

Władysław JANUSZ*, Ewa SKWAREK*

ADSORPTION OF Ni (II) IONS AT THE FeTiO₃/NaCl INTERFACE – STRUCTURE OF ELECTRICAL DOUBLE LAYER

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The influence of ionic strength, pH, and presence of ions on adsorption of Ni(II) at the FeTiO₃/NaCl solution interface was investigated. Measurements of adsorption of Ni(II) ions at the FeTiO₃/electrolyte solution interface was presented. ζ potential, surface charge density, adsorption density, pH_{50%} and Δ pH_{10-90%} parameters for different concentrations of carrying electrolyte were presented. The adsorption constants of surface hydroxyl groups were determined using numerical optimization.

Key words: ilmenite, electrical double layer, Ni(II) adsorption, surface charge density and zeta potential

INTRODUCTION

The ilmenite is the most widely used titanium mineral that plays an important role in the titanium industry. The preparation of synthetic rutile containing more than 90% titanium dioxide from ilmenite involves oxidation roast, reduction roast and leaching (Mackey, 1994). The processing of ilmenite incorporates crushing and milling, in order to liberate the ilmenite mineral from waste, and after that concentration by flotation, leaching other techniques. Most of them process aqueous dispersions of ilmenite where the various reactions at the mineral solution interface have take place. Among these is the adsorption of divalent metal ions at mineral surface and this process has great influence on the electrical properties of the interface and in this way on stability of dispersion. Pure FeTiO₃ has technical application as ferroelectric and semiconductor material.

The investigation of adsorption of Ni (II) on the FeTiO₃ surface may be interesting from practical point of view because nickel ore occurs in natural entertainment next to

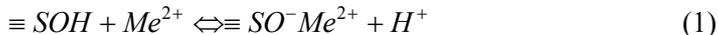
* Uniwersytet Marii Curie-Skłodowskiej, Wydział Chemii, Pl. M.C. Skłodowskiej 3, 20-031 Lublin, Poland

ilmenite (Surowce mineralne świata, 1985). The association of nickel with ilmenite is important for various processes with nickel extraction. Ilmenite is consisted of two simple oxides: TiO_2 and Fe_2O_3 . This is the reason of its different surface properties.

Hydrogen ions are released as a result of the adsorption process of metal cations at the metal oxide surface.

Process of uptake of hydrolysable metal ions at the solid/aqueous solution interface according to (R.O. James et al., 1975) may be described of metal ions at the metal oxide electrolyte interface by four different models: reactions exchange of free metal ions with hydrogen of surface hydroxyl groups, specific adsorption of hydrolysis species of metal ions, adsorption of metal ions and then surface hydrolysis and at high concentrations of metal cation adsorption of its low to high molecular weight polymeric hydrolysis products (James et al., 1975).

According to site binding theory of edl the divalent ions can be adsorbed specifically on the metal oxide surface by forming the coordinate bonds between the surface oxygen atoms and the adsorbed cation. Some of them are adsorbed so strongly that there is no water molecules between the adsorbed ion and the surface, so-called inner-sphere complexes the outer-sphere complex is formed, when a water molecule is present between the adsorbed ion and the surface, then the outer-sphere complex is formed. Divalent ions may adsorb at the metal oxide surface on one or two surface sites (P.W. Schindler et al., 1976). It is assumed that the following reactions are responsible for the adsorption of bivalent cations at the oxide/electrolyte interface:



As may be noticed from Eq 1 and 2 the adsorption of cations releases the hydrogen ions from hydroxyl groups, so the increase of pH in the system will favor the adsorption of cations at the metal oxide/electrolyte interface. Consequently, the sharp increase of the cation adsorption from 0% to 100%, with increase of pH of the electrolyte as much as 1, 2 units is observed. This relationship is called “edge of adsorption” and Robertson and Leckie (1997) have proposed very useful parameters to characterize it:

- $dpMe/dpH$ – parameter that shows the activity of cations; must vary when pH of the solution changes to maintain the constant adsorption of the cation.
- $pH_{50\%}$ - the value of pH when 50% of initial concentration of cation adsorbs, this parameter characterizes the position of adsorption edge on the pH scale.
- $pH_{10-90\%}$ - the range of pH where the adsorption changes from 10% to 90%, it characterizes the slope of the edge.

