Regulation of clay particles charge for design of protective electrokinetic barriers

V.A. Korolev, D.S. Nesterov*

Lomonosov Moscow State University, Faculty of Geology, Department of Engineering and Ecological Geology, 119991, Leninskiye Gory, 1-1, Moscow, Russia

A B S T R A C T

Coupled electrokinetic protective reactive barriers (PRB) are considered as a perspective technology for the treatment of contaminated groundwater. Design of PRB is directly connected with a problem of barrier material choice. Clays can be considered as an appropriate material due to high adsorptive properties and relative cheapness. The barrier internals are formed by clay surface charge properties. We revealed that acidic and alkaline treatment of clay is an effective way to affect its protective properties so that clay can be used to treat various pollutants. Surface charge and electrokinetic properties of clays were characterized by point of zero charge (p.z.c.), point of zero net proton charge (p.z.n.p.c.) and ζ-potential at different pH. Suspensions of 3 main clay types were studied by microelectrophoresis and potentiometric titration methods. At pH > p.z.n.p.c. clayey barrier adsorbs predominantly cationic toxicants and at pH < p.z.c. – anionic ones. The barrier is seemed to be the least effective in pH range between p.z.c. and p.z.n.p.c. Given the physicochemical and electrokinetic parameters, the most efficient clays for barrier design are Cambrian illite and all montmorillonite clays.

1. Introduction

Pollution of ground water and soils by heavy-metal cations, various anionic species and organics is a real threat for people's health and environmental development. The sources of these pollutions are mines, plants, dumpsters of solid wastes, etc. The sewage from these objects is usually represented by acidic solutions where heavy metals reside in dissolved species and can spread to long distances [1].

Various protective technologies are applied to solve these ecological problems. One of them is electrokinetic barriers, which design technologies are developed widely recent time [2–4]. Electrokinetic barrier is a natural or artificial soil wall at which opposite sides electrical potential difference is created. Due to created potential difference, electroosmic (EO) and electromigration (EM) flows are created in the body of barrier in an opposite direction to groundwater flow. Thus, electrokinetic barrier makes a hurdle on a migration path of contaminated groundwater and protects the area from polluted flow [3]. Combined electrokinetic protective reactive barrier (PRB) is an example of the efficient technology. This coupled barrier works on a migration path of pollution as a semipermeable screen that binds toxicants (by their adsorption, ionic exchange, neutralization, oxidation, etc.) but passes water. Perspective protection technology is a 'funnel-gate' principle barrier where a raw of electrodes collects and passes polluted groundwater flow through reactive part of the barrier that binds toxicants [4].

In present time many researches successfully model and create these barriers [3–5]. Nevertheless, in many cases problem of material for these barriers is still unsolved.

One of the most appropriate materials for these barriers is clays due to their high adsorptive properties and specific surface area. In addition, clays are widely spread and are a relatively cheap material, but their appliance to this role is complicated by some circumstances. First, various clays show different efficiency to a specific toxicant due to clay mineral composition wherein clays of one mineral type may differ greatly by their adsorptive properties. Second, the same barrier can treat different toxicants (cationic or anionic, etc.) in appliance with change of medium conditions. The latter circumstance makes possible to change properties of the barrier directly for more efficient treat of polluted ground water.

Behavior of clays toward changes of medium conditions can be characterized by surface charge and electrokinetic characteristics: various components of surface charge, points of zero charge and ζ-potential. Knowledge of surface charge characteristics of clay soils may help in selection of clay material for creation of protective barrier against specific toxicant.

The surface charge components have different origin among clays. Isomorphic substitutions in clays cause a structural charge. Surface charge of hydroxyl groups originates from protonation/deprotonation reactions on the side surfaces of the particles or neutralization reactions

	List of used symbols		M_c	Sherer crystallinity index, units
			Eh	oxidation/reduction potential, mV
σ_p	total net charge surface density, C/m^2		k	specific electrical conductivity, S/m
σ_0	structural charge surface density, C/m^2		TDS	total dissolved solids, ppm
σ_H	pH-dependent hydroxylation surface charge density, C/m^2		C	concentration, mol/L ($=$ M)
σ_{IS}	inner-sphere surface charge density, C/m^2		V	residual volume of titrant used in suspense and blank solution titration, L
σ_{OS}	outer-sphere surface charge density, C/m^2			
ζ	electrokinetical potential, mV		$F \approx 96485.33\ C\ mol^{-1}$	Faraday constant
CEC	cation exchange capscity, meq/100 g ($=$ cmol kg^{-1});		m	mass of clay sample, g
SSA	specific surface area, m^2/g		z	equivalent number
HI	Hinkley index (X-ray structure index of kaolinite crystallinity), units;		p.z.c.	point of zero charge, units of pH
			p.z.n.p.c.	point of zero net proton charge, units of pH

on base and side clay particle surfaces resulted from disruption of Si-O-Si or Al-O-Al bonds and hydrolysis of boundary O atoms. Inner-sphere charge is caused by specific ions adsorption directly on the particle's surface whereas outer-sphere charge arises due to ions bound through molecules of water. In general, total net charge of clays σ_p consists of these four components [6–8]:

$$\sigma_p = \sigma_0 + \sigma_H + \sigma_{IS} + \sigma_{OS}, \tag{1}$$

where σ_0 is structural charge, σ_H – pH-dependent hydroxylation surface charge, σ_{IS} – inner-sphere charge, σ_{OS} – outer-sphere charge.

