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# Ion-exchange of amino- and aqua-complexes of nickel and cobalt in natural clinoptilolite

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# A R T I C L E I N F O

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# ABSTRACT

Natural clinoptilolite from Caimanes deposit (Cuba) modified to ammonium form was used for removal and recuperation of nickel and cobalt by ion-exchange from residual ammoniacal liquors of the nickel hydrometallurgical industry. Metal cations in these residual solutions exist in amino- and aqua-complex form, such as  $[Ni(H_2O)_6]^{2+}$ ,  $[Ni(NH_3)_6]^{2+}$  and  $[Co(NH_3)_6]^{3+}$ . The subject of the present study is to analyze the influence both of the nature of these complex-cations and the temperature on its ion-exchange in the ammonia modified clinoptilolite. The main kinetic parameters associated with these exchanges were determined. An increase in the attraction interaction between the metallic-cation (Ni<sup>2+</sup> and Co<sup>3+</sup>) and their ligands (H<sub>2</sub>O and NH<sub>3</sub>) affect the complex-cations exchange. Kinetic of these sexchanges is favored in the following order:  $[Ni(H_2O)_6]^{2+} > [Ni(NH_3)_6]^{2+} > [Co(NH_3)_6]^{3+}$ . For steric reasons the exchange of these complex-ions from solution must occur via cations of smaller size, i.e. single Ni<sup>2+</sup> and Co<sup>3+</sup> and/or cations with a number of water or ammoniac molecules smaller than 6. The exchanges are favored by an increasing of the temperature, which is confirmed by a substantial raise of the rates of the diffusive processes and increased amounts of removed from the solutions ions of nickel and cobalt. This effect in the case of nickel is especially pronounced, probably due to increasing of exchange site's accessibility compared with exchange at low temperature.

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#### Introduction

The ion exchange property is one of the main features that zeolites exhibit. This feature is important from two points of view. First of all, cations introduced in zeolite matrices by ion exchange treatment allow subsequent development of materials for catalytic, medical and antibacterial applications, between many others [1–6]. Secondly, one of the most important applications is the processes of removing of pollutants such as heavy metals from the wastewater of industrial plants, soil, and other sources [7–12]. For the first branch of zeolite applications synthetic zeolites are used mainly due to their uniformity in phase and chemical composition, and absence of impurities. As a consequence, it made their price higher. In turns, chip and abundant natural zeolites are very suitable material for harmful ions removal, because polimetallic cation mixture inherent to natural zeolitic rock, mineral impurities, and as a rule several zeolitic phases presenting in the row natural mineral do not hinder their use for accumulation of undesired cations in the ambient, because any future use of this material is not assumed.

Cation exchange properties are very important applications, for

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example in environment protection to trap radioactive cations. It is well known that after Chernobyl catastrophe "permeable reactive barriers" made from natural zeolites, especially from clinoptilolites [13] were applied to prevent diffusion of the radionuclides [14,15]. The authors [14] summarized the consequences of Chernobyl catastrophe for people and the environment and information on successful treatment using widely available natural zeolites. Similar methods were used to tolerate Fukushima nuclear contamination. The Japanese government hopes that the zeolites help reduce radioactive contamination of the sea. Zeolites have previously been used in cleaning the anthropogenic accidents in the world, such as the realized in the Soviet Union 1978 underground nuclear explosion "Kraton-3" in Vilyuy, Yakutia [13], and 1979 "Three Mile Island" nuclear disaster in the United States [15]. Availability and reasonable cost of natural clinoptilolite together with its high selectivity towards Sr<sup>2+</sup> and Cs<sup>+</sup> radionuclides make possible the use of a clinoptilolite tuff as a barrier.

The potential use of natural zeolites as cation exchangers in environmental protection include scavenging of fall-out products from living hosts [15], ammonium removal from municipal sewage [7], desalination treatment of seawater [16], or remediation of hazardous heavy metal-polluted soils [17] or sediments [18].

