Physicochem. Probl. Miner. Process. 46(2011) 73-82

journal homepage
www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

Index No. 32213X ISSN 1643-1049

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ADSORPTION OF Ca(II) AND Fe(III) IONS AT THE SnO_2/ELECTROLYTE SOLUTION INTERFACE

Received May 7, 2010; reviewed; accepted June 25, 2010

Adsorption of Ca(II) and Fe(III) ions at the SnO_2/NaCl solution interface as well as the effect of adsorption on the structure of electrical double layer were presented in this paper. The influence of ionic strength, pH and presence of ions on adsorption of Ca(II) and Fe(III) at the SnO_2/NaCl solution interface were also investigated. Adsorption was investigated in the pH range of 2 to 10. The zeta potential, surface charge density, adsorption density, $pH_{50\%}$ and $\Delta pH_{10\text{-}90\%}$ parameters for different concentrations of carrying electrolyte were presented. The adsorption reaction constants involving the surface hydroxyl groups were determined using the numerical optimization method.

keywords: SnO_2, electrical double layer, surface charge density, zeta potential, Ca(II) adsorption, Fe(III)adsorption

1. INTRODUCTION

Tin is a chemical element which is not widely spread in the Earth's crust ($4\cdot10^{-3}$ wt. %). There are few more than ten minerals containing tin and the most important is cassiterite (tin dioxide SnO_2), a source of tin as well as other tin compounds (Bielański, 1998). Tin dioxide has been used for a long time in ceramics, sensors for environment pollutants control in chromatographic detectors as well as catalysts (Dobrzański and Zawadzki, 1981). Tin dioxide has also been used in production of

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semiconducting solar cells (Suppan, 1997). Since present natural resources of tin are small, the role of tin recycling increases significantly. Control of stability of tin dioxide dispersion during enrichment process is very important and this is possible by means of changes of electrokinetic potential that depends on concentration of potential determining and specifically adsorbing ions (Janusz at al., 2007). Adsorption or desorption of calcium and iron ions on the SnO_2 surface is related not only to the hydrogen ions concentration but also to the surface potential. Adsorption has a great influence on the surface potential and through it, on SnO_2 particles aggregation and heteroaggregation with other particles. The multivalent ions can be adsorbed specifically on one or two surface sites (hydroxyl groups) of metal oxide surface via hydrogen exchange, but number of sites usually occupied by a single ion is smaller than two (Schindler et al., 1981). Adsorption of such ions may lead to formation of inner-sphere or, when the adsorbed cation is separated from the surface by a water molecule, outer-sphere complexes. Usually a sharp increase of cations adsorption from 0 to 100%, with an increase of pH of the electrolyte, is observed. This relationship is called “the edge of adsorption” Robertson and Leckie (1997) proposed very useful parameters to characterize it:

- d(pMe)/d(pH) – parameter that shows the activity of cations; must vary when pH of the solution changes to maintain the constant adsorption of the cations
- $pH_{50\%}$ - the value of pH when 50% of the initial concentration of cations is adsorbed; this parameter characterizes the position of adsorption edge on the pH scale
- $pH_{10\text{-}90\%}$ - the range of pH where the adsorption changes from 10 to 90%; it characterizes the slope of the edge.

Heavy metal cations belong to ions possessing a great adsorption affinity for mixed oxide surfaces and create inner-sphere complexes. The DLM (double layer) and TLM (triple layer) models describe specific adsorption of ions. According to the DLM, the specific adsorption of ions is possible with the creation of the inner-sphere complexes, where ions are situated inside the surface plane. According to the TLM (model SCM, site binding), also absorption of background electrolyte ions may be considered as specific and nonspecific. The ions, taking part in the ionization and complexation reactions, increase the surface charge density on the oxide and adsorb specifically, but those in the diffusion part of the electrical double layer (EDL) are adsorbed nonspecifically (Hayes and Katz, 1996). In the present paper we report the influence of ionic strength, pH and presence of ions on the adsorption of Ca(II) and Fe(III) and the structure of the EDL at the SnO_2/electrolyte interface. Adsorption measurements are complemented with the surface charge density and ζ potential determinations. The effect of Ca(II) and Fe(III) adsorption on the properties of the EDL is discussed. To determine the constants of surface reaction by numerical optimization, the ion adsorption data and triple layer model of the EDL were used.

