)^{n_f} exp\left(\frac{E^f}{RT}\right),$$

where A^f - is the frequency factor; T_{ref} - relative temperature 1°K; n_f - reflects the stoichiometry of the process varies from 0 to; E^f – is the activation energy.

The SF extraction of REM was simulated using the program for calculating the equilibrium in heterogeneous systems[2]. The results of modeling the extraction of yttrium and lanthanum, depending on the initial content of nitric acid in the system, are presented in Fig. 1.

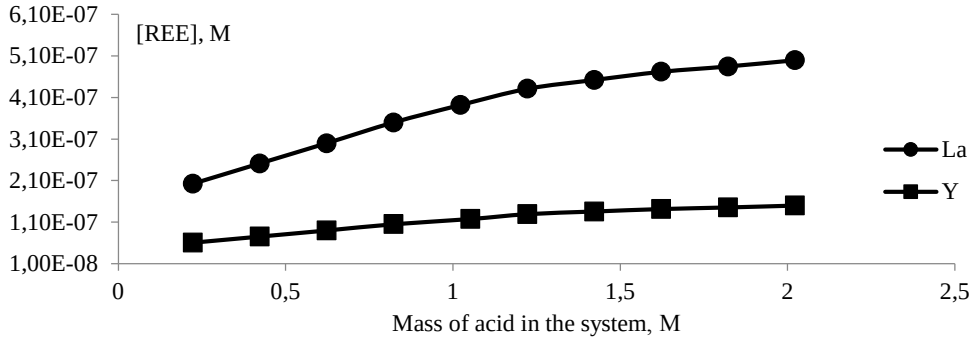

Figure 1. Change in the equilibrium concentrations of lanthanum and yttrium in the system depending on the initial acid content

It can be seen from the Fig. 1 that increasing of acid content in the system, the equilibrium concentration of rare-earth metals increases in the liquid phase. At the same time, the equilibrium content of rare-earth metals in comparison with the experimental values obtained in leach mixtures is lower. This is explained by the fact that in practice we used more concentrated solutions of acids, which made it possible to increase the equilibrium concentration of metals in the organic phase of the solution. It has been established that with a decrease in the concentration of water in the system and an increase in the concentration of leaching acid, the content of REM in the phase of sc-CO_2-TBP increases.

3. Conclusions

Modeling taking into account the equilibrium in a complex system based on raw materials - phosphogypsum, obtained at the “Kazphosphate” LLP showed the possibility of applying model calculations to optimize the composition of the extractants sc-CO_2 in the presence of TBP, which allows speeding up the search for optimal conditions for extracting REM from man-made phosphogypsum raw materials.

References

1. D.V. Sevastyanov, M.S. Doriomedov, I.V. Sutubalov, G.S Kulagina. Directions of development of industrial technologies in the field of rare-earth metals // Trudy VIAM. - 2018. - №1. - P 61.
2. Vasiliev V.P., Borodin V.A., Kozlovsky E.V. The use of computers in chemical and analytical calculations, M: Higher school. - 1993. - 112 p.