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Experimental Study of Acido-Basic Surface Equilibria in Zeolitized Brick: Theoretical Approach and Magnetic Behaviour of Framework Protons



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ABSTRACT

A metakaolinite-rich brick was treated with sodium hydroxydes in order to generate sodic sites that were found to participate actively in the removal of heavy metals from aqueous solutions. The ESEM/EDS analysis of the treated material revealed first the formation of Na-zeolites and second, the preferential bindings of cationic metals like nickel(II) and cadmium(II) with the surface zeolitic structures. Because of the amphoteric behaviour of the modified brick, an electric charge distribution existed at the solid surface. On the basis of surface charge (σ) / surface acidity and surface equilibria, the reactivity of zeolitized brick toward Ni²⁺ ions and Cd²⁺ ions was examined theoretically in single systems. These investigations permitted to identify the different physicochemical phenomena involved at the solution-brick interface and to quantify them. Using the SciLab program, the dimensionless pH sensitivity parameter (β) and the pH at the Point of Zero Charge (pH_{PZC}) were determined and these values were used for assessing the surface equilibrium constants for the protonation and dissociation reactions ($K_{\alpha 1}$ and $K_{\alpha 2}$). ¹H MAS NMR revealed that water protons distribution within the network of (sodic) zeolitized brick occurred no-uniformly through channels and cavities with the formation and scission of hydrogen bonds, thus enabling efficient protons propagation. As for the protonic form of the material, the protonation of negatively charged zeolite sites led to stronger ionic bonds, which contributed to reduce the mobility and transport of water protons within the network and to give rise to higher overlapping of the magnetic resonances of framework protons.

INTRODUCTION

Numerous attempts to elucidate the adsorptive behaviour of oxide and (alumino-)silicate mineral surfaces in water had previously been made in terms of surface complexes [1-7]. In order to understand interfacial complexation processes on oxides, it was evidenced that surface protonation/deprotonation reactions at the surfaces of these solids played an important role for explaining Physico-chemical phenomena [8-9]. Thus, heterogeneous reactions took place at water-mineral interfaces with equilibria between surface species: $>S-O^-$, >S-OH and $>S-OH_2^+$ and H^+ in solution (where ">S-O" represents a reactive hydroxyl site, either silanol or aluminol).

Some works were devoted to the charge characteristics of zeolitic materials in the aim to better comprehend their surface reactivity [10-11]. Their electric charge distribution was found to be intimately related to the acid-base behaviour of the surface hydroxyl groups [11]. The magnitude of the formed surface charge was further dependent on the pH and ionic strength of the background electrolyte solution. And because of the amphoteric properties of the zeolitic material, the surface functional group, -OH, can be transformed into either $-O^-$ or $-OH_2^+$.

The raw brick from Central African Republic presents a heterogeneous surface and its weak surface charge changes as a function of pH (pH_{PZC} \approx 5.3 [12]). After the hydroxylation of metakaolinite present in this brick by NaOH treatment, an increase of the charge density of anion framework of the raw brick occurs as a result of the formation of NaA and NaP crystals at the brick surface. The pH_{PZC} of raw brick is then increased from ~5.3 to 5.85 [12]. Depending upon the pH and the ionic strength of the solution, specific interactions between protons, water molecules (H-bondings) and negatively charged sites take place at the brick surface. These interactions cause changes in the acidity strength of the brick and in the magnitude of the surface constant values.

On this view, efforts had been made in this paper to gain a more detailed theoretical insight into key physicochemical parameters controlling the magnitudes of surface protonation equilibrium constants and their implications on metals removals by (sodic) zeolitized brick from aqueous solutions. From the Gouy-Chapmann-Stern theory of the electrical double layer (and applying a single site-type model), we focused our attention on the importance of some

parameters in the adsorption mechanism: solution and interface pH; pH_{PZC}; surface potential of the adsorbent, Ψ_0 ; and dimensionless pH sensitivity parameter, β .

The application of mathematical surface protonation models to the metal-adsorption process by zeolitized brick was undertaken in the aim to provide fits to experimental surface charge (σ) and surface potential (Ψ_o) *versus* equilibrium pH data. The objective of this approach was to lead us to equations with a theoretical basis that was consistent with experimental results and predicted surface protonation equilibrium constants. On this basis and from the experimental and computational study, we attempted here to re-determinate the pH_{PZC} and to evaluate the (intrinsic) surface acidity equilibrium constants (K_{a1} and K_{a2}).