2. EXPERIMENTAL

Experiments were carried out using a commercial SnO_2 sample purchased from Aldrich Chemical Company. The roentgen diffraction analysis revealed a rutile type structure of the studied dioxide. The size distribution analysis by the photo correlation spectroscopy (PCS) method showed that particle sizes ranged from 300 nm to >3000 nm and the arithmetic mean diameter of the particles was 458 nm. The specific surface of the SnO_2 sample determined by nitrogen desorption was 7.4 m^2/g. The BJH (Barret, Joyner, Halenda) analysis of the isotherm obtained by adsorption-desorption of nitrogen did not reveal micropores in the examined SnO_2 sample.

Adsorption densities of Ca(II) and Fe(III) ions were measured using a radiotracer technique with ^{45}Ca and ^{55}Fe radioisotopes supplied by Polatom (Świerk, Poland). Specific adsorption of Ca(II) and Fe(III) ions at the /SnO_2 interface was studied as a function of Ca(II) and Fe(III) ions concentration, NaCl concentration and pH. The initial concentration of Ca(II) and Fe(III) ions ranged from 10^{-6} to 10^{-3} M, pH was changed from 2.0 to 10.0. NaCl solution was used as a background electrolyte. The adsorption measurements were complemented by potentiometric titration of SnO_2 suspensions and electrokinetic measurements.

Adsorption and surface charge measurements were carried out simultaneously in a thermostated Teflon vessel at 25°C. To eliminate the influence of CO_2 all potentiometric measurements were performed under nitrogen atmosphere. pH values were measured using a PHM240 Research pH-meter (G202C and K401 electrodes). The surface charge density was calculated from the difference between the amounts of added acid or base to obtain the same pH value of suspension as for the background electrolyte.

The zeta potential of SnO_2 dispersions was determined by electrophoresis with Zetasizer 3000 by Malvern. Diluted SnO_2 suspensions containing 100 ppm of solids in the electrolyte solution were used. Before measurements the suspensions were dispersed using Sonicator XL2020 made by Misonix.

3. RESULTS AND DISCUSSION

The characteristic parameter of the EDL for the tin dioxide (SnO_2)/NaCl system is the shift of the point of zero charge (pH_{pzc}) with the background electrolyte concentration which decreases from 4.8 for 0.001 M NaCl to 4.0 for 0.1 M NaCl. This effect is caused by specific adsorption of cation. The pH_{iep} shifts from 4.5 for the solution 0.1 M to 4.0 for 0.001 M NaCl. The ionization constants, calculated from the charge density as a function of pH and electrolyte concentration, are $pK_{a1}=0.154$, $pK_{a2}=7.984$ and the complexation constants are $pK_{Cl}=1.765$, $pK_{Na}= 5.173$.

3.1. SPECIFIC ADSORPTION OF CA(II) IONS AT THE SnO_2/NaCl SOLUTION INTERFACE

Specific adsorption of multivalent/heavy ions at the metal oxide/electrolyte solution interface significantly influences the EDL structure. Influence of calcium ions on the EDL of the SnO_2/electrolyte solution interface has been presented by Ardizzone and Trasatti (1996). In this paper a comprehensive study on the influence of calcium ions Ca(II) adsorption on the EDL properties for the tin dioxide/electrolyte solution interface is presented. Figure 1 presents a dependence of characteristic parameters of the adsorption edge on the initial Ca(II) concentration for the SnO_2/0.1 M NaCl solution system. The position of the adsorption edge, characterized by $pH_{50\%}$, shifts from pH 4.2 to pH 5.5 for the 0.001 M NaCl concentration. With the increase of initial Ca^{2+} ions concentration, the adsorption edge slightly flattens, as indicated by parameter $pH_{10-90\%}$. For more concentrated NaCl solution the shift of the Ca^{2+} ions adsorption edge in the SnO_2/electrolyte solution system is more complicated due to competition in Na^+ and Ca^{2+} ions adsorption.