$$*K_1^S = \frac{[H^+][\equiv SO^-Me^{2+}]}{[Me^{2+}][\equiv SOH]} \frac{\gamma_H\gamma_1}{\gamma_{Me}\gamma_0} \times \exp\left(\frac{e(2\psi_1 - \psi_H)}{kT}\right) \quad (4)$$

$$*\beta_{21}^S = \frac{[H^+]^2[(\equiv SO^-)_2Me^{2+}]}{[Me^{2+}][\equiv SOH]^2} \frac{\gamma_H^2\gamma_2}{\gamma_{Me}\gamma_0^2} \times \exp\left(\frac{e(2\psi_2 - \psi_H)}{kT}\right) \quad (5)$$

$$*K_{MeOH}^S = \frac{[H^+]^2[\equiv SOMeOH]}{[Me^{2+}][\equiv SOH]} \frac{\gamma_H^2\gamma_1}{\gamma_{Me}\gamma_0} \times \exp\left(\frac{e(\psi_1 - \psi_H)}{kT}\right) \quad (6)$$

were:

- γ_1, γ_2 – activity coefficients of $\equiv SOH^{(z-1)+}$ and $(\equiv SO)_2H^{(z-2)+}$ groups,
 ψ_1, ψ_2 – means potentials in the planes of adsorption of Me^{2+} bounded to $\equiv SOH^{(z-1)+}$
 and $(\equiv SO)_2H^{(z-2)+}$ surface species respectively,
 γ_0 – activity coefficients of $\equiv SOH$ group,
 γ_H – activity coefficients of H^+ ions,
 γ_{Me} – activity coefficients of metal cation,
 k – Boltzman constant.

The value of reaction constants may be determined by (Schindler, 1981) method as well as by use of numerical optimization procedures.

Results of specific adsorption of ions at electrical double layer structure may be described by means of DLM (*double layer model*) and TLM (*triple layer model*). According to DLM model, specific adsorption of ions is impossible with creation of inner-sphere complexes, when ions take position at inner surface plane. According to the SCM model, site-binding (*s-b*) theory, the adsorption of background electrolyte ions may be considered both as specific adsorption and as the unspecific one. Background electrolyte ions undergo so-called ionization and complexation reactions increasing surface charge density on the surface of oxides. Ions found in diffusion plane edl adsorbed unspecific ally (K.F. Hayes et al., 1996).

The specific adsorption ions may lead to creation of the inner sphere or outer-sphere surface complexes. In case of the outer sphere, complexes are adsorbed in the Inner Helmholtz Plane (IHP). These ions are separated from the solid surface by a water molecule; inner-sphere complexes ions take place in surface plane (A.P. Robertson, 1997).

EXPERIMENTAL

Experiments were performed on a commercial ilmenite sample from Alfa Aesar that contain about pure 99.9% of ilmenite. XRF analysis of the sample showed the presence of the following elements 34.3 % Fe and 27.7 % Ti. The specific surface of

the FeTiO₃ sample, determined by nitrogen desorption, was 1.28 m²/g. BJH analysis of the isotherm obtained by adsorption-desorption of nitrogen did not reveal micropores, only mesopores of the rise of 52 Å in the examined FeTiO₃ sample were detected. Roentgen diffraction analysis revealed that crystallographic structure of measured substance is ilmenite. Nickel ions adsorption was performed with ⁶³Ni isotope as a tracer. The specific adsorption of Ni(II) ions at FeTiO₃ interface was investigated by the means of radioisotope method as a function of Ni(II) concentration ions, NaCl concentration and pH. The initial concentration of Ni(II) ions ranged from 1x10⁻⁶ to 1x10⁻³ mol dm⁻³, pH was changed from 3 to 10. As a background electrolyte NaCl solution was used of concentrations 0.1, 0.01, 0.001 mol dm⁻³. The adsorption measurements were complemented by the potentiometric titration of FeTiO₃ suspensions and electrophoresis measurements.