Considering the structure and topology of the zeolitic material, the ¹H MAS NMR technique was employed in order to obtain information about the localization/distribution/mobility of protons and their chemical environment inside the sodic zeolitized brick and its protonic (acidified) form.

MATERIALS AND METHODS

2.1 Zeolitized-brick synthesis and characterization

The raw material used in the experiments was obtained from a brick made locally in Bangui region (Central African Republic). This brick contains mainly quartz (60-65 w%) and metakaolinite (20-26 w%) and, to a lesser extent, iron oxide/hydroxide, illite and titanium dioxide [13]. The brick was broken into grains and seized and the 0.7-1.0 mm fraction was selected. 10 g of this fraction were treated with 40 mL of sodium hydroxide (0.6 mol.L⁻¹) at room temperature for one night under slow shaking at a speed of 120 rpm. This procedure was afterwards followed by a fixed-temperature increase of the mixture at 90°C for a constant reaction time of six days. The recovered grains were afterwards rinsed several times with MilliQ water and dried at 90°C for 24 hours. The transformation of brick metakaolinite into zeolites NaA and NaP was previously confirmed by X-ray diffraction and scanning electron microscopy [12].

Chemicals

All chemicals employed in the experiments were analytical grades. Sodium hydroxide, Cd(NO₃)₂.4H₂O and Ni(NO₃)₂.6H₂O were supplied by DISLAB (France).

2.2. ICP-AES analyses

During adsorption studies, recovered solutions were analyzed for element contents using ICP-AES (Inductively Coupled Plasma – Atomic Emission Spectroscopy; model Varian Pro Axial View).

2.3. Adsorption experiments

Metal-adsorption runs were conducted on the above zeolitized brick sample and the experimental details are as follows. In order to perform adsorption experiments, we prepared a series of metal cation solutions with concentrations ranging from 0.798 to 1.645 mmol.L⁻¹ for cadmium(II) and from 0.499 to 0.952 mmol.L⁻¹ for nickel(II). We took about 50 mL of each of these metal solutions and added to it 1g of modified brick pellets (with average diameters varying from 0.7 to 1.0 mm). These experiments were carried out at room temperature. The different suspensions were continuously and gingerly mixed for 24 hours, allowing the adsorption to reach the equilibrium state. At the beginning and end of adsorption experiments, pH was measured. The resulting supernatants were filtered through a 0.45 μ m pore diameter (cellulose nitrate filter) and analyzed for the determination of metal level by ICP-AES.

2.4. Solid-state NMR studies

The ¹H MAS-NMR spectra were recorded at 800 MHz on a 18.8 T Bruker Avance III spectrometer. The ¹H MAS-NMR experiments were recorded with a $\pi/2$ pulse length of 3.5 μ s, 128 transients and a 5s rd using the DEPTH sequence in order to suppress the signal coming from the measurement probe. All the ¹H chemical shifts were referenced as 0 ppm to TMS.

2.5. Electron Microscopy analysis

Micrographies of representative specimens of zeolitized brick were recorded by using an environmental scanning electron microscope (ESEM, Quanta 200 FEI). Elemental analysis was performed using ESEM/EDS (ESEM, model: QUANTA–200–FEI, equipped with an Energy Dispersive X-Ray Spectrometer EDS X flash 3001 and monitored by QUANTA–400 software elaborated by Bruker). EDS measurements were carried out at 20 kV at low vacuum (1.00 Torr) and the maximum pulse throughput was 20 kcps. Different surface areas ranging from 0.5 to 3.5 mm² were targeted on alkali-brick grains and examined by ESEM/EDS. For that, a narrow beam scanned selected areas of brick pellets for chemical analysis. Atomic quantifications and mathematical treatments were undertaken using QUANTA-400 software in order to determine the averaged elemental composition of the surface brick and to detect chemical/elemental variabilities.

RESULTS AND DISCUSSION

3.1. ESEM/EDS analysis

The chemical determination of the minerals in the brick samples was carried out by means of elemental chemical mapping using an Environmental Scanning Electron Microscope (ESEM) equipped with an Energy-Dispersive Spectroscopy (EDS) device. This technique permitted particularly to show the surface heterogeneity of the brick material. Conventional Back-Scattered Electron (BSE)-imaging allowed localising grains rich in elements of high atomic number. The chemistry of the different minerals constituting the brick material was assessed by estimating the element proportions obtained from the map averaged values yielded by ESEM–EDS scanning; and chemically coded colour imaging helped to visualize the mineral grains according to their chemical composition.

