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# Selective ion exchange onto Slovakian natural zeolites in aqueous solutions

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**Abstract** Ion exchange isotherms have been measured and plotted for the uptake of cesium, barium, cobalt, zinc, silver and amonium onto clinoptilolite- and mordenite-rich tuffs of Slovakian origin selectively for both the natural and near homoionic Na form as well, using the radioanalytical determination. The higher quality clinoptilolite-rich tuff has been proven to be effective for a potential radionucleides removal in native form according to the following selectivity sequence: $Ag^{+}$,$Ba^{2}$,$Cs^{+}$>$NH_4^{+}$>$Co^{2+}$, while parent tuff in Na exchanged variety exhibited a little different sequence according to: $Ag^{+} > NH_4^{+} > Ba^{2+} > Cs^{+}$. The raw and Na exchanged mordenite-rich tuffs proved subsequently more or less similar selectivity : $Ag^{+} > Zn^{2+} > Cs^{+}$, $Ba^{2+} > Co^{2+}$ and $Ag^{+} > Zn^{2+}$.

**Keywords** Clinoptilolite- and mordenite-rich tuffs · Ammonium and some radioisotopes · Ion exchange · Selectivity sequence · Radioanalytical determination · Radionucleides

## Introduction

Although, If the process of ion exchange may remain for the globe history as discovered in the year 1850, it has not been certainly applied as an industrial separation process untill 1905, when the German inventor Richard Gans demonstrated it as a unique process for water softening as well as removal of iron and manganese from polluted waters. About 50 years passed, mainly after the second WW II, when an extensive development of the new organic ion exchangers, e.g. sulfonated and aminated copolymers of styrene and divinyl benzene with superior stability and easier recovery or their regeneration, fabricated usually in oil refineries or petrochemical companies, enabled to expand rapidly all the ion exchange processes for plenty of industrial applications [1].

Nevertheless, the higher thermal and radiation resistance of some natural zeolites in regard to synthetic ion exchange resins and their excellent selectivity for large weakly hydrated cations and noxious radioisotopes allowed to combine a development of entirely new technological applications of natural zeolites in the next decades. This phenomenon has not generally displaced competetive synthetic ion exchangers in existing environmental applications. Oppositively, initiated a development of entirely new processes for which the synthetic resins were not well suited till that time [2].

In the 1950s the Union Carbide Corporation (currently Dow Chemicals) and some oil companies like Shell Development Companies in USA, Canada and Mexico started to use the natural zeolites (erionite, chabazite and mordenite preferentially) as cheap molecular sieve amendments for purification and desiccation of low grade natural gases [3].

Although, the zeolites possessed outstanding ion exchange properties, they have not found any significant use

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commercially as ion exchangers until the early 1960s. This was largely due to the lack of availability and lack of knowledge about their properties. The first environmental application was developed by Ames in 1961 for the treatment of high level alkaline wastes from the Purex Processing of spent nuclear fuel. Here, zeolite's high stability against ionizing radiation in aqueous solutions at elevated temperatures and pH levels together with their excellent selectivities for certain radioisotopes, caused that these minerals have been applied for recovery and concentration of Cs (137) and Sr (90) radioisotopes in long term storage [4].

A zeolite ion exchange process was used also in the Hanford Atomic Energy Project for the separation of radioactive cesium from highly radioactive liquid waste. That waste had a cesium content in order of 0.1 mmol per liter and approximately 4.5 mol per liter of sodium concentration. Separation of the radioactive cesium from high level liquid waste prior to evaporation and solidification of the waste in large underground storage tanks was necessary, on account of the excessive heat generation, resulting from Cs (137) fission reactions in salt cake. Consequently to that the liquid waste was pumped downflow through a bed of chabazite-bearing rock until the cesium breakthrough occurred [5].

At the Idaho National Engineering Laboratory, a low-level radioactive waste water from an irradiated fuel storage basin was passed through four clinoptilolite-rich tuff columns in parallel. Each column consisted of two drums connected in series. When radionucleides broke through the bottom drums, the top drums were replaced and removed from use, sealed and burried as the solid waste [4].

Clinoptilolite-rich tuff helped to lower the threat of radiation impact of the Chernobyl accident in 1986, when about a half million tonnes of clinoptilolite-bearing rocks from all former Soviet Union zeolite open mines were successfully used to reduce and buffer the huge radioactive explosion [5, 6]. In addition, filters of clinoptilolite-rich tuffs were suggested to extract radionucleides from the drainage water of the encapsulated Chernobyl nuclear power plant. The filtration reduced radiocesium (137) by 95% and radiostrontium (90) by 50–60%. The decontamination of potable water from Dneper river using a combination of dust-like clinoptilolite with aluminium sulphate coagulation and followed by clinoptilolite filtration led to substantial decrease of radioactivity [6, 7].

