ADSORPTION OF LANTHANIDES ON Na-MORDENITE

Agnieszka GŁADYSZ-PŁASKA, Marek MAJDAN

Faculty of Chemistry UMCS, 20-031 Lublin, Maria Curie-Skłodowska square 2, Poland

The adsorption of the lanthanides (except for Pm) on the mordenite was investigated under various solution conditions of nitrate ion concentrations ($[NO_3^-]$: 0.001-2 mol/dm³) and total lanthanide concentrations 0.0005 mol/dm³. Zeolite CBV 10 A (mordenite) in the form of powder has been delivered by Zeolyst International. Chemical composition of the samples has been reported by the supplier as: Na₂O – w/w 6.6%, SiO₂ /Al₂O₃ = 13.

EXPERIMENTAL

The aqueous phases (100 cm³ volume) containing lanthanide nitrates (0.0005 mol/dm³; 99.9% purity, Sigma Aldrich) dissolved in sodium nitrate with concentrations ranging from 0.001 mol/dm³ to 2 mol/dm³ (pure, Sigma Aldrich) were equilibrated through 4h with 100 mg samples of the sodium form of the mordenite in temperature $23\pm1^{\circ}$ C. The aqueous phase was separated from the solid residue by filtration (paper filter Filtrak 390, Polskie Odczynniki Chemiczne) and the concentration of the lanthanides was determined spectrophotometrically using Arsenazo III [1]. The concentration of the lanthanide in the solid phase c_{Ze} was found as the difference between the initial concentration c_{in} and the concentration in the equilibrium aqueous phase c_{aq} . The initial and equilibrium pH values were controlled using combined glass electrode (Sigma Chemical Co.) connected to the pH meter (CX-731 type, Elmetron Co.).

RESULTS AND DISCUSSION

The change of the distribution constants of the lanthanides in the system $Ln(NO_3)_3$ -NaNO₃-mordenite with the nitrates concentrations is given in Figure. The distribution constants K_d are defined as:

 $K_d = (c_{Ze}/c_{aq})V/m.$ (1) where: V and m denote the volume of aqueous phase and the mass of the adsorbent respectively.

The nonmonotous change of log K_d values with the atomic number of the tripositive lanthanides is evident. For the first tetrad of the lanthanides (La-Nd) the concave deviation from the interpolation straightline in the run of K_d values is observed. Second tetrad (Pm-Gd) was not considered since we do not have the data for Pm. For the third tetrad (Gd-Ho) the negative deviation from the interpolation



line is noticed. For the fourth tetrad (Er-Lu), similarly as in the case of the first tetrad, concave deviations are evident especially for higher concentrations of nitrates $(0.2 - 2 \text{ mol/dm}^3)$. According to Kawabe [2-6], the concave tetrad is observed when the covalency in lanthanide ion-ligand in products of the complexation reaction is Fig.1. The changes of distribution constants (K_d) of the lanthanides in the system NaNO₃ – mordenite with nitrate concentrations.

weaker, i.e. Racah parameters are higher, than in the substrates. Therefore for the ions: $La^{3+}-Nd^{3+}$, when the ion exchange-complexation reaction of the aquoions $Ln(H_2O)_9^{-3+}$ with the sodium form NaZe of the zeolite is considered: $Ln(H_2O)_9^{-3+} + 3NaZe \leftrightarrow Ln(H_2O)_x Ze_3 + 3Na^+ + (9-x) H_2O$ (2)

 $Ln(H_2O)_9^{3+} + 3NaZe \leftrightarrow Ln(H_2O)_x Ze_3 + 3 Na^+ + (9-x) H_2O$ (2) covalency of the Ln-O bond in the $Ln(H_2O)_x Ze_3$ species is weaker than in aquocomplex $Ln(H_2O)_9^{3+}$.

Apart from above mentioned reactions the complexation of the lanthanide ions by nitrates should be taken into account, according to general reaction:

 $Ln(H_2O)_n^{3+} + NO_3^{-} \leftrightarrow Ln(H_2O)_x NO_3^{2+} + (n-x) H_2O$ (3) where n=9 and 8 for the light and heavy lanthanides [7].

REFERENCES

- 1. Z. Marczenko, M. Balcerzak. "Spektrofotometryczne metody w analizie nieorganicznej", Wydawnictwo PWN SA, Warszawa 1998, p.353
- 2. A. Ohta, I. Kawabe, Geochem. J., 34(2000)455
- 3. A. Ohta, I. Kawabe, Geochem. J., 34(2000)439
- 4. I. Kawabe, A. Ohta, N. Miura, Geochem. J., 33(1999)181
- 5. A. Ohta, S. Ishii, M. Sakakibara, A. Mizuno, I. Kawabe, *Geochem. J.*, 33(1999)339
- 6. I. Kawabe, T. Toriumi, A. Ohta, N. Miura, Geochem. J., 32(1998)213
- M. Majdan, A. Gładysz-Płaska, S. Pikus, D. Sternik, O. Maryuk, E. Zięba, P. Sadowski, J. Mol. Struct. 702(2004)95