*Raw brick*__The ESEM micrograph of raw brick exhibits highly porous and non-uniform textural surfaces with major fissures and cracks, except for some micro – specimens that were well - identified as quartz (not shown here). ESEM/EDS analyses were carried out in large circled regions of raw brick with diameters of *ca* 300 μ m and, resulting data revealed that Al, Si, O and Fe were the principal elements constituting this material at its surfaces while K, Ti, Mg and Ca were minor elements.

NaOH-treated brick The ESEM micrographs of the NaOH-treated brick showed that the surface morphology of the material changed noticeably by the apparition of cubic and spherical micro-particles at its surfaces (see Fig. 1).



Figure No. 1: ESEM micrograph of (sodic) zeolitized brick, showing cubic and spherical specimens ascribed to NaA and NaP zeolites, respectively.

Their sizes varied from 8 μ m to 10 μ m for cubic micro-specimens and from 3 μ m to 6 μ m for spherical micro-specimens. Quantitative ESEM/EDS study revealed that the elemental composition of these micro-specimens corresponded well to that of zeolite with an atomic ratio Si: Al \approx 1 [14]. Averaged EDS data further indicated a significant increase of sodium on the surfaces of these cubic and spherical particles, suggesting the formation of Na-zeolites [14]. The identification of these zeolites was made by means of the X-ray diffraction analysis, revealing the formation of crystalline Na-zeolites: NaA and NaP [14].

Cd(*II*) or *Ni*(*II*)-doped zeolitized brick_ The spatial distribution of the framework elements Al, Si, Ti and Na and the adsorbed metal (Cd or Ni) at the brick surface was displayed in Fig. 2. The ESEM/EDS mapping procedure gave the color overlay shown in this figure, where the elemental distributions for Al, Si, Na, Ti and Cd are represented in red, blue, yellow, light blue and green, respectively. Element distribution images indicate a positive correlation

between Al, Na and Cd (Fig. 2). This observation confirms previous results indicative of the significant role of sodic alumino-silicates like Na-zeolites in the adsorption removal of heavy metals from aqueous solutions in their applications to water treatments [15].



Figure No. 2: Spatial distribution of the framework elements Al, Na, Si and Ti and the adsorbed metal (cadmium) at the brick surface; and the reconstituted ESM/EDS mapping. (Note that, as evidenced recently [14], titanium is also present in the material in the crystalline form of rutile: TiO₂).

Conversely, there is a negative correlation between cationic metal and silicon in Si-rich zones (composed mainly of quartz), suggesting lower contributions to metal adsorption by silicate(s). The reconstituted ESEM/EDS mapping image clearly highlights discrete Cd-Na-Al combinations which are localized in light regions where 'green' and 'yellow' colors predominate. In other words, Cd image is more superimposed to the images of Al and Na. Whereas quartz grains (SiO₂) appears in blue regions where Cd atoms are not present. A similar elements distribution and reconstituted ESEM/EDS mapping were also observed for Ni(II)-doped zeolitized brick, showing as well that Ni atoms were preferentially adsorbed onto zeolitic crystals (Fig. 3).



Figure No. 3: Reconstituted ESM/EDS mapping relative to the spatial distribution of the framework elements Al, Na and Si and the adsorbed metal (nickel) at the brick surface.

3.2. Choice of cadmium(II) and nickel(II) for the theoretical study of surface equilibria

The pH of the aqueous solution is an important parameter that controls cationic adsorption on to zeolitized brick. This is due to changes of brick-surface characteristics and metallic species taking place in water with an increase of pH.

On the other hand, it is well known that divalent metal ions in aqueous solution hydrolyze to form a series of mononuclear and poly-nuclear hydroxyl complexes [16]. Previously, we examined the equilibrium species distributions (in single-metal systems) of cationic metals such as: Cd^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} as a function of the solution pH at batch and kinetics concentrations employed for metal adsorption [17]. From the drawn diagrams, we revealed that free metal ion was the major species in acidic medium and remained stable up to pH values ranging from ~5.5 to ~8.0, depending upon the divalent metal studied. Thus, free metal ion remained the dominant species up to reach a maximal pH value of ~5.5 for Pb^{2+} , ~7.0 for Zn^{2+} , ~7.2 for Fe^{2+} , ~7.5 for Co^{2+} and ~8.2 for Ni^{2+} , Cd^{2+} and Mn^{2+} . This finding is in fact related to the acid properties of cationic metal in water, indicating particularly that $Me(OH)^+$ is the first hydroxy complex appearing in the medium with pH increase according to the hydrolysis reaction: $Me^{2+} + H_2O \leftrightarrow Me(OH)^+ + H^+$.