To remove ionic type contaminations, which might influence the ion adsorption measurements, the ilmenite was washed with double distilled water until constant conductivity about 2 μS/cm was achieved. Adsorption and surface charge measurements were performed simultaneously in the suspension of the same solid content, to keep the identical conditions of the experiments in a thermostated Teflon vessel in 25°C. To eliminate the influence of CO₂ all potentiometric measurements were performed under nitrogen atmosphere. pH values were measured using a set of glass REF 451 and calomel pHG201-8 electrodes with Radiometer assembly. Surface charge density was calculated from the difference of the amounts of added acid or base to obtain the same pH value of suspension as for the background electrolyte.

The zeta potential of the ilmenite dispersions was determined by electrophoresis with Zetasizer 3000 by Malvern. The measurements were performed at 100 ppm solid concentration ultrasonication of the suspension.

RESULTS AND DISCUSSION

A structure of the electrical double layer at the ilmenite /electrolyte solution interface is poorly described; (M. Kosmulski, 2001) in his comprehensive review cited only few papers. One of them (M.A. Butler et. al. 1978) the value pH_{pzc}=6.3, in the second has obtained pH_{IEP}=3.3. (M.A. Blesa at al.,1997) determined for FeTiO₃ in solution 0.01 mol/dm⁻³ KCl pH_{IEP}=3.8. As it is seen these values are scattered and further investigation of this system is necessary.

Fig. 1 presents the surface charge density of ilmenite as a function of pH for three concentrations of NaCl solution as a background electrolyte. Surface charge density versus pH dependence as a function of electrolyte concentration at the FeTiO₃/NaCl solution interface is presented on Fig.1. As can be seen CIP (*Common Intersection Point*) is at pH=7.19 and lie above line indicated σ₀=0. The point pH_{pzc} shifts with increase of the concentration of background electrolyte towards higher values of pH. The difference between common intersection point CIP and pzc indicate that density of adsorption of Na and Cl at the FeTiO₃ in the pH_{pzc} is not the same and the anions

have stronger adsorption affinity than cation. So assumption of specific anion adsorption is additionally supported by greater increase of surface charge density below pH_{pzc} . The increase of background electrolyte concentration results in a shift of pH_{pzc} . Because this effect depends on complexation reactions that may indicate that chloride ions adsorb stronger than sodium ones.

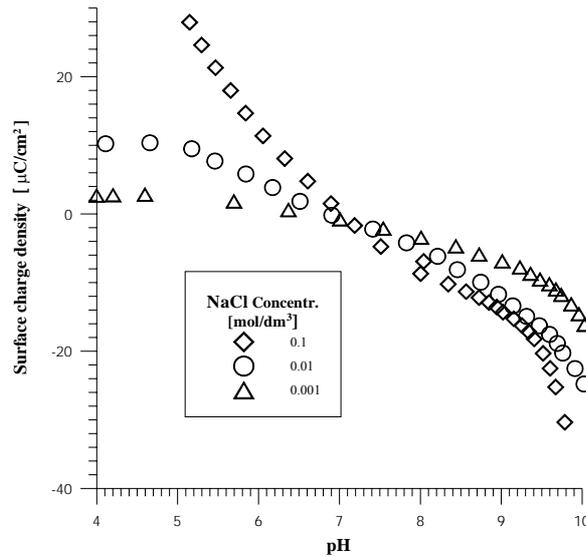


Fig. 1. Surface charge density at the FeTiO₃/NaCl solution interface as a function of pH

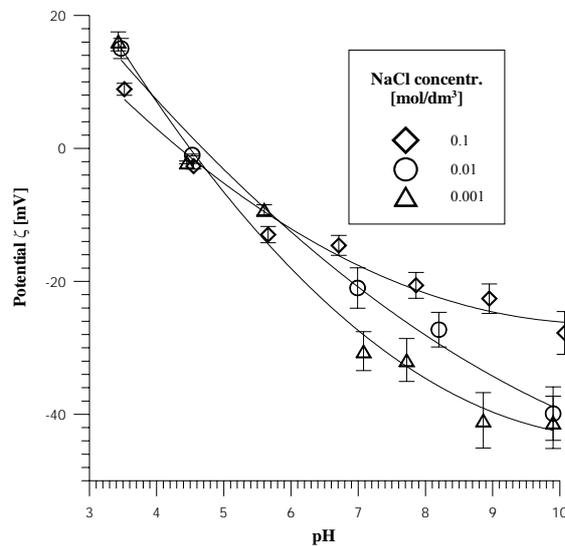


Fig.2. The ζ potential as a function pH at the ilmenite particles in solution NaCl

Potentiometric titration of FeTiO_3 was carried out for the same ionic strength electrolyte but different concentration of the adsorbent to eliminate in calculation of surface charge density consumption of H^+ ions in the solubility of oxide reactions.