The presence of clinoptilolite and mordenite in undersaturated tuffs at Yucca Mountain in Nevada drew attention as a possible high level radioactive waste repository. These two zeolites suppose to retard radionucleides migration through a cation exchange due to their exchange capabilities as high as 2.0 meq per gram for Cs (137) and Sr (90), since a significant hazard to environment from waste canisters allowing reliable containment, may expose for over 1,000 years [8].

Some later environmental application of natural clinoptilolite by Ames and Mercer concerned the excellent ammonium ion selectivity of clinoptilolite and led in the early 1970s to the development of the ammonium removal process for municipal wastewater. These authors, together with The Plant Engineering Service $CH_2M$-Hill, proposed a tertiary treatment unit for Battelle Northwest/South Tahoe Public Utility District to protect the quality of the Truckee river in California. The regional facility became fully operational in the early 1980s and remained under operation since that time as only one natural zeolite working industrial facility of the world [9].

Current rapid escalation of the raw resource prices and world recession suppose to place the volcanogenic rocks in an improving price-performance position even in near future, comparing to those materials, which are produced synthetically, materials with permanently increasing number, based on the crystalline zeolite or amorphous hydrocarbon matrices. Later ones are known under the trade marks Lewatite, Wofatite, Dowex, Duolite, Amberlite and are fabricated by worlwide recognized Dow Chemicals, Mitsubishi, Merck, Rohm and Haas, Infilco, Philips, Bayer and some other companies.

Based on chemical and mineralogical variabilities of the specific zeolitic rocks and thus their moderate ion exchange and selectivity properties, the exploration of new zeolite ores in several regions of the globe (nowadays over 1,000 occurrences of zeolite minerals reported in more than 40 countries) has initiated an unpredictably wide national research, leading to the versatile industrial applications of these tuffaceous materials, simultaneously [10].

Consequently to above short historical excurse and on the base of encouraging results of Slovakian natural clinoptilolite producer, recently achieved, topic of this paper is to review and characterize the basic ion exchange and selectivity properties of inland (Slovakian) clinoptilolite- and mordenite-rich tuffs.

## Experimental

### Geological features and characterization of inland natural zeolites studied

Zeolite-bearing formations are generally at or close to the surface and require the removal of only small amounts of over burden to expose the ore. In this respect, a mining the zeolitic rocks is relatively simple compared to mining most other mineral commodities. Most zeolites in sedimentary rocks are formed from volcanic ashes or other pyroclastics

**Table 1** The mineralogical and chemical composition of the clinoptilolite-rich tuff from the repository Nižný Hrabovec

| Species | | % | |
|---|---|---|---|
| Clinoptilolite | | 70–85 | |
| Volcanic glass | | 15–20 | |
| Feldspar | | 7–10 | |
| Cristobalite | | 2–4 | |
| Alfa–quartz | | 2–3 | |
| Oxides | % | Metal | % |
| $SiO_2$ | 67.16 | Zn | 0.0024 |
| $Al_2O_3$ | 12.3 | Ba | 0.0353 |
| CaO | 2.91 | Pb | 0.001 |
| $K_2O$ | 2.28 | Sr | 0.01 |
| $Na_2O$ | 0.66 | Cs | 0.0004 |
| $Fe_2O_3$ | 2.3 | Cr | 0.0008 |
| MgO | 1.1 | | |
| $P_2O_5$ | 0.11 | | |
| MnO | 0.14 | | |
| $TiO_2$ | 0.17 | | |
| $H_20$ | 10.9 | | |

**Table 2** The mineralogical and chemical composition of the mordenite-rich tuff from the repository Bartošova Lehôtka–Jastrabá

| Species | | | % |
|---|---|---|---|
| Mordenite | | | 38–40 |
| Cristobalite, volcanic glass, quartz | | | 30 |
| Clay mica | | | 6 |
| Feldspar | | | 8 |
| Plagioclass | | | 6 |
| Montmorillonite | | | 6 |
| Chloritized biotite | | | 4 |
| Kaolinite | | | 2 |
| Oxides | % | Metals | % |
| $Si0_2$ | 70.04 | Sr, Y, Yb, Be, Zr, La, Pb, B, V, Cu, Zn, Ga | 0.01–0.001 |
| $Ti0_2$ | 0.12 | | |
| $Al_2O_3$ | 12.23 | Mn, Ba, P, Ti | 0.1–0.01 |
| $Fe_20_3$ (total) | 1.31 | | |
| CaO | 1.90 | Hg, As | Traces |
| MgO | 0.37 | | |
| $Na_20$ | 0.78 | MnO | 0.03 |
| $K_20$ | 3.43 | | |
| $H_2O$ | 9.64 | $SO_3$ (total) | 0.02–0.05 |
| BaO | 0.09–0.12 | | |
| SrO | 0.04–0.06 | $P_2O_5$ | 0.01–0.03 |

by reaction of the amorphous aluminosilicate glasses and by pervading pore water [11].