In this work, we had chosen nickel(II) and cadmium(II) for studying metal adsorption by zeolitized brick because the different hydroxyl complexes of these metals barely existed in the reaction medium under experimental pH conditions (*i.e.*, at pH > pH_{PZC} and pH < 8.2); And, consequently, only their free ionic forms were presumed to interact predominantly with de-protonated hydroxyl groups (>S–O⁻) on the brick surface [17].

3.3. Theoretical approach of the brick-surface effects on the metal-adsorption process

According to our theoretical approach, brick surface was considered to be amphoteric, which means it can act as a proton acceptor or a proton donor. The acidic and basic properties of a neutral brick site (>S–OH), can then be expressed by the two equilibrium reactions:

$$>S-OH_2^+ \leftrightarrow >S-OH + H^+_{(s)}$$
 (1)

$$>S-OH \leftrightarrow >S-O^{-} + H^{+}_{(s)}$$
 (2)

Where ">S" represents an active surface functional group including the silanol (SiO⁻) and aluminol (AlO⁻) sites. The equilibrium constants for reactions (1) and (2) are given by:

$$K_{\alpha 1} = \frac{[>S - OH]^* [H^+]_s}{[>S - OH_2^+]}$$
(3)

$$K_{\alpha 2} = \frac{[>S - O^{-}] * [H^{+}]_{s}}{[>S - OH]}$$
(4)

where $[H^+]_s$ is the surface concentration of H^+ ions. $[H^+]_s$ is related to the concentration of H^+ ions in the bulk solution by the Botzmann-statistics equation:

$$[H^{+}]_{(s)} = [H^{+}]_{bulk} \cdot \exp(-\frac{e \cdot \Psi_{o}}{kT})$$
(5)

in which Ψ_0 is the surface potential; k the Boltzmann constant (1.38x10⁻²³ J.K⁻¹); e the electron charge (1.602x10⁻¹⁹ C); and T the absolute temperature.

Moreover, the brick-surface charge can be determined from the equation:

$$\sigma(C/m^2) = eN_s \frac{([>S - OH_2^+] - [>S - O^-])}{([>S - OH] + [>S - OH_2^+] + [>S - O^-])}$$
(6)

where N_s represents the surface site density (sites/m²). In this study, we considered sodic zeolitized brick, >S–O⁻Na⁺, as adsorbent for heavy metals adsorption removals. We conducted a series of experiments on adsorption of Ni²⁺ and Cd²⁺ ions by sodic zeolitized brick (1.0 g of brick in 45 mL) with increasing concentrations of these metals (see the *Experimental Section*). Initial metal concentrations (in ppm) and adsorbed metal concentrations (in ppm) are given in Table 1.

NICKEL(II)			CADMIUM(II)				
[Ni ²⁺] _{initia} 1 (ppm)	[Ni ²⁺] _{ads} (ppm)	Fraction of occupie d sites (%)	Free sites (mmol/1 g of brick)	[Cd ²⁺]initia 1 (ppm)	[Cd ²⁺] _{ads} (ppm)	Fraction of occupie d sites (%)	Free sites (mmol/1 g of brick)
29.311	28.934	37.44	0.08237	123.99	119.74	47.84	0.16160
32.955	31.929	41.28	0.07739	139.11	132.68	53.00	0.10469
44.246	41.837	54.12	0.06043	148.63	139.01	55.31	0.09992
47.146	38.153	49.38	0.06663	168.04	158.24	63.05	0.08250
49.957	46.974	60.86	0.05147	172.99	157.65	62.78	0.08314
55.891	51.795	66.82	0.04381	184.88	163.21	65.12	0.07778

 Table No. 1: Experimental data on the removal of cadmium(II) and nickel (II) by sodic

 zeolitized brick from water at room temperature.

In the reaction medium, the ion-exchange mechanism occurred according to the following stoichiometric process:

$$2(>S-O^{-}Na^{+}) + Me^{2+} \to (>S-O)_{2}Me + 2Na^{+}$$
(7)

in which $2Na^+$ ions were released in the solution for 1 Me²⁺ ion adsorbed. Note that the number of (sodic) reactive sites in the modified brick was evaluated: $N_s = 0.049$ mmol per gram of brick material (Poumaye et al., *unpublished work*). Note further that from the specific surface area of the modified brick (S_{BET}) measured by the BET technique (in m²/g), N_s could also be expressed in mmol/m². Note that the Ns value permitted to assess the fraction of occupied sites (in %) see Table 1.