The series of potentiometric titration characterized by a different mass of the solid but the same ionic strength of electrolyte were conducted in order to control FeTiO_3 solubility. (E. Olanipekun, 1999) a kinetic study of the leaching of powdered ilmenite ore by hydrochloric acid had been investigated. The reaches had resulted the following: temperature and concentration of hydrochloric acid have a significant effect on the rate of dissolution of titanium and iron from the ilmenite ore. In all tests, not more than 80% of titanium and 85% of iron dissolved. Apparently, this is due to the used reaction conditions which were not vigorous. The actual amount of element leached depends on ilmenite mineralogy and reaction variables. (A.F. White, et al. 1994) ascertained that FeTiO_3 is a very stable compound, 10^7 year old. It is a geological champion.

The ionization and complexation constants of the surface hydroxyl groups were calculated according to the method of (J.A. Davis et al., 1978), Schwarzenbach modified by (W. Janusz, 1991), and using numerically optimization procedures, on the basis of surface charge density versus pH and electrolyte concentration data (W. Janusz, 1994). The obtained values are collected in Table 1.

Table 1. The values of surface ionization and complexation constants for $\text{FeTiO}_3/\text{NaCl}$ solution system

Constants	Method		
	Davis <i>et al.</i>	Modified Schwarzenbach's	Numerical Optimization
pK_{a1}	5.09	5.10	0.003
pK_{a2}	9.15	9.14	10.52
pK_{Cl}	5.41	5.97	5.81
pK_{Na}	8.01	7.67	7.12

One can see a good agreement with values calculation method Davis *et al.*, and Schwarzenbach. Constants were calculated according to the method of numerically with except pK_{Cl} were differed, however that sets of constants give the best fit with experimental data. The systems were reaches characterized by a big ΔpK difference between pK_{a1} and pK_{a2} ionization constants. The great value of $\Delta\text{pK}_{\text{FeTiO}_3} = 4.04$ is typical for the systems about low participation groups with charge start up ionization hydroxyls groups in balance surface charge. Analysis of the constances indicates that there is larger number of anionic surface groups than cationic ones, especially for FeTiO_3 system.

The contribution of the particular surface groups in the surface charge of the FeTiO_3 is depicted in Fig. 3. It can be noticed that for this electrolyte concentration the contribution of the ionized groups ($[\equiv\text{SOH}_2^+]$, $[\equiv\text{SO}^-]$) in the surface charge

formation is very small. As it is seen, the calculated concentration of surface charge density with data obtained experimentally shows acceptable consistence of both values (Fig.3) in the range pH from 5 to 9.

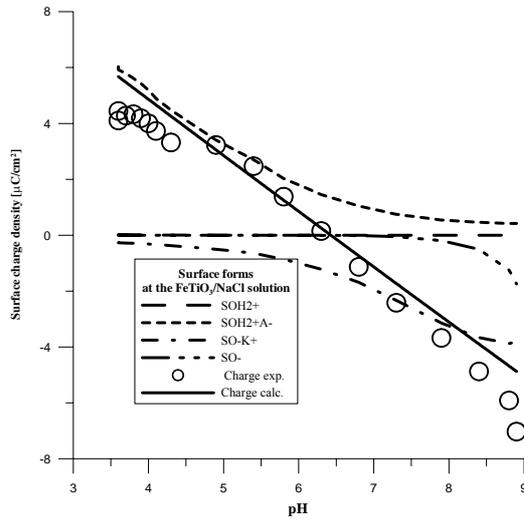


Fig. 3. Model calculation of surface charged forms at the FeTiO₃ surface in the 0,1 mol/dm³ solution of NaCl of concentration