Electrokinetic or ζ-potential represents an electrical potential at the boundary in aqueous phase on which the shift of pore solution relatively to soil particle occurs when outer electrical field is applied [2,9].

The most common types of clays (kaolinite, illite and smectite) significantly differ in their surface charge properties [9]. These differences should be taken into account in design of protective clay barriers. Various clay types react differently the change of physicochemical medium parameters: pH, oxidation/reduction potential, total dissolved solids. Change of these parameters causes great change of surface charge and electrokinetic properties of clays. Partially for the change of clay barrier properties solutions with different pH values may be required, for instance, solutions of acid or alkali.

Summing up, the main purpose of this paper is to study surface charge and electrokinetic properties of different clay types under the treatment by acidic and alkaline solutions of different concentrations, and to make recommendations for usage of these clays as a material for the electrokinetic PRB.

2. Materials and methods

2.1. Objects of the study

Studied clayey soils show a wide variety of the mineral composition as it can be seen from Table 1. Three of them represent monomineral clays: Polozhsk kaolin, kil and Makharadzian montmorillonite clays. Glukhovetsk kaolin and Biyasalin's illite clay contains about 70% of their main mineral and a significant admixtures of quarts or other clay minerals. Cambrian illite and Oglanly montmorillonite clays are polimineral soils with contain of main mineral in a range about 40–50%.

Adsorptive properties of clays were characterized by cation-exchange capacity (CEC) and specific surface area (SSA). Hinkley index of crystallinity degree was determined for kaolins. According to Hinkley index Glukhovetsk kaolin is well-crystallized, whereas Polozhsk kaolin is poor-crystallized. Hinkley and Sherer index values were given by our colleagues who used for a research the same samples of kaolins and Cambrian illite clay [13]. Sherer index is a number of elementary crystallites in a single defect-free layer of clay mineral. Physicochemical and crystal structure parameters of studied clays are given in Table 2.

Both kaolins were obtained from Ukraine (villages Polozhky and Glukhovtsy respectively). Biyasalin's and kil clays were taken from Crimea (village Prohladnoe). Cambrian clay was gotten from Saint-

Petersburg suburbs. Oglanly and Makharadzian montmorillonite clays were obtained from Turkmenistan (village Oglanly) and Georgia (village Makharadze) respectively. Kaolins have eluvial, whereas kil and both illite clays have marine genesis. Oglanly clay has hybrid eluvial-marine genesis. Makharadzian clay is of hydrothermal origination. Polozhsk kaolin, both illite clays, kil and Makharadzian montmorillonite clays were represented by Ca-forms whereas Oglanly clay was presented by Na-form. Glukhovetsk kaolin was studied both in Na- and Ca-forms.

2.2. Methods

The mineral composition was studied by X-ray diffraction method on ULTIMA-IV. Specific surface area was measured by Brunauer-Emmett-Teller method (BET). Cation-exchange capacity was determined by methylene blue adsorption method.

The ζ-potential values were measured by microelectrophoresis on instrument Horiba SZ-100 in electrode cell. For experiment suspensions with wide range of pH were prepared. Clay samples of 0.5 g were suspended in distilled water, HCl or alkali solutions of different concentrations. Polozhsk and Na-form of Glukhovetsk kaolins, Biyasalin's illite clay, kil and Oglanly clays were suspended in NaOH as an alkali whereas the rest soils were suspended in $Ca(OH)_2$. Solid/aqueous phase mass relation was 1:20 for Polozhsk, Na-Glukhovetsk kaolins, Biyasalin's, kil and Oglanly clays and 1:40 for other clayey suspensions.

Determination of pH of suspensions was done with pH-061 instrument. Oxidation/reduction potential (Eh), total dissolved solids and electrical conductivity values of suspensions were measured on instruments ORP-169B, HM Digital COM-80 and conductometer MMZ4-04 respectively. These parameters were determined for blank acid and alkali solutions with same concentrations as were used for suspensions. Acidic and alkaline solutions were used with ionic strength values in range 0.0001-0.1 $mol \cdot L^{-1}$, but not with some constant value.

Acidic-basic potentiometric titrations were carried out in two series of samples. The first included Polozhsk and Na-form of Glukhovetsk kaolins, Biyasalin's illite, kil and Oglanly montmorillonite clays. Samples weighing 5.0 g were suspended in buffer $NaNO_3$ solutions of 3 ionic strengths (0.1, 0.01, 0.001 $mol\ L^{-1}$). Then suspensions were

Table 1
Mineral composition of studied clays, mass %.