On the other hand, the number of negatively] charged sites (not bound to metal cations) can be determined approximately from the relationship:

$$[>SO^{-}]_{\text{free}} \approx [>SO^{-}]_{\text{total}} - 2[(>SO)_2Me]$$
(8)

where $[>SO^-]_{total}$ represents the total concentration of reactive (sodic) sites at brick surfaces (in mmol per gram of brick); and $[(>SO)_2Me]$ is the concentration of metal associated with the brick (in mmol per gram of brick). For the different performed brick-metal mixtures, the numbers of free sites (in mmol per gram of brick) are listed in Table 1.

Taking into account Eq.(8), Eq.(6) becomes:

$$\sigma \approx eN_s \frac{(-[>S-O^-]_{free})}{([>S-O]_{total})} \approx eN_s \frac{([>SO]_{total} - 2[(>SO)_2Me])}{([>SO]_{total})}$$
(9)

Besides, from Gouy-Chapman diffuse layer theory [18], the charge in the diffuse layer can be expressed as:

$$\sigma(C/m^2) = (8.\varepsilon_o.\varepsilon_w.R.T.I_c)^{1/2}\sinh(\frac{F.\Psi_o}{2R.T})$$
(10)

where ε_0 is the permittivity of vacuum (8.854188.10⁻¹² C²J⁻¹m⁻¹); ε_w the relative permittivity of water (78.5); and I_c the ionic strength of the influent solution; R the gas constant (8.314 J.mol⁻¹.K⁻¹); and F the Faraday constant (96487 C.mol⁻¹). Hence, from Eq.(10) the surface potential (Ψ_0) can be assessed from the mathematical expression:

$$\Psi_o = \frac{2R.T}{F} \cdot \sinh^{-1} \left(\left[\frac{\sigma}{\left(8.\varepsilon_o \varepsilon_w \cdot R.T.I_c\right)^{1/2}} \right] \right)$$
(11)

Moreover, the pH-dependence of the surface potential (Ψ_o) can be expressed from the relationship [19-22]:

$$pH = pH_{PZC} - \frac{1}{2.303} \left[\frac{\Psi_o \cdot e}{kT} + \sinh^{-1} \left(\frac{e \cdot \Psi_o}{\beta kT} \right) \right]$$
(12)

where β is a dimensionless pH sensitivity parameter. The β parameter is given by:

$$\beta = \frac{2e^2 N_s}{k.T.C_{DL}} (\frac{K_{\alpha 2}}{K_{\alpha 1}})^{1/2}$$
(13)

In Eq. (13), N_s is the surface site density; C_{DL} is the linearized double-layer capacitance; and $K_{\alpha 1}$ and $K_{\alpha 2}$ represent the surface equilibrium constants for reactions (1) and (2), respectively.

The "equilibrium pH" modelling equation used in this study, Eq. (12), is given as a nonlinear equation. Modelling data were then fitted to experimental results using nonlinear regression analysis. The goodness-of-fit between the model and experimental observations was

ascertained in terms of sum of square residuals (SSR) and mean chi-square error (χ^2) using Eqs. (14) and (15), respectively:

$$SSR = \sum_{j=1}^{n} [pH_{eqj}(\exp.) - pH_{eqj}(pred.)]^{2}$$
(14)

$$\chi^{2} = \frac{1}{n} \sum_{j=1}^{n} \frac{\left[pH_{eqj}(pred.) - pH_{eqj}(\exp.)\right]^{2}}{pH_{eqj}(pred.)}$$
(15)

where $pH_{eqj}(exp.)$ and $pH_{eqj}(pred.)$ represent the experimental and the predicted (or calculated) values of the "equilibrium adsorption pH", respectively; j is the integer index denoting the successiveness of experimental data; and n is the number of data points. The best fitting was calculated by minimizing SSR and χ^2 values by using an algorithm programmed in Scilab 6.0.2 software. For each performed experiment, the values of surface charge (σ), surface potential (Ψ_0) and experimental and simulated pH_{final} are given in Table 2.

Table No. 2: Determination of surface charge (σ), surface potential (Ψ_0) and pH_{final} involved in Ni(II) and Cd(II) adsorptions (in single system) from the Gouy-Chapmann-Stern theory of the electrical double layer.