Ion-exchange processes in zeolites are affected by several factors such as concentration and nature of cations and anions, complexing agents, pH, temperature and structure of the zeolite. Many reports

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on influence of these factors are available in the literature [19-23] but most of them have been carried out with water solutions of single salts, where the cations are in single form or forming low-stable aqueous complexes. There are considerably less of the available information about exchange in zeolites from mixed solutions and their exchange mechanism, as well as with ion-exchange of stable complex cations. However, this knowledge is very important because it can alter the selectivity and other qualities of the zeolitic exchange material. For example, most of zeolites prefer the Ag<sup>+</sup> cation instead of Na<sup>+</sup>, but they retain the Na<sup>+</sup> instead of  $[Ag(NH_3)_2]^+$  complex cation [24]. A study on ion exchange process of Cu<sup>2+</sup>, Cr<sup>3+</sup> and Fe<sup>3+</sup> in natural clinoptilolite using organic solvents (ethanol and acetone) instead of water, showed that the selectivity of exchange of the complex cations formed in the presence of the certain solvent may change radically [25]. It was reported [26] that the presence of Cr(VI) significantly diminished the removal of  $Pb^{2+}$  and  $Cd^{2+}$  in clinoptilolite, which is attributed to the formation of anionic complexes, between Cr(VI) and the metallic cations ( $Pb^{2+}$  and  $Cd^{2+}$ ), with little affinity for cationic exchange sites. Studies on uptake of platinum and copper tetra-ammine complexes ( $[Pt(NH_3)_4]^{2+}$  and  $[Cu(NH_3)_4]^{2+}$ ) into zeolites (Y, MOR and MFI) reported [27] that an over-exchange of both metals take place. The authors suggest that these metal cations interact with zeolites by two mechanisms, ion exchange at the Al exchange sites and electrostatic adsorption at silanol groups. It is outlined that the  $[Cu(NH_3)_4]^{2+}$  complex is converted to the dimer  $Cu_2(OH)^{2+}$  due to the weaker stability of this ammine complex and the decrease in local pH near the zeolite surface, which do not take place for the platinum.

In addition, the processes that include formation of complexcations on zeolites are important to develop materials with industrially important properties, such as catalysts, medicine, adsorbents, etc. For example, the ammonia oxidation process to nitrogen and water over Cu–Y zeolites in the range from 160 to 185 °C is favored by in situ formation of  $[Cu(NH_3)_4]^{2+}$  complex during this process [28]. Other example is that Y zeolite modified with 1-(2-pyridylazo)-2-naphthol transition metal complexes of cobalt(II), nickel(II), copper(II) and zinc(II) showed to have catalytic activity for the oxidation reactions of cyclohexene and cyclohexanol, by using tert-butylhydroperoxide as the oxidizing agent [29].

The use of Cuban natural clinoptilolite for removal and recuperation of nickel and other heavy metals from watery solutions and ammoniacal-carbonate residual liquors of the nickel hydrometallurgical industry by ion exchange has been the subject of several studies [30–32]. In this case the aim is not only removing of harmful cations, but recuperation of valuable metals too. Influence of the temperature, cation concentrations, presence of carbonate anions and formation of low soluble phases during the ion-exchange in the clinoptilolite with watery solutions of single salts, where the cations are in single form, was analyzed in such studies. But, metallic cations in these residual solutions are present, fundamentally, in form of amino complexes, at temperatures of 80 °C. Among all these amino complexes, the nickel(II) and cobalt(III) complex-cations attract special attention due to their dominant contents and economic value, especially for nickel. However, an in-depth study of this process to explain the behavior of ion-exchange of these complex-cations in the zeolite has not been reported yet. Such study is important because it has direct relationship to the efficiency of removing of nickel and cobalt from industrial waste solutions, where the metals are present in the form of amino-complexes to prevent environmental contamination and accomplish simultaneous extraction of high-value products.

The present work is aimed at gaining information on the ionexchange process of hexacoordinated amino- and aqua-complexes of nickel(II) and cobalt(III) in the clinoptilolite from Caimanes deposit (Moa, Cuba) modified to ammonium form. The influence of the nature of the exchanged cations and the temperature during the ionexchange between  $NH_4^+$  and these complex cations is analyzed. The main kinetic parameters associated with ion-exchange processes are determined and a mechanism of ion exchange is proposed.

#### Experimental

# Materials and preparation

The main phase present in the zeolitic rock (raw mineral) from Caimanes deposit, Moa, Cuba, is clinoptilolite (Framework Type Code applied by International Zeolite association for Clinoptilolite is HEU). From this rock, a purified sample with particles size class + 0.25– 0.5 mm was obtained following a procedure similar to described elsewhere [31,32]. This sample resulted in a mixture of about 85% clinoptilolite, 5.5% quartz and 9.5% of other phases (mordenite, montmorillonite, feldspar, etc.). The chemical composition of this purified sample in oxide form is: 63.2% SiO<sub>2</sub>, 10.13% Al<sub>2</sub>O<sub>3</sub>, 3.92% CaO, 3.05% Fe<sub>2</sub>O<sub>3</sub>, 1.3% MgO, 1.42% K<sub>2</sub>O, 0.93% Na<sub>2</sub>O and 13.9% H<sub>2</sub>O. Herein this purified zeolite is referred to as clinoptilolite (CLI).