Figure 2 shows the adsorption isotherms as the log-log plot for adsorption versus concentration at the SnO_2/0.1M NaCl interface for three selected pH values (5, 7 and 9). A linear approximation of the log-log adsorption vs. concentration plot, indicated by a dashed line, for the lowest concentration shows that the slope of the straight line differs distinctly from 1, being a characteristic value for the isotherms based on either Henry or Langmuir equations. It means that these isotherms cannot be used for this system and quantitative description of adsorption requires taking into consideration interactions connected with the presence of double electric layer or energetic heterogeneity of the surface. The surface charge density at the SnO_2/NaCl electrolyte interface in the presence of Ca(II) ions for 0.001M NaCl is shown in Fig. 3.

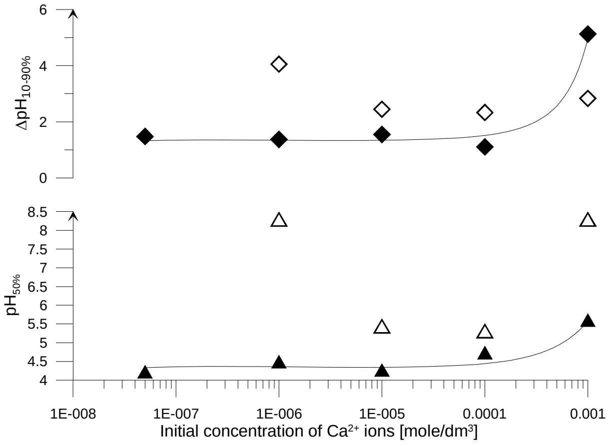

Fig. 1. Parameters of adsorption edge vs. initial concentration of Ca^{2+} ions for the SnO_2/0.001 M NaCl solution system. Closed symbols - 0.001 M NaCl, open symbols - 0.1 M NaCl

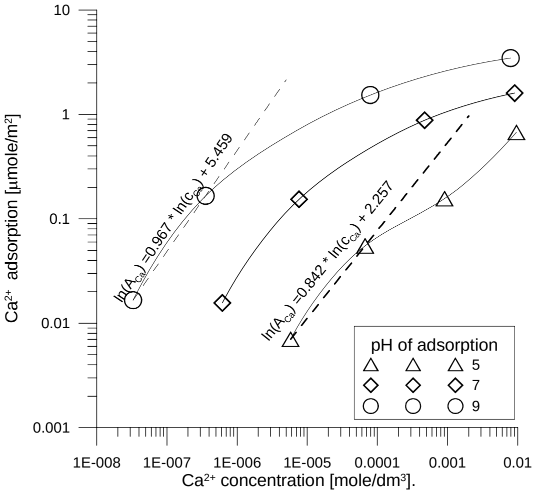

Fig. 2. Ca^{2+} adsorption isotherms for the SnO$_2$/0.1 M NaCl solution system

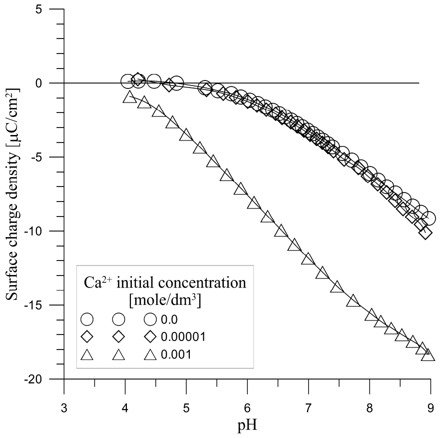

Fig. 3. Surface charge density as a function of pH in the presence of Ca^{2+} for the SnO$_2$/0.001M NaCl solution system