THAT IN THE								
NICKEL(II)			CADMIUM(II)					
σ	Ψo	$\mathbf{pH}_{\mathrm{final}}$	$\mathbf{pH}_{\mathbf{final}}$	σ	Ψo	\mathbf{pH}_{final}	$\mathbf{pH}_{\mathrm{final}}$	
(C.m ⁻²)	(Volt)	(experi.)	(SciLab)	(C.m ⁻²)	(Volt)	(experi.)	(SciLab)	
0 04967	-0 175	8 88	8.81 ±	0 04194	-0 140	8.01	$8.02 \pm$	
0.04707	0.175	0.00	<0.01	-0.140	0.01	< 0.01		
0.04667	0 172	8 66	$8.77 \pm$	0.03779	0.03770	0.122	7.07	7.91 ±
0.04007 -0.	-0.172	8.00	< 0.01		-0.132	1.91	< 0.01	
0.03644 -0.15	0.150	8 50	$8.58 \pm$	0.03593	-0.128	7.88	7.85 ±	
	-0.139	0.39	< 0.01				< 0.01	
0.04018	0.164	8.65	8.65 ±	$\begin{array}{c c} 8.65 \pm \\ < 0.01 \end{array} 0.02971 \end{array}$	-0.115	7.72	7.68 ±	
0.04018 -0.104	-0.104		< 0.01				< 0.01	
0.03104 -0.	0.151	8 15	8.47 ±	0.02992	-0.114	7.60	7.66 ±	
	-0.131	0.43	< 0.01				< 0.01	
0.02642	-0.143	8.42	8.35 ±	$\begin{array}{c c} 8.35 \pm \\ < 0.01 \end{array} 0.02805 \end{array}$	-0.110	7.55	7.61 ±	
			< 0.01				< 0.01	

The β parameter and pH_{PZC} were then estimated by profile optimization minimizing the sum of square residuals (SSR) and chi-square test (χ^2) between experimental and calculated / predicted "pH_{eq}"data. The predicted values of the dimensionless pH sensitivity parameter (β) from Scilab program analyses were: $\beta = 0.04345 \pm 0.00325$ for nickel(II)-brick system and β

= 0.04490 ± 0.03237 for cadmium(II)-brick system. As for the pH at the point of zero charge (pH_{PZC}), its value estimated from Scilab program was: pH_{PZC} = 5.77 ± 0.03 for nickel(II)-brick system and pH_{PZC} = $5.77(5) \pm 0.02(5)$ for cadmium(II)-brick system (see Table 3). These pH_{PZC} values agreed well with that determined by Zetametric measurements: pH_{PZC} = 5.80 ± 0.10 [17].

Table No. 3: Assessment of the dimensionless pH sensitivity parameter (β), the pH at zero charge (pH_{PZC}) and the surface equilibrium constants for the protonation and dissociation reactions (K_{a1} and K_{a2}) from SciLab program analysis.

Systems		Scilab program		
Nickel(II)- adsorption by zeolitized brick	β	0.04020-0.04670		
	pHpzc	5.74-5.80		
	pKα1	2.76-2.88		
	pK _{α2}	8.66-8.78		
Cadmium(II) adsorption by zeolitized brick	β	0.01253-0.07727		
	pHpzc	5.75-5.80		
	pK _{α1}	2.23-3.07		
	pK _{α2}	8.53-9.27		

On the other hand, before determining the $K_{\alpha 2}/K_{\alpha 1}$ ratio from Eq.(13), it was necessary to evaluate the linearized double-layer capacitance, C_{DL} . For that purpose, we used the theoretical formulae established by Bousse and his coworkers [19]:

$$\frac{1}{C_{DL}} = \frac{2kT}{e.(8\varepsilon_o.\varepsilon_w.RT.I_c)^{1/2}} + \frac{1}{C_{Stern}}$$
(16)

where, C_{Stern} (0.2 F/m²) represents the Stern capacitance. We found $C_{DL} \approx 0.0595$ F/m² for nickel(II)-brick system and $C_{DL} \approx 0.0740$ F/m² for cadmium(II)-brick system. From the β and pH_{PZC} values reported in Table 1, the equilibrium constants (K_{a1} and K_{a2}) for reactions (1) and (2) could then be evaluated by using Eqs. (13), (16) and pH_{PZC} = $\frac{1}{2}((pK_{a1} + pK_{a2}))$. We found: $pK_{a1} = 2.82 \pm 0.06$ and $pK_{a2} = 8.72 \pm 0.06$ for nickel(II)-brick system and $pK_{a1} = 2.65 \pm 0.42$ and $pK_{a2} = 8.90 \pm 0.37$ for cadmium(II)-brick system (see Table 3).

The values of pH_{PZC} , $pK_{\alpha 1}$ and $pK_{\alpha 2}$ calculated for NaOH-treated brick were afterwards compared with those reported in the literature for some aluminate/silicate minerals (see Table 4).