Mineralogical and chemical composition of the clinoptilolite-rich tuff from the open mine nearby Nižný Hrabovec presents Table 1 and of the mordenite-rich tuff from the vicinity of Bartošova Lehôtka-Jastrabá Table 2. As can be seen from the date tabelled, the mordenite-rich tuff from Central Slovakian deposit belongs only to the low grade, not valuable zeolitic rock, but the clinoptilolite-rich tuff situated in Eastern Slovakian municipality nearby Nižný Hrabovec contains significant percentage of active mineral clinoptilolite and is consequently classified as an excellent one.

This clinoptilolite-rich tuff has been started to mine industrially even in former Czecho-Slovakia 40 years ego by Zeocem Bystré. The company is producing 90,000 metric tons annually, what is consequently placing the factory to the top natural zeolite producer of the European Union nowaday [12].

## Pretreatment of zeolite samples prior to plotting the ion exchange isotherms

Native zeolite samples were preconditioned into near homoionic sodium form by equilibrating them by means of periodic shaking machine in 10% aqueous sodium chloride solution (10 g in 1L) in a series of batchwise steps during the 3 days everyone, then washed them in distilled water thoroughly untill any precipitate of AgCl with the $AgNO_3$ solution appeared and finally dried at 105 °C for 2 h in laboratory dryer. The raw tuffs, crushed and grinded into the fraction of 0.4–1 mm (35–16 mesh) has been supplied for laboratory experiments from Zeocem Bystré and Geological Survey Banská Bystrica.

## Analytical procedures

Chemicals necessary for the stock solution preparation were purchased mostly from Lachema Brno (made in Czech Republic) with analytical grade quality. Aqueous model solutions of the pollutants examined in adsorption experiments (as chlorides of metallic cations of Cs, Ba, Co and Zn, except the $AgNO_3$, labelled with the adequate radioisotopes of $^{137}Cs$, $^{133}Ba$, $^{65}Zn$ and $^{60}Co$) were determined by means of radio indicator method (spectrometrical set of EG and G Berthold Ortec, USA with a scintillation detector NaI (Tl)). Ammonium ions in the solution have been determined using the Nessler reagent at the wavelength 420 nm on the Diode Array HP Spectrometer 8452A and silver cations by means of AAS Spectrometer using Varian SpectrAA 10 Apparatus with the flame technique.

## Laboratory setup

In order to determine the equilibrium distribution of the cations between the solid and aqueous phases, following laboratory setup was proposed. Equilibrium adsorption and isotherm measurements at the laboratory were done with aqueous model solutions of above labelled cations vs. native and Na-pretreated clinoptilolite-rich as well as mordenite-rich tuffs with the solid-to-liquid ratio 1 g/100 mL, at $T = 23 \pm 0{,}1\ ^\circ C$. All experiments were run in triplicate, keeping the suspensions equilibrated up to 7 h. The total solution normality for each experimentally determined ion exchange isotherm with different zeolitic tuffs (raw and near homoionic Na variety) was 0.1 N.

The equilibrium uptake capacity a (in mg/g) for each sample was calculated according to following mass balance equation:

$$a(eq) = [\{c(i) - c(eq)\}/m] \cdot V$$

where c(i) and c(eq) were initial and equilibrium concentrations of cation examined (in mg/L), m was the mass of zeolite sample (in g) and V was volume of the solution in liters (L).

## Results and discussion

Over the past decades the sieving or partial sieving effects of natural zeolites to various cations have been attributed to following mechanisms or scenario mostly controlling the ion exchange [3, 6, 7, 10, 14, 16]: (i) the cation may be to large to enter smaller channels and cavities within the zeolite structure or in some zeolites the extraframework cation may remained locked and thus not to be replaced, (ii) the charge distribution of zeolitic aluminosilicate framework may be unfavorable for the cation (in uni-univalent cation exchanges, siliceous zeolites, which have a relatively low field strength, are selective for cations with lower charge density, whereas aluminous ones, which have a relatively high field strength, prefer cations with higher charge density, (iii) the size of the hydrated cation in aqueous solution may influence and retard the exchange of cation, since an exchange of solvent molecules occurs with cations, both diffusing through apertures (zeolite cavities and channels are to small for the solvated cation accomodation), (iv) selectivity of zeolite is markedly dependent on its original cationic composition, as not all the cationic sites in the structure can be made available for exchange, (v) the temperature at which exchange is carried out can influence the removal of water of hydration and thus accessibility of sites and improve ion exchange kinetics.