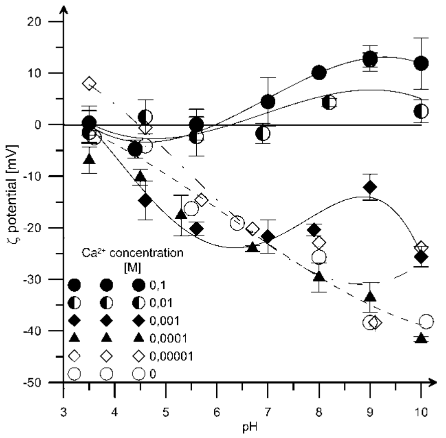

Fig. 4. Zeta potential vs. pH and initial Ca^{2+} concentration for SnO$_2$/0.1 M NaCl solution system

As result from Fig. 3, at a low initial concentration of Ca(II) ions, there is no effect of Ca^{2+} ions adsorption on the surface charge density at the SnO$_2$/NaCl solution interface because one can expect that for the adsorption density of 0.17 μmol/m^2 for the initial concentration of 10^{-4} M Ca^{2+} at pH>7, assuming that one Ca^{2+} ion replaces on the SnO$_2$ surface one hydrogen atom in one hydroxyl group, it should cause a surface charge density decrease by about 1.6 μC/cm^2. When the initial concentration of Ca^{2+} ions exceeds 10^{-3} M , then a significant decrease of the surface charge density and a shift of pH$_{\mathrm{pzc}}$ towards lower values of pH are observed. This is a result of negatively charged groups formation due to complexation of calcium ions by the surface hydroxyl groups. Reaction of calcium ions proceeds via release of H^+ ions form the surface hydroxyl groups. This causes an exchange of the H^+ ions of the hydroxyl groups with Ca^{2+} ions. The dependence shown in Fig. 3 indicates that Ca^{2+} ions are partially absorbed onto ionized ($\equiv SnO^-$) or complexed ($\equiv SnO^-Na^+$) and partially onto $\equiv SiOH$ groups with H^+ ions release.

Similarly, adsorption of Ca^{2+} ions from the solution of low initial concentrations of Ca^{2+} ions did not bring about within the experimental error any change of ζ potential. When the initial concentration of Ca^{2+} ions is equal to 0.001 M NaCl, then an increase of zeta potential above pH=7 is observed. For higher initial concentrations the charge reversal point (CR2) (change from negative to positive values of zeta potential) was observed. This is caused by a considerable compensation of the electric charge by the Ca^{2+} ions in the compact part of the electrical double layer. The calcium ion, being adsorbed onto one hydroxyl group, introduces two charge units into the compact layer of EDL.

Using adsorption density of Ca^{2+} ions as a function of pH the equilibrium constants for the reactions of Ca^{2+} ions in the SnO_2/0.001 M NaCl solution system (Eqs 1 and 2) were calculated by the method proposed by Schindler (1976), taking into account the ionized and complexed forms at the SnO_2 surface:

$$^{*}K_1^S = \frac{\left[\mathrm{H}^+\right]\left[\equiv \mathrm{SO}^-\mathrm{Me}^{2+}\right]}{\left[\mathrm{Me}^{2+}\right]\left[\equiv \mathrm{SOH}\right]}\frac{\gamma_{\mathrm{H}}\gamma_1}{\gamma_{\mathrm{Me}}\gamma_0}\times \exp\left(\frac{e(2\psi_1-\psi_H)}{\mathrm{k}T}\right) \tag{1}$$

$$^{*}\beta_{21}^S = \frac{\left[\mathrm{H}^+\right]^2\left[(\equiv \mathrm{SO}^-)_2\mathrm{Me}^{2+}\right]}{\left[\mathrm{Me}^{2+}\right]\left[\equiv \mathrm{SOH}\right]^2}\frac{\gamma_{\mathrm{H}}^2\gamma_2}{\gamma_{\mathrm{Me}}\gamma_0^2}\times \exp\left(\frac{e(2\psi_2-\psi_H)}{\mathrm{k}T}\right) \tag{2}$$

where: γ_1, γ_2 – activity coefficients of $\equiv SOH^{(z-1)+}$ and $(\equiv SO)_2H^{(z-2)+}$ groups, ψ_1, ψ_2 – denotes 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 – Boltzmann constant. The values of the reaction constants determined by a numerical optimization procedure are collected in Table 1.