Table No. 4: Comparison of pH_{PZC} , $pK_{\alpha 1}$ and $pK_{\alpha 2}$ calculated for zeolitized brick with those reported in the literature for some aluminate/silicate minerals.

Aluminate/					
silicate pH _{PZC}		pK α1	pK α2	References	
minerals					
SiO ₂	2	20 (TIM)	72 (TIM)	[23]	
(quartz)	3*	$2.0(1\mathrm{Livi})$	7.2 (1 LIVI)		
AlOOH	8.5	7.38 (CCM)	9.09 (CCM)	[24_ 25]	
(γ-Al 2O3)	8.1*	5.0 (TLM)	11.2 (TLM)	[24-23]	
Amorphous		5.6 (CCM)	7.9 (CCM)		
alumino-	4.1	5.0 (CCM) 6.02 (TLM)	7.9 (CCM) 8.13 (TLM)	[10]	
silicate		0.02(1LWI)	0.13 (1LWI)		
Amorphous					
alumino-	1.1	4.1 (CCM)	6.5 (CCM)	[10]	
silicate coated	4.4	3.46 (TLM)	7.16 (TLM)	[10]	
with iron oxide		1			
Acid-treated					
natural zeolite	2.0	27	2.0	[11]	
(from Chilean	2.9	2.1	5.0		
mining)		HUMAN			
NaOH-treated		numan			
brick (from	5.77 ± 0.03	2.65 ± 0.42	8.90 ± 0.37	This work	
Bangui region)					

CCM: Constant Capacitance Model; DLM: Double Layer Model; TLM: Triple Layer Model.

*: see Ref. 9: Sverjensky and Sahai, 1996.

Significant discrepancies were nevertheless noticed, thus revealing the importance of both the chemical and crystalline nature of the minerals and chemical treatments carried out on these materials on the magnitude of the surface acidity equilibrium constants and the pH at zero charge.

3.4. On the structure/topology/acidity of brick zeolites and protons localization/mobility

3.4.1. Chemical structure/acidity dependence

ESM/EDS and X-ray diffraction studies permitted to identify the presence of NaA and NaP crystals in NaOH-treated brick. These zeolites are considered as among the richest zeolitic

structures in Al and Na since their atomic Al/Si ratios (~1) are maximal. In addition, as pointed out previously [26] zeolites become more ionic as their structure contains more Al atoms. Hence, ionic interactions between silicate species and aluminium(III) would occur essentially for NaA and NaP brick zeolites with maximum atomic Al/Si in their lattices. Such a chemical behaviour then yields more polar (than covalent) structures which can be assimilated roughly to ionic combinations of aluminium, sodium, orthosilicate[26]. As orthosilicate is a relatively strong base, its acidic form (orthosilicic acid, H₄SiO₄) is a weak acid: pK_a \approx 9.5 [27]. This pKa value is close to the equilibrium constant pK_{a2} obtained for the protonic form of (sodic) zeolitized brick (the pK_{a2} value ranges from 8.53 to 9.27; see Table 3). This would reveal the importance of the H-form of orthosilicate brick fragments on the global acid characteristics of the H-zeolitized brick.

3.4.2. Protons propagation/distribution/mobility within brick framework

The structure and topology of zeolites as well as the chemical environment of their hydroxyl groups have to be considered in studying protons propagation/distribution within zeolitic networks as well as the implication of these phenomena on framework acidity/basicity [28].

Zeolites are known to possess three-dimensional frameworks that contain open cavities in the form of channels and cages [15]. Inside these cavities, water molecules and extra-framework cations such as Na⁺ ions have some freedom of movement, thus enabling ion exchange and adsorption. However, because water molecules have a polar nature and dipole moment, zeolites also possess the ability to generate hydrogen bonds inside channels/tunnels through electrostatic interactions with framework negative charges. To evidence the different types of water protons introduced into negatively charged aluminosilicate cavities and to differentiate them, ¹H MAS NMR spectroscopy was used. Note that ¹H MAS NMR was found in the past to be a good technique for identifying and localizing protons in zeolitic lattices [26, 29, 30].

In the present work, ¹H MAS NMR was applied first to NaOH-treated brick and second to its acidic form.

¹*H* MAS NMR analysis of NaOH-treated brick__The ¹H MAS NMR spectrum of NaOH-treated brick exhibits three resonances centered at 3.8 ppm, 4.3 ppm and 4.8 ppm (see Fig. 4a).



Figure No. 4: ¹H MAS NMR spectra of (sodic) zeolitized brick (a) and its protonic form (b).