Obviously, naturally occurring zeolites use to prove better selectivity to some monovalent over common divalent cations. A decreasing of the aluminium content in the zeolitic rock increases the average distance between the adjacent anionic sites of the zeolite framework, and thus the difficulty of a single divalent cation to satisfy the field of two adjacent anionic sites [3, 7]. Consequently to that, the preference of the zeolite for divalent cations falls down and that for univalent cations arises. In general, while a zeolite favors the least hydrated ion, the solution phase favors the most highly hydrated ion, by the other words, water molecules in solution compete with the zeolite framework to attract some cations. Large, poorly hydrated cations are preferred in “weak” field zeolites, i.e. those with lower aluminium content and thus lower framework charge density. However, even among those zeolites the relative selectivities to cations in the series differ considerably [14–20].

Exchange of multivalent metal ions is rather complicated due to maintaining the pH level in solution low enough to avoid the solubility limit of metals and high enough to minimize proton exchange or hydrolysis of the zeolite framework. Thus the exchange reactions are primarily accomplished in the most acid resistant clinoptilolite- and mordenite-rich tuffs. The ion exchange affinity is often found to be in agreement with the hydrated ionic radius and follows obviously below patterns [21–23]: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and for divalent cations: $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$.

An ion exchange process is basically the stoichiometric, reversible exchange of ions between the aqueous and solid phases, which does not produce any significant changes in the solid structure, while approaching gradually between the both phases steady-state conditions.

In a binary system the mass action equilibria may be written as follows [3, 6, 7, 16]: $A + BZ \leftrightarrow AZ + B$ and the equilibrium coefficient based on above reaction as:

$$K = \frac{AZ \times B}{A \times BZ}$$

where A, B are ions and Z zeolite (the cation’s valence has been omitted).

Quantitatively the selectivity of the zeolite for an ion A instead of an ion B can be simplified according to the equation:

$$K \approx \frac{q_{eq}}{C_{eq}} = \frac{Y_A . X_B}{X_A . Y_B}$$

while $X = C_{eq}/C_o$ equals to equivalent fraction (simplex) of ions A, B in solution and $Y = q_{eq}/q_{max}$ equals to equivalent fraction (simplex) of parent ions in zeolitic phase. Variables of the total and equilibrium solution concentrations $C_o$ and $C_{eq}$ are in mmol/L and of the total and equilibrium ion exchange capacities of zeolite $q_{max}$ and $q_{eq}$ are in mmol/g.

The preference of an ion exchange for one ion relatively to another in binary systems is often expressed as the “separation factor” α. If the equivalent fraction of ion A in the solid phase $Y_A$ is plotted against the equivalent fraction of A in the solution $X_A$, three cases may be identified corresponding to $\alpha < 1$, $\alpha = 1$ and $\alpha > 1$. Isotherms which are concave