Table 1. Reaction constants for adsorption involving one and two hydroxyl groups in 0.1M NaCl aqueous solution

C_{Ca}, mol/dm^3	pK_i	pK_B
0.000001	4.0	6.0
0.00001	3.88	6.0
0.0001	3.13	0.0
0.001	3.42	4.9
0.01	5.99	0.0

3.2. SPECIFIC ADSORPTION OF Fe(III) IONS AT THE SnO_2/NaCl SOLUTION INTERFACE

Distribution of iron(III) ions in aqueous solutions analyzed by Baes and Mesmer (1976) shows that hydrolysis starts at pH about 1 and $Fe(OH)_2^+$ appears at pH=1. From pH 3 to 6 the main form of iron(III) ions is $Fe(OH)_2^+$, then from pH 6 to 9 it is replaced with $Fe(OH)_3$ and over that value of pH with $Fe(OH)_4^-$. These charged species may interact with the surface of tin dioxide electrically and chemically.

For high iron salt concentrations in weakly acidic solutions one may expect appearance of solid iron hydroxide whose solubility product is $10^{-38.6}$. A study of iron(III) ions adsorption on SiO_2 carried out by Schindler et al. (1976) showed that the adsorption edge for iron ions occurs in the largely acidic environment ($pH_{50\%}$=2.0). They assumed that iron ion absorbs on the silica gel surface exchanging from 1 hydrogen atom at pH=1 to about 2 at pH=2. Fe(III) ions adsorb on the metal oxide forming the so-called inner sphere complexes, located in the surface plane. Due to the assumption $\psi_1=\psi_H$, the exponential term in Eqs 1 and 2 is equal to 1. In such a case the equilibrium constants can be calculated using the adsorption data and neglecting the electrostatic interaction, for example using the James et al. (1975) model. The values of equilibrium constants of nonstoichiometric exchange are collected in Table 2.

Table 2. Nonelectrostatic model parameters for Fe(III) ions adsorption at the SnO_2/electrolyte solution interface (James et al., 1975)

C_{Fe} mol/dm^3	pK_n	n_{H+}	pH_{50}
0.000001	5.356±1.011	2.89	1.973
0.00001	4.555±0.160	2.75	2.103
0.0001	1.439±0.145	1.64	2.239
0.001	-0.258±0.092	0.81	1.645

As can be seen from Table 2, the reaction equilibrium constants decrease with the increase of the initial concentration. A similar decrease is found for the number of released hydrogen ions (smaller than 3 for the lowest concentration). The number of hydrogen ions released at the highest concentration is surprisingly low. The characteristic parameter for the adsorption edge ($pH_{50\%}$) is also shown in Table 2. Its value grows with the initial Fe(III) concentration towards higher pH values, but not for the highest iron ions concentration. This shift is not as large as that for Ca(II) ions, where $pH_{50\%}$ of the adsorption edge is over pH=4. Figure 5 depicts the iron ions adsorption isotherms for the selected pH values, that is pH=3, pH=5, pH=7. According to the previous prerequisites, the isotherms shape indicates that precipitation occurs at higher iron ions concentrations (Hayes et al., 1996).

Figure 6 shows the dependence of charge density on pH in the presence of Fe(III) ions. Iron ions adsorption in the solution with the initial concentration of 10^{-4} M

Fe(III) causes accumulation of negatively charged groups at the surface (in comparison with the system in which iron ions are absent). In addition, an increase of surface concentration of negatively charged groups is observed with the pH increase, which indicates change in the form of the adsorbed Fe(III) ions (formation of surface hydroxyl complexes of Fe ions). Iron ions at the initial concentration of 10^{-3} M, as mentioned before, causes precipitation of iron compounds and growth of iron ions consumption. Figure 7 shows a contribution of individual complex forms on the SnO_2 surface as a function of pH for the initial concentration of Fe ions equal to 10^{-4} M.