The presence of several types of protons revealed unambiguously that protons propagation/distribution occurs no-uniformly inside the zeolite framework, although the largest part of brick protons gave rise to an intense and broad NMR signal at 4.8 ppm. This broad resonance indicated that a majority of adsorbed water molecules interacted more strongly and thereby, at a more reduced mobility with negatively charged sites ($>S-O^-$) within zeolitized-brick framework. While the sharp peaks at 4.3 pm and 3.8 ppm were rather attributed to mobile protons in brick framework.

To support this, in what follows we attempted to differentiate water molecules adsorbed into zeolitized brick by employing ¹H rotor-synchronized echo MAS NMR spectroscopy. For that, we applied the ¹H-synchronised echo pulse sequence described by Greiger and his coworkers [29]. Fig. 5 shows five ¹H rotor-synchronized echo spectra for a zeolitized brick sample. Spectrum '*a*' represents the echo experiment with the shortest echo time of 50µs. Spectra '*b*-*d*' were recorded at longer echo times ranging from 250 µs to 2 ms.



Figure No. 5: ¹H rotor-synchronized echo MAS NMR spectra of the zeolitized brick after different echo times ranging from 50 µs to 2 ms.

As can be seen in Fig. 5, the peaks at 4.3 ppm and 3.8 ppm have much higher echo stabilities than the broad signal at 4.8 ppm. This suggested that the latter signal should result from the magnetic resonances of water protons involved in strong hydrogen bonds within α -cages of brick zeolite(s), in agreement with Greiser et al.'s data on geopolymer-zeolite composites [29] and Glid et al.'s data on alkali metakaolinite [30]. The peak at 4.3 ppm was instead assigned to water molecules which were more freely involved in β -cages of brick zeolite(s), as pointed out for zeolite A in Greiser et al.'s works [30]. As for the weak peak at 3.8 ppm, its resonance should probably be caused by water molecules strongly complexed with Na⁺ cations and associated with other clays of the studied brick (but not identified) [31].

¹*H* MAS NMR analysis of protonic zeolitized brick_____ In the polar hydrogen forms of the modified brick (with acid sites), adsorbed water molecules underwent a protonation from which the resulting H_3O^+ became firmly attached to negatively charged zeolite framework by means of strong ionic bonds. In this case, the mobility of protons resonating at the chemical shifts 4.3 ppm and 3.8 ppm (see fig. 4a) were substantially reduced, which led to signal broadenings and thereby to the disappearance of these two sharp peaks (see Fig.4b).

However, the ¹H MAS NMR spectrum of the H-form of the modified brick still displays a unique and large resonance centered at 4.5 ppm (Fig. 4b), which is slightly broader than that observed for sodic zeolitized brick and centred at 4.8 ppm (see Fig. 4a). It could be conceived that the observed signal (at 4.5 ppm; see Fig.4b) resulted globally from the resonances of protons of both hydroxyl groups and water molecules present in zeolitic pores. The magnetic resonances of these protons were highly overlapped because of the occurrence of H-bondings between -OH and H₂O molecules and delocalization of H₃O⁺ ions on negatively charged zeolite framework.

CONCLUSION

On the basis of surface site dissociation and complexation concepts, we have discussed in the present work an important aspect of the reactions occurring on the surface of a zeolitized brick, namely the formation of surface complexes of negatively charged sites with divalent $(Ni^{2+} and Cd^{2+} ions)$. It became possible to make predictions of averaged surface-protonation equilibrium constants for surface zeolites (NaA and NaP) present in the modified brick. The predictive methods employed here had made it easier to fit experimental data. Firstly, a theoretical approach for determining the surface potential (Ψ o) was used at the equilibrium state of metal cation-zeolitized systems. And secondly, from "Vo/final pH" measurements, computational calculations permitted to evaluate the following surface chemical parameters: (i) the pH at the point of zero charge, $pH_{PZC} = 5.74 - 5.80$; and (ii) the dimensionless pH sensitivity parameter (β). Knowledge of the pH_{PZC} value and the β parameter enabled the K_{a1} and $K_{\alpha 2}$ constants to be calculated: $pK_{\alpha 1} = 2.65 \pm 0.42$ and $pK_{\alpha 2} = 8.90 \pm 0.37$. With the ¹H MAS NMR technique, it had been evidenced the existence of hydrogen bonds between water protons and negatively charged sites (>S $-O^{-}$), and particularly those located inside α -cages and β -cages of brick zeolite(s). As for the protonic form of the zeolitized brick, an unique and broad ¹H NMR signal detected suggested the involvement of protons release, H⁺ exchange and stronger ionic bonds between proton species and negatively charged aluminosilicate framework.

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