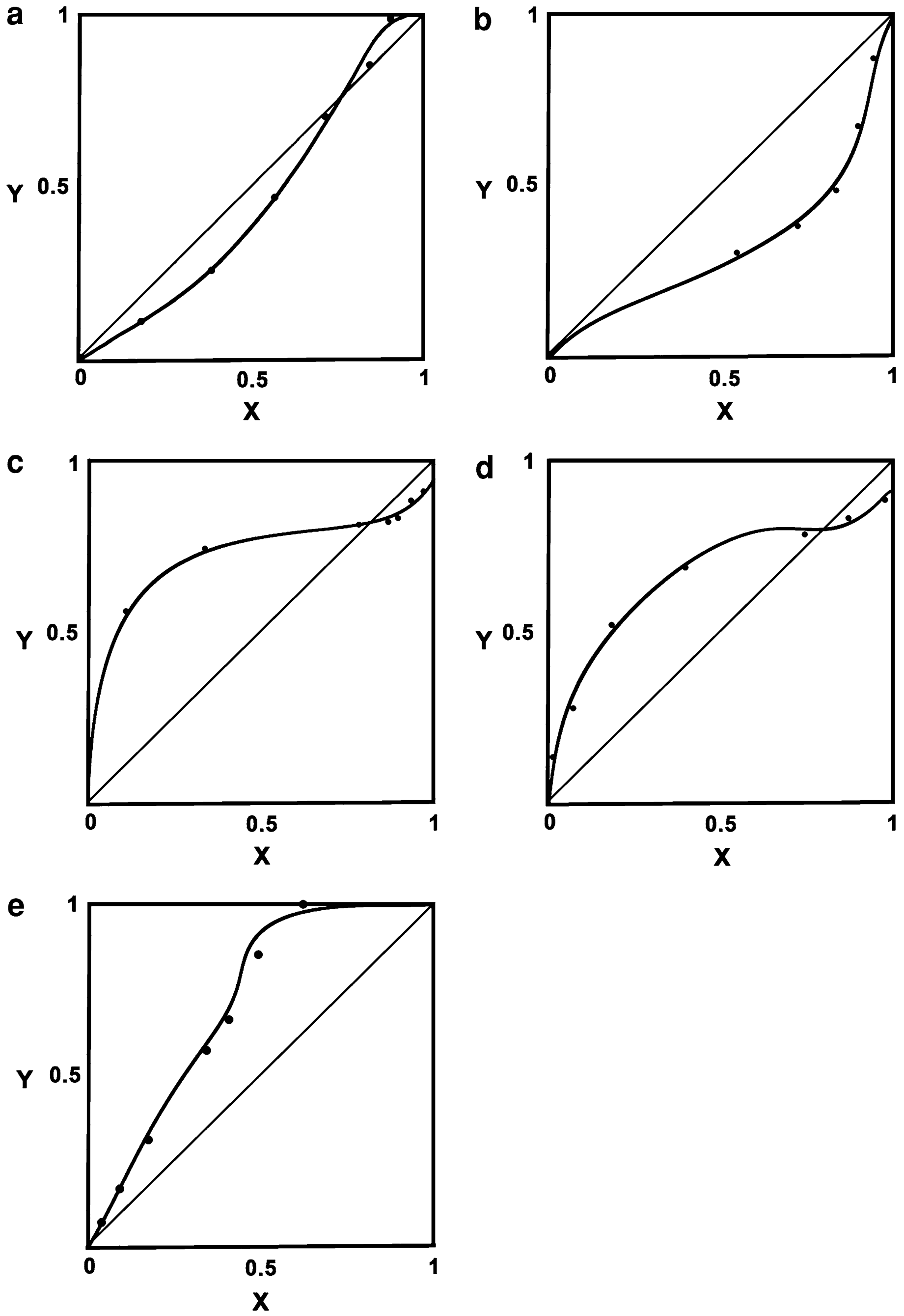

**Fig. 1** **a** Ion exchange isotherm at 23 °C for the exchange of ammonium cation into natural clinoptilolite at 0.1 total normality, **b** Ion exchange isotherm at 23 °C for the exchange of cobalt cation into natural clinoptilolite at 0.1 total normality, **c** Ion exchange isotherm at 23 °C for the exchange of barium cation into natural clinoptilolite at 0.1 total normality, **d** Ion exchange isotherm at 23 °C for the exchange of cesium cation into natural clinoptilolite at 0.1 total normality, **e** Ion exchange isotherm at 23 °C for the exchange of silver cation into natural clinoptilolite at 0.1 total normality

upward $\alpha < 1$ are designated as being "unfavorable" to the uptake of ion A; those which fall along the rising diagonal $\alpha = 1$ are termed "linear" and exhibit no preference for ion A or B and curves which are concave downward $\alpha > 1$ are referred to as favorable (convex) isotherms since the solid prefers ion A before ion B [3, 6, 7, 16].

Figures 1, 2, 3 and 4 illustrate the all ion exchange isotherms measured and plotted as Y upon X on both clinoptilolite- and mordenite-rich tuffs from Slovakian sedimentary deposits, as described under the Sect. 2.4. Based on the shapes of these isotherms, the selectivity series with decreasing preference for exchange of different cations onto the raw and Na exchanged clinoptilolite-rich tuffs can be expressed by following sequences: $Ag^+$, $Ba^{2+}$, $Cs^+ > NH_4{}^+ > Co^{2+}$ and $Ag^+ > NH_4{}^+ > Ba^{2+} > Cs^+$ and for raw and Na exchanged mordenite-rich tuffs subsequently as: $Ag^+ > Zn^{2+} > Cs^+$, $Ba^{2+} > Co^{2+}$ and $Ag^+ > Zn^{2+}$.

Taking into consideration that the variety of extra-framework cations for clinoptilolite-rich tuff was analysed as Ca > K > Mg > Na and for mordenite-rich tuff as K > Ca > Na > Mg, as well as on the base of different mineralogical composition of both tuffs following conclusions may be drawn [24]:

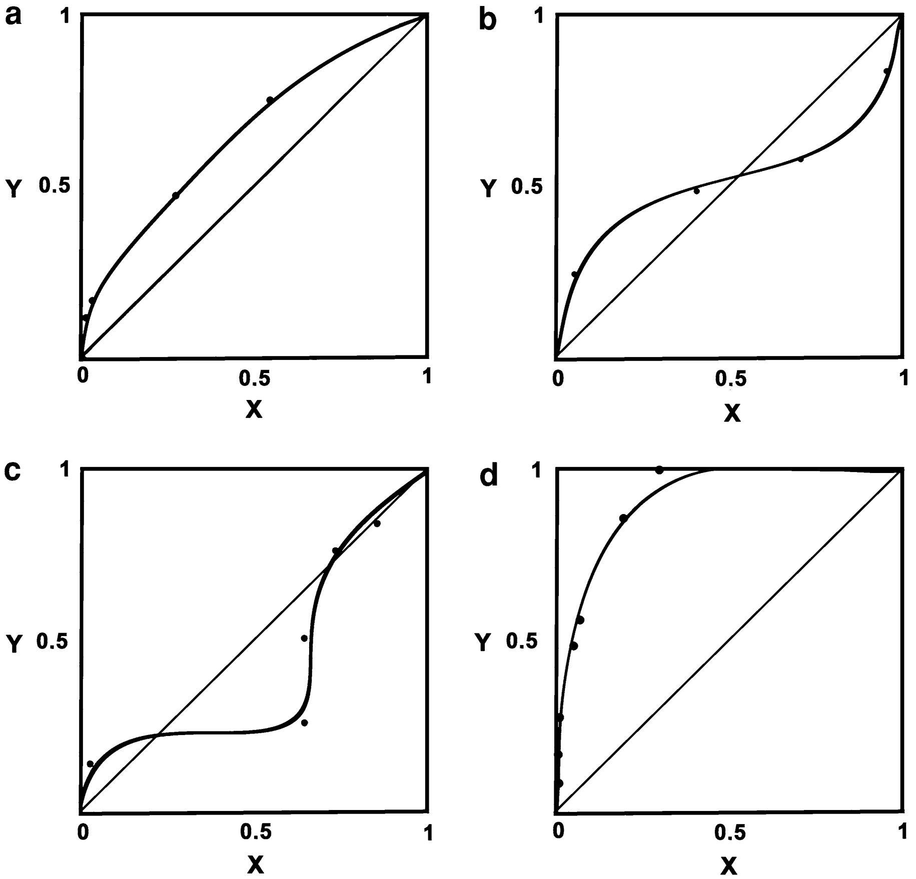

**Fig. 2** **a** Ion exchange isotherm at 23 °C for the exchange of ammonium cation into Na-clinoptilolite at 0.1 total normality, **b** Ion exchange isotherm at 23 °C for the exchange of barium cation into Na-clinoptilolite at 0.1 total normality, **c** Ion exchange isotherm at 23 °C for the exchange of cesium cation into Na-clinoptilolite at 0.1 total normality, **d** Ion exchange isotherm at 23 °C for the exchange of silver cation into Na-clinoptilolite at 0.1 total normality

(i) Despite the fact that the kinetic and thermodynamic studies are providing relevant information about the affinity of a zeolite towards a cation, the attention in this study was limited only to equilibrium measurements.

(ii) The nature of hosting exchangable cations and the Si/Al ratio, which in case of inland clinoptilolite-rich tuff varied between 4.8 and 5.4 [29], modulated the selectivity and ion exchange properties predominantly, i.e. high silica content zeolite with sufficiently weak framework favoured large, poorly hydrated cations like $Ba^{2+}$ and $Cs^{+}$.

(iii) Godelitsas labelled in the HEU-type clinoptilolite three types of extraframework cations according to the channel indicated as A, B and C [11]. Because the C channels connect the A and B channels essentially, all extra framework or hosting cation sites are also a part of the C channels, arranged as two dimensional channel system. In the A channels created by the ten membered rings of tetrahedra with the pore dimensions of 3.0 × 7.6 Å, there are localized three potential cation sites, i.e. A1 on the mirror planes, A3 in the centre inbetween and A2 situated on the two-fold axis with two bonds to adjacent oxygen sites of the framework incl. additional coordinating $H_2O$ molecules oppositely. Relatively small cations like $K^{+}$, $NH_4{}^{+}$, $Zn^{2+}$, $Ag^{+}$, $Co^{2+}$, $Ca^{2+}$ prefer the A3 sites according to several authors [11, 15], while large cations $Cs^{+}$, $Ba^{2+}$ prefer the B sites, localized also on the mirror planes of B channels, which consist of eight membered rings, having the pore dimensions of 3.3 × 4.6 Å. C-type of channels forming also eight membered rings of tetrahedra posses the pore dimension of 2.7 × 4.7 Å. According to structural and physicochemical investigations of heulandite by Godelitsas [11] $Ag^{+}$ and $Na^{+}$ cations with corresponding octahedral ionic radii used to occupy in case of $Na^{+}$ the site A1 by 47%, the site B by 44% and C position by 9%, while $Ag^{+}$ cations occupy A1 position by 56% and B position by 43%. These results support the easier exchange of $Ag^{+}$ and $Na^{+}$ ions by the clinoptilolite-rich tuff, confirmed simultaneously by our study.

(iv) There is important to note that the mordenite-rich tuff currently studied posses rather variable mineralogical composition, whereas clay minerals with different ion exchange behaviours and much broader spatial voids incl. structural sheets distance predominate [26–28, 32]. These phenomena incl. nature of hosting extraframework cations were probably responsible for lower Cs and Ba affinity in regard to higher quality clinoptilolite-rich tuff, which does not contain such a high percentage of mineral impurities.