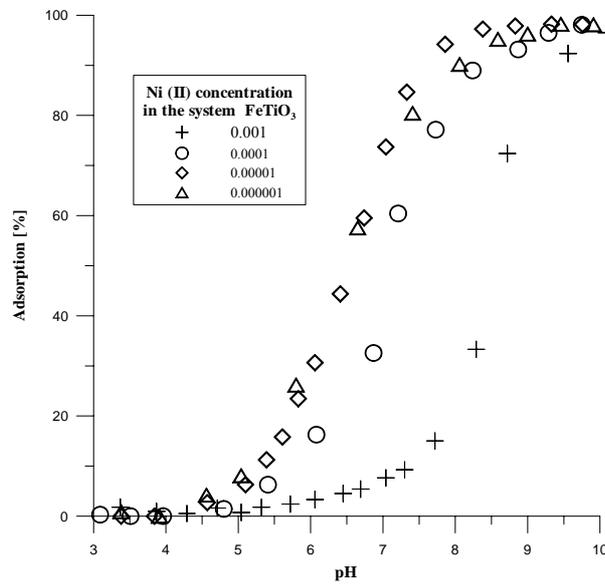


Fig. 4. Adsorption of Ni (II) ions at FeTiO₃/0.001 mol dm⁻³ NaCl interface vs pH

The adsorption density of Ni (II) ions as a function of pH in the FeTiO₃/NaCl solution system is presented in Fig. 4. The adsorption edge of the nickel ion adsorption plot in the studied system is characteristic for adsorption of divalent cations on the oxides. With increasing initial concentration of nickel ions the adsorption edge shifts toward higher pH values. For pH≈10 adsorption reaches 100% that means that almost all nickel ions are on the solid phase. The property surface hydroxyl groups on mixed oxides depends on number and kind of metal atoms the in vicinity of hydroxyl group. In both case hydroxyl groups would had different acid-base character.

Table 2. Values of pH_{50%} and ΔpH_{10-90%} parameters for the system FeTiO₃/0.001 mol dm⁻³ NaCl solution, Ni (II) ions

Parameters of Adsorption Edge	C _{Ni(II)} mol dm ⁻³			
	0.001	0.0001	0.00001	0.000001
pH _{50%}	8.31	7.02	6.43	6.48
ΔpH _{10-90%}	2.14	2.21	2.43	2.58

Characteristic adsorption edge parameters pH_{50%} and ΔpH_{10-90%} are listed in Table 2. These data show the shift of the adsorption edge towards higher pH values with the increase starting concentration of nickel ions. The adsorption edge slope is characterized by the ΔpH_{10-90%} parameter. It increases when nickel ions initial concentration decreases in the system.

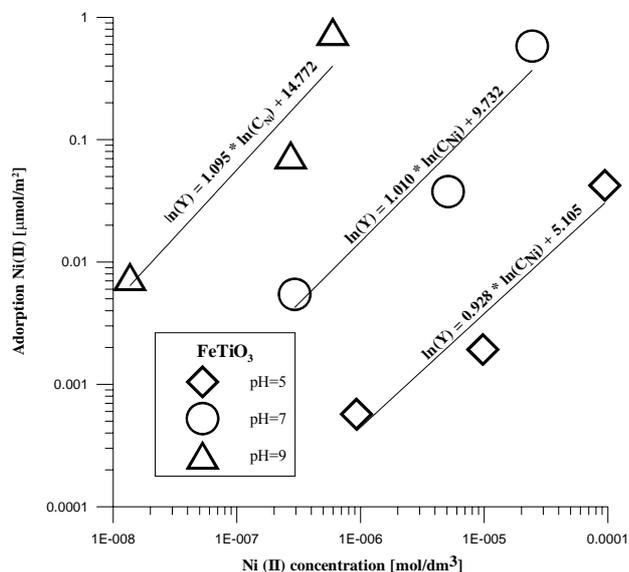


Fig. 5. Adsorption of Ni (II) at FeTiO₃ /0.001 NaCl solution interface as a function of equilibrium concentration for selected pH values (5,7 and 9)

Fig. 5 shows the adsorption isotherms of Ni(II) ions for selected pH values (5, 7 and 9). In the low pH range the log-log plot of the isotherm is linear and is characterized by smaller than one slope coefficient. When pH increases the slope of the isotherms decreases. Dependence log number of adsorbent ions nickel from log concentration ions in solution has carried *Krurbatow plots*, for small concentration ions has a linear character, from here usually described by Freundlich isotherm.