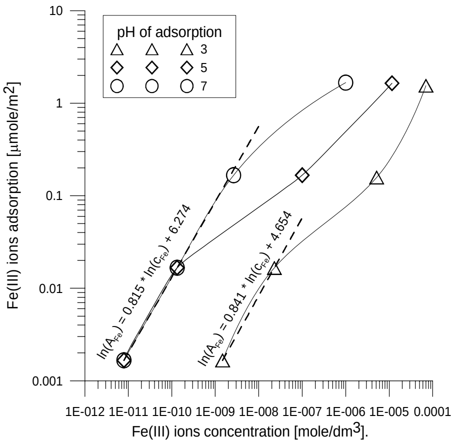

Fig. 5. Fe(III) ions adsorption as a function of Fe(III) equilibrium concentration at the SnO_2/0.1 M NaCl solution interface

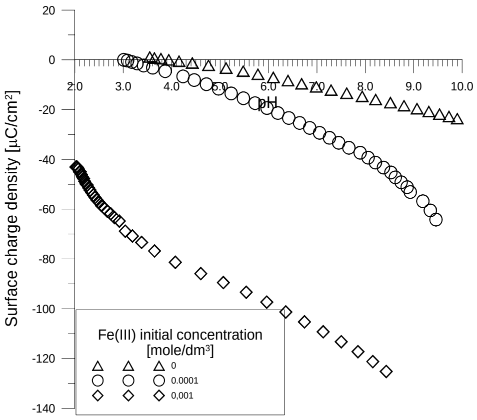

Fig. 6. Surface charge density as a function of pH in the presence of Fe(III) for the SnO_2/0.1 M NaCl solution interface

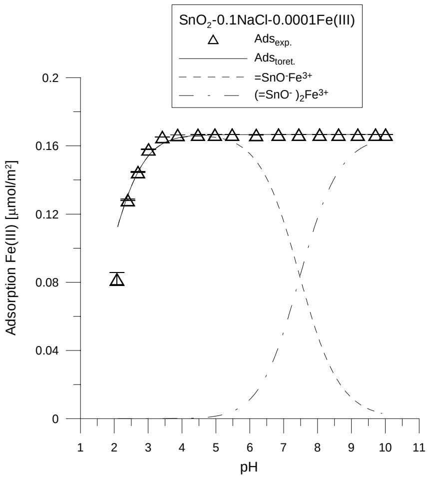

Fig. 7. Adsorption density of Fe(III) ions for the SnO_2/0.1M NaCl-0.0001M Fe(III) solution system

For Fe ions of the initial concentration of 10^{-4} M and pH=6 the form of Fe adsorbed on one hydroxyl group dominates while at pH=8 and over the dominating form is Fe adsorbed on two groups. This effect may result from iron ions abundance at a low equilibrium concentration, which is more beneficial for the adsorption on two groups than on one. The above statement is based on the Schindler model, taking adsorption on one and two hydroxyl groups into account (Schindler et al., 1981).

3. CONCLUSIONS

The investigations carried out in this paper can be summed up as follows.

1. The electrical double layer for the SnO_2/NaCl solution system can be characterized by the point of zero charge, pH_{pzc}, which shifts with the electrolyte concentration and increases from 4.8 for 0.001 M NaCl to 4.0 for 0.1 M NaCl. This effect is caused by specific adsorption of cation (Na^+). The pH_{iep} shifts from 4.5 for 0.1 M NaCl solution to 4.0 for 0.001 M NaCl.
2. The ionization constants, calculated from the charge density dependence on pH and electrolyte concentration, are pK_{a1}=0.154, pK_{a2}=7.984. The complexation constants are pK_{Cl} = 1.765, pK_{Na} = 5.173, respectively.
3. Calcium ions adsorbing on the tin dioxide surface release hydrogen ions. The number of ions released depends on pH and calcium ions concentration.
4. The adsorption isotherms for Ca(II) ions reveal mutual interactions of ions in the adsorption layer. The direction coefficient of the isotherm for the log-log plot of adsorption vs. the balance equilibrium concentration is lower than 1.
5. The adsorption of calcium ions on one hydroxyl group from the solution of high Ca(II) concentrations causes overcharging the EDL condensed layer leading to the positive ζ potential over pH_{pzc}, and even under alkaline conditions.
6. Fe(III) ions, up to 0.0001M, are absorbed on the tin dioxide releasing hydrogen ions (H^+). An increase of negatively charged groups density on the surface takes place.
7. Fe^{+3} adsorption edge at the tin dioxide/electrolyte solution interface occurs in acidic environment at pH about 2.
8. Precipitation of iron hydroxide on the tin dioxide surface occurs at the initial concentration of 0.001 M Fe(III) ions.