Ammonium form of clinoptilolite (NH<sub>4</sub>-CLI) was obtained from CLI by treatment with NH<sub>4</sub>Cl solution at 100 °C with reflux, using ratio of 5  $\times$  10<sup>-3</sup> equiv. NH<sub>4</sub><sup>+</sup> / g clinoptilolite, during 72 h. The NH<sub>4</sub>Cl solution was replaced six times. The solid was filtered and washed with distilled water until the Cl<sup>-</sup> ions were totally removed, then oven-dried at 110 °C, and stored in a desiccator to ensure constant water content. The total amount of exchanged ammonium ions in the NH<sub>4</sub>-CLI sample was 1.45  $\pm$  0.15 NH<sub>4</sub><sup>+</sup> mequiv. per gram of zeolite (1.45  $\pm$  0.15 mequiv./g). The Ca, Na, K and Mg contents presents in the NH<sub>4</sub>-CLI sample, expressed in oxide form, are 0.39% CaO, 0.97% MgO, 1.07% K<sub>2</sub>O and 0.79% Na<sub>2</sub>O. These percents were determined using atomic absorption spectrometry. The concentration of ammonium ions was determined using the Nessler reagent.

Ion-exchange between  $\mathrm{NH_4}^+$  and the amino- and aqua-complex cations of nickel and cobalt

NH<sub>4</sub>-CLI samples were combined with NiCl<sub>2</sub>,  $[Ni(NH_3)_6]Cl_2$  and  $[Co(NH_3)_6]Cl_3$  solutions in a relation of 1 g of NH<sub>4</sub>-CLI by 20 mL of solution, applying constant agitation. The equivalent molar concentration of Ni<sup>2+</sup> and Co<sup>3+</sup> in the respective solutions was 0.15 equiv./L. The experiments were conducted for each cation in study, i.e.  $[Co(NH_3)_6]^{3+}$ ,  $[Ni(NH_3)_6]^{2+}$  and  $[Ni(H_2O)_6]^{2+}$ , at the temperature of 25 °C and 80 °C. At different times, the solutions and the solid phase (zeolite) were separated by filtration. The nickel and cobalt concentrations in the zeolite and liquid phase after the treatment were determined using atomic absorption spectrometry.

The main kinetic parameters associated with exchange of complex-cations were determined. The maximum estimated errors for these parameters were calculated carrying out a propagation of the experimental errors.

# **Results and discussion**

The results of the treatment of the ammonium form of clinoptilolite (NH<sub>4</sub>-CLI) with NiCl<sub>2</sub>, [Ni(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>2</sub> and [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> solutions at 25 °C and 80 °C are shown as kinetic curves in Fig. 1a–c. These curves show the variations of the Ni<sup>2+</sup> and Co<sup>3+</sup> mequiv. retained per gram of NH<sub>4</sub>-CLI ( $Q_t$ ) as a function of time (t) during the treatment. The nickel and cobalt retention can be explained by exchange of the corresponding metallic complex cations with the NH<sub>4</sub><sup>+</sup> ions from zeolitic exchanger (NH<sub>4</sub>-CLI), according to the following general reactions:

 $[Ni(H_2O)_6]^{2+}_{(aq)} + (NH_4)_2 - CLI_{(S)} = = [Ni(H_2O)_n] - CLI_{(S)} + 2NH_4^+_{(aq)} + mH_2O$ (1)

 $[Ni(NH_3)_6]^{2+}(aq) + (NH_4)_2 - CLI_{(S)} = = [Ni(NH_{3n}] - CLI_{(S)} + 2NH_4^+(aq) + mNH_3 (2)]$ 

 $[Co(NH_3)_6]^{3+}{}_{(aq)} + (NH_4)_3 - CLI_{(S)} = = [Co(NH_{3n}] - CLI_{(S)} + 3NH_4^{+}{}_{(aq)} + mNH_3 (3)$ 

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