The values of equilibrium constants of the adsorption reactions, calculated on the basis of the TLM model of edl using numerical optimization procedure, are collected in Table 3. As it is seen, the calculated concentrations of the complexing nickel cations (Fig.6) show acceptable consistence with the adsorption data obtained experimentally.

Table 3. Values of the adsorption constants for Ni (II) ions for FeTiO₃/0.001 mol dm⁻³ NaCl solution, Ni (II) ions

Constans	$C_{Ni(II)} \text{ mol dm}^{-3}$			
	0.001	0.0001	0.00001	0.000001
pK ₁	5.00	5.22	4.00	4.29
pβ ₁	9.54	12.00	9.72	10.07

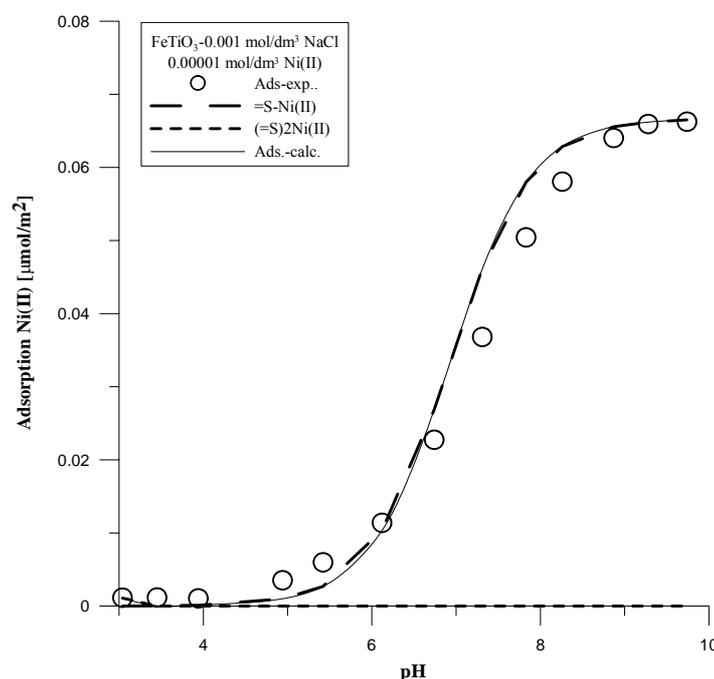


Fig. 6. Model calculation of adsorption forms Ni (II) at the FeTiO₃ surface in the 0.001 mol/dm³ solution NaCl – 0.00001 mol/dm³ Ni (II)

On Fig. 6 one can see share of Ni(II) forms adsorbed on FeTiO_3 surface in the pH function for start concentration $0.00001 \text{ mol dm}^{-3}\text{Ni(II)}$. Nickel ions are adsorbed onto one hydroxyl group.

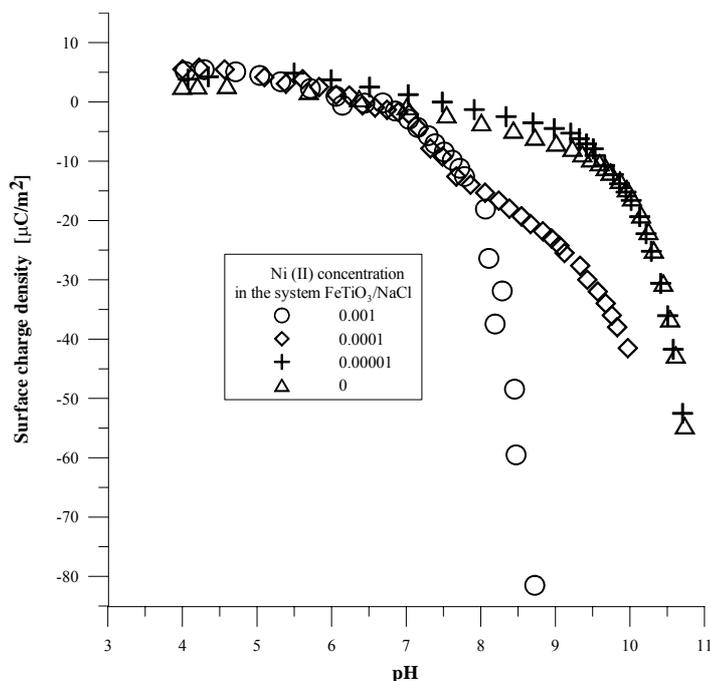


Fig.7. The surface charge density $\text{FeTiO}_3/\text{NaCl}$ solution interface as a function of pH