(v) Feasible explanation for the equilibrium data obtained regarding the raw and Na exchanged clinoptilolite-rich tuffs and the shapes of their isotherms were concluded. Relatively

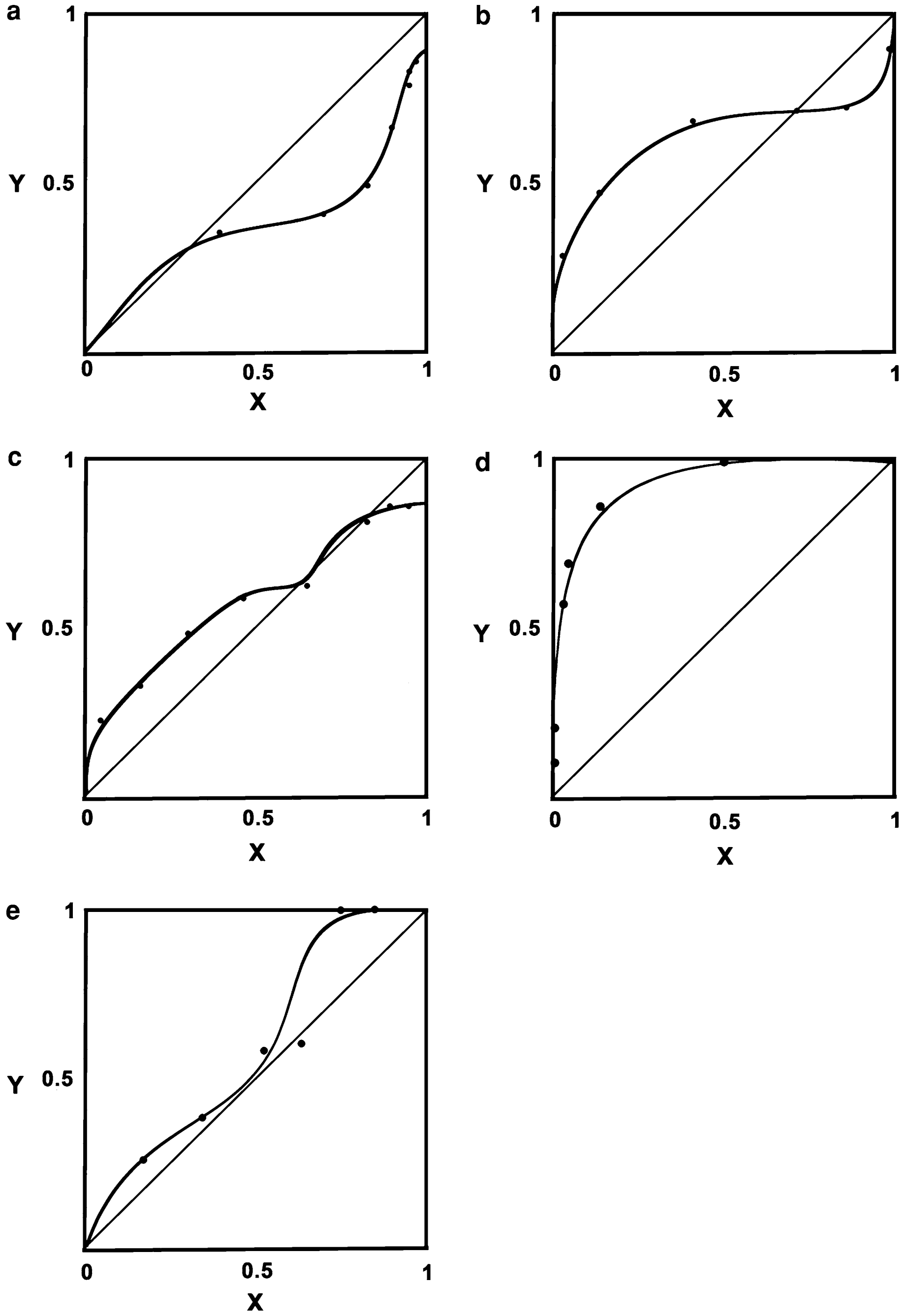

**Fig. 3** **a** Ion exchange isotherm at 23 °C for the exchange of cobalt cation into natural mordenite at 0,1 total normality, **b** Ion exchange isotherm at 23 °C for the exchange of barium cation into natural mordenite at 0.1 total normality, **c** Ion exchange isotherm at 23 °C for the exchange of cesium cation into natural mordenite at 0.1 total normality, **d** Ion exchange isotherm at 23 °C for the exchange of silver cation into natural mordenite at 0.1 total normality, **e** Ion exchange isotherm at 23 °C for the exchange of zinc cation into natural mordenite at 0.1 total normality