REFERENCES

ARDIZZONE S., TRASATTI S. (1996), Interfacial Properties of Oxides with Technological Impact in Electrochemistry, Adv. Colloid Interface Sci., 64, 173-251.

BAES C.F. and MESMER R.E ,The Hydrolysis of Cations, Wiley-Interscience, New York (1976).

BIELAŃSKI A. Podstawy chemii nieorganicznej Wydawnictwa Naukowe PWN część 3, Warszawa (1998).

DOBRZAŃSKI B., ZAWADZKI S. (1981). Gleboznawstwo, Państwowe Wydawnictwa Rolnicze i Leśne, Warszawa

HAYES K.F., KATZ L.E, (1996) Application of X-ray absorption spectroscopy for Surface Complexation modeling of Metal Ion Sorption in: Physics and Chemistry of Mineral Surfaces, Ed. P.V. Brady, CRC Press, New York, pp 147-224.

JAMES R.O, STIGLICH P.J., and HEALY T.W., (1975) Characterization of Aqueous Colloids by Their Electrical Double –Layer and Intrinsic Surface Chemical Properties Disc. Faraday Soc., 59, 142.

JANUSZ W., SKWAREK E., ZARKO V.I., GUN'KO V.M., (2007), *Structure of electrical double layer at the* Al_2O_3*-*SiO_2*/electrolyte solution interface*, Physicochem. Probl. Miner. Process. 41, 215-225.

SCHINDLER P.W., FÜRST B., DICK R., WOLF P.U., (1976) Ligand properties of silanol groups J. Colloid Interface Sci. 55-469.

SUPPAN, P. Chemia i Światło, PWN , Warszawa (1997).

ROBERTSON A.P., LECKIE J.O., (1997) Cation binding predictions of surface complexation models: effects of pH, ionic strength, cation loading, surface complex and model fit, J. Colloid Interface Sci. 88, 444.

Janusz, W., Skwarek, E., *Adsorpcja jonów Ca(II) i Fe(III) na granicy faz* SnO_2*/roztwór elektrolitu*, Physicochem. Probl. Miner. Process., 46 (2011) 73-82, (w jęz. ang),http://www.minproc.pwr.wroc.pl/journal

Cyna i jej związki mają szereg praktycznych i istotnych zastosowań od wielu lat. Obecnie zasoby naturalne cyny są nieduże. Szacuje się, że wystarczą na około 40 lat. Dlatego należy podjąć próbę odzysku cyny z materiałów zawierających ten pierwiastek. Przeprowadzono pomiary adsorpcji jonów wapnia i żelaza, dla jego różnych stężeń początkowych, w funkcji pH dla układu SnO_2/roztwór NaCl. Kształt krzywej adsorpcji w funkcji pH ma postać krawędzi adsorpcji. Wzrost stężenia początkowego jonów Ca(II) i Fe(III) powoduje przesunięcie krawędzi w kierunku zasadowym w skali pH. Wyznaczono charakterystyczne parametry krawędzi adsorpcji tj. $pH_{50\%}$ i $\Delta pH_{10-90\%}$. W oparciu o zależność adsorpcji od pH obliczono również stałe adsorpcji jonów Ca(II) i Fe(III). Zależność gęstości ładunku powierzchniowego od pH w obecności jonów Ca(II) i Fe(III) jest w dobrej korelacji z zależnością adsorpcji jonów Ca(II) i Fe(III) od pH. Adsorpcja jonów Ca(II) i Fe(III) na powierzchni SnO_2 prowadzi do wzrostu stężenia grup ujemnie naładowanych

słowa kluczowe: SnO_2*, podwójna warstwa elektryczna, gęstość ładunku powierzchniowego, potencjał dzeta, adsorpcja Ca(II), adsorpcja Fe(III)*