The charge density dependence versus pH in the presence of Ni(II) ions is shown on Fig. 8. As it can be seen, the charge density as a function of pH for the lowest concentrations of Ni (II) is the same as for the system without the absent nickel ions. For initial concentration of $0.001 \text{ mol dm}^{-3}\text{Ni(II)}$ the increase of concentration of negatively charged groups is observed on Fig. 7.

The surface charge decreases above $\text{pH}=7.5$, is covering with “adsorption edge” of nickel (II) ions in this pH range. Fig. 7 show increase of the concentration of negatively charged groups. This was caused adsorption cations Ni(II), who is to associate with get rid H^+ ions with hydroxyl group.

The charge density versus pH dependence in the presence of Ni(II) ions is well correlated with adsorption of nickel ions versus pH. When pH value reaches pH_{pzc} , however for lower concentration, the charge density dependence versus pH is the same, when there is no nickel ions, Fig.7. Higher surface charge density concentration surface charge density is reduced to -80 μC/cm^2 . To sum up nickel adsorption causes decreasing of negatively charged groups concentration on the surface of ilmenite. Another consequence of this fact is dissociation of hydroxyl groups.

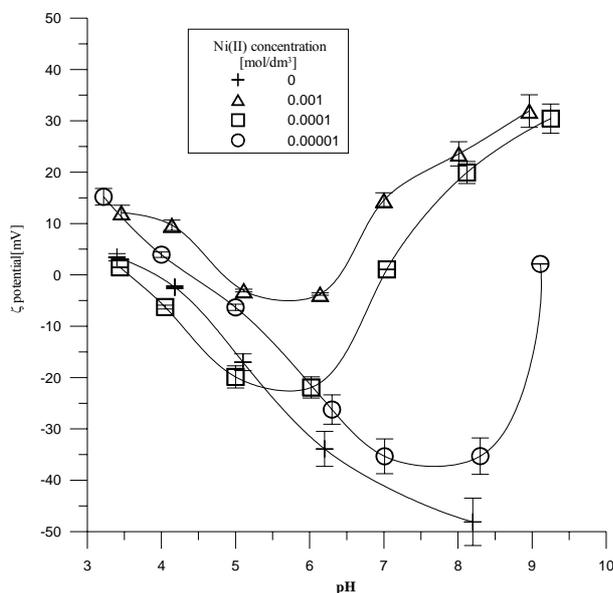


Fig. 8. ζ potential at FeTiO₃/NaCl solution interface as a function pH

The increase of nickel ions concentration in the system causes the lowering of the zeta potential (Fig. 8). It is visible from initial concentration of 0.00001 mol dm⁻³, while for initial concentration of 0.0001 mol dm⁻³ charge reversal point can be noticed (point CR2) for pH =6. Such point is characteristic for the overcharged compact layer caused by the specific adsorption of divalent cations.

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W środowisku naturalnym rudy niklu występują obok ilmenitu, dlatego też badania adsorpcji niklu na powierzchni FeTiO₃ mogą mieć pewne znaczenie praktyczne. Materiał wykorzystany do badań był komercyjny, metody analityczne stosowane to miareczkowanie potencjometryczne oraz pomiary elektrokinetyczne. Adsorpcję jonów niklu prowadzono w różnym stężeniu na granicy faz FeTiO₃/NaCl. Określono wpływ: pH, siły jonowej elektrolitu na obecność jonów niklu w roztworze. Wyznaczono następujące parametry charakteryzujące pwe: potencjał ζ, gęstość ładunku powierzchniowego, gęstość adsorpcji oraz parametry krawędzi adsorpcji: pH_{50%} i ΔpH_{10-90%}. Na podstawie zmian ładunku powierzchniowego w skali pH obliczono stałe jonizacji i kompleksowania grup hydroksylowych na granicy faz ilmenit/roztwór metodami: Devisa, Schwanbacha i optymalizacji numerycznej.