large cations $Cs^+$, $Ba^{2+}$ but also $Ag^+$ due to coordination effects and due to the original, mostly $Ca^{2+}$, $K^+$ cations, were exchanged and hosted much easier rather in all sites, what was in agreement with the highly selective, convex type of isotherms plotted (Fig. 1c–e). On the other hand, those cations accessibility was practically hindered to some extent and correspondingly their isotherms presented except for $Ag^+$ ions the inflection points as well as not complete degree of ion exchange (estimated to about 80%) under the higher saturation degree of zeolite. The same concerns also the clinoptilolite-rich tuff vs. $NH_4^+$, however in opposite shape and feature of isotherm for raw and Na exchanged variety. More or less, the native tuff does not prove rather any selectivity to $NH_4^+$, but oppositively in the homoionic Na exchanged form the selectivity of clinoptilolite-rich tuff was increased in the whole concentration range (Figs. 1a, 2a). While the selectivity of Na exchanged clinoptilolite-rich tuff towards $Ag^+$ ions even arised regarding to the raw clinoptilolite-rich tuff, the affinity of such a tuff towards $Cs^+$ and $Ba^{2+}$ cations decreased, whereas their isotherms became characteristic with inflex points. By the other words, native form of clinoptilolite-rich tuff, predominantly Ca, K, favours

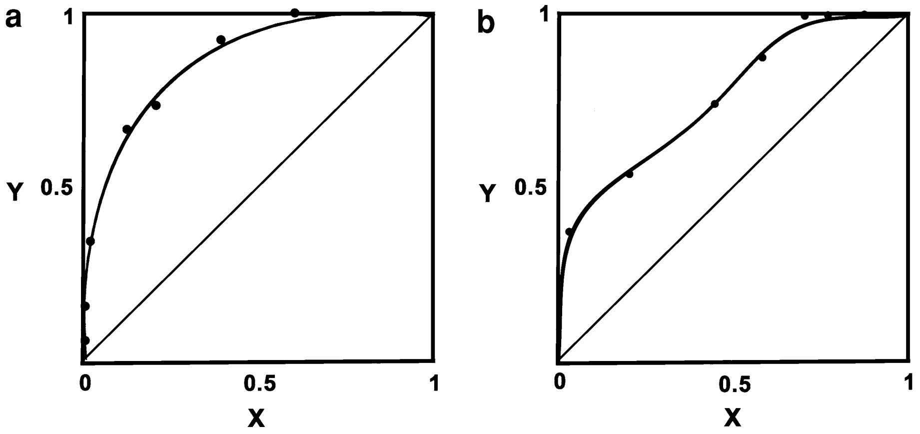

**Fig. 4** **a** Ion exchange isotherm at 23 °C for the exchange of silver cation into Na-mordenite at 0.1 total normality, **b** Ion exchange isotherm at 23 °C for the exchange of zinc cation into Na-mordenite at 0.1 total normality

$Ag^+$, $Ba^{2+}$, $Cs^+$ cation exchange, while Na variety easier exchanges and favours smaller cations like $Ag^+$ and $NH_4^+$ before $Ba^{2+}$ and $Cs^+$ [11, 13, 23, 25, 30].

(vi) Neither natural clinoptilolite- nor mordenite-rich tuff proved any selectivity towards $Co^{2+}$ ions, moreover in mordenite-rich tuff some incompletness of exchange was observed by the higher saturation degree of solids (Figs. 1b, 3a).

(vii) From the isotherm shapes (Figs. 3d–e, 4a–b), $Ag^+$ and with less extent also $Zn^{2+}$ cations can be preferentially exchanged into raw mordenite-rich tuff before $K^+$ and $Ca^{2+}$ ions, but even before $Na^+$ ions, when the mordenite-rich tuff was Na exchanged. The raw mordenite-rich tuff, as illustrated in Fig. 3b–c, shows a slight preference for $Ba^{2+}$ and $Cs^+$ ions, while the isotherms shape recorded some sigmoidal charakter, indicating probably a heterogeneity of cation exchange sites in the mordenite structure [31, 32].

## Conclusion

Summing up, the Slovakian zeolite-rich tuffs prove a high selectivity towards noxious radionucleids of Cs and Ba in moderate extent depending on the extra framework or hosting cations in their structures. While the selectivity of Na exchanged clinoptilolite-rich tuff towards $Ag^+$ ions even arised regarding to the raw clinoptilolite-rich tuff, the affinity of such a tuff towards $Cs^+$ and $Ba^{2+}$ cations decreased, whereas their isotherms became characteristic with inflex points. By the other words, native form of clinoptilolite-rich tuff, predominantly Ca, K, favours $Ag^+$, $Ba^{2+}$, $Cs^+$ cation exchange, while Na variety easier exchanges and favours smaller cations like $Ag^+$ and $NH_4^+$ before $Ba^{2+}$ and $Cs^+$. A lower Cs and Ba affinity of mordente-rich tuff in regard to higher quality clinoptilolite-rich tuff, which does not contain such a high percentage of mineral impurities, was found.

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