Clay soil	K	Il	Sm	Ch	Q	Pf	Pl	C	G
Polozhsk kaolin	98	0	0	0	2	0	0	0	0
Glukhovetsk kaolin	75	5	0	0	18	0	0	0	2
Biyasalin's illite clay	10	70	5	10	4	0	0	1	0
Cambrian illite clay	8	53	4	3	24	7	1	0	0
Oglanly montmorillonite clay	27	0	41	0	32	0	0	0	0
Kil montmorillonite clay	0	0	95	2	0	0	0	3	0
Makharadzian montmorillonite clay	0	0	100	0	0	0	0	0	0

Note. K – kaolinite, Il – illite, Sm – smectite, Ch – chlorite, Q – quartz, Pf – potassium feldspar, Pl – plagioclases, C – carbonates, G – gypsum.

Table 2
Physicochemical parameters of studied clays [10–13].

Clay soil	CEC, meq/ 100 g	SSA, m^2/g	Hinkley index HI, units	Sherer index M_c, units
Glukhovetsk kaolin	3.1	17.6	0.90	50
Polozhsk kaolin*	4.0	22.9	0.58	35
Cambrian illite clay	10.7	51.6	–	12**
Biyasalin's illite clay	13.0	74.4	–	–
Oglanly montmorillonite clay*	81.5	202.0	–	–
Kil smectite clay*	127.0	530.0	–	–
Makharadzian montmorillonite clay	99.7	910.0	–	–

Notes. *Physicochemical parameters for some of clays were taken from literature where researches used natural clays from the same deposits and in same ion-forms as presented in our research. CEC and SSA values for Ca-form of Polozhsk kaolin were taken from [10]. These parameters for Biyasalin's illite clay were taken from [11]. CEC and SSA values for Oglanly montmorillonite clay were taken from [12]. Kil clay parameters and crystallinity index values were given by [13].
**Sherer index for illite crystals is 12 and for chlorite crystals is 10.

titrated by 0.001 M HCl and 0.001 M NaOH solutions. Solid/aqueous phase mass relation was 1:10. The second series included Ca-form of Glukhovetsk kaolin, Cambrian illite and Makharadzian montmorillonite clays. Their samples of 5.0 g were suspended in buffer $CaCl_2$ solutions with ionic strengths of 0.3, 0.03 and 0.003 mol L^{-1} and titrated by 0.01 M HCl and 0.009 M $Ca(OH)_2$ solutions. Solid/aqueous phase mass relation was 1:20 for these series. Experiments were held by continuous titration scheme. The exposition for all titrations was 3 min. Each addition of titrant was about 0.2-0.5 mL. Determination of pH was held on pH-061 instrument.

3. Theory of surface charge properties of clays

3.1. Electrical charge origin in clays

Previously, the surface charge properties of clay minerals have been studied extensively [2,9]. The most common three types of clays demonstrate different surface properties from each other. Isomorphic substitutions are poorly developed in kaolinites and presented by $Si^{4+} \rightarrow Al^{3+}$ substitutions in tetrahedral layers of 1:1 kaolinite structures [9]. So structural charge σ_0 has a small value or is absent [14]. Illite clays have 2:1 crystal structure where the octahedral layer is located between two tetrahedral layers. Illite isomorphic substitutions mainly represented by $Si^{4+} \rightarrow Al^{3+}$ in outer tetrahedral layers too but the amount of them is more than in kaolinites [9,15]. Smectite (montmorillonite) clays are characterized by a great number of isomorphic substitutions in their 2:1 structure located in inner octahedral layer. The last circumstance reduces markedly the influence of structural charge so its values on the surface may be comparable to these of illites. On the other hand, montmorillonites have great specific area so their σ_H values are higher than for other clays [16,17]. In addition, all components of surface charge depend on a crystallinity degree of clay minerals [14].

Point of zero charge is pH value, at which $\sigma_p = 0$ [6]. The point of $\zeta = f(pH)$ curve, where $\zeta = 0$, is isoelectric point (at this pH value electrophoretic mobility is zero). Also near this pH $\sigma_p = 0$ because $\zeta = f(\sigma_p)$. In our case isoelectric point is comparable to point of zero charge (p.z.c.) value within measuring error. Point of zero net proton charge is pH value at which $\sigma_H = 0$ [6].

3.2. Calculations

There was about 4–5 measurements of ζ-potential for each pH value.

Arithmetical average values were calculated, after that ζ-potential vs pH curves were plotted for each clay. P.z.c. values for arithmetical average values were taken from $\zeta = f(pH)$ curve.

Potentiometric titration curves were plotted for each value of ionic strength with a simplified equation that accuracy is enough for aims of present study:

$$\sigma_H = \Delta V \cdot C \cdot F / (z \cdot SSA \cdot m), \qquad (2)$$

where σ_H represents hydroxylation electrical charge surface density, C/ m^2; ΔV – residual volume of titrant used for titration of suspension and blank solution respectively, L; C – titrant concentration, mol/L; $F \approx 96485.33$ C mol^{-1} – Faraday constant; z – equivalent number; SSA – specific surface area, m^2/g; m – mass of clay sample, g. P.z.n.p.c. values were taken from $\sigma_H = f(pH)$ curves for each ionic strength value of buffer solution.

4. Results and discussion

A main concept for regulation of the protective clayey barrier properties is associated with interactions between clay particles and acidic or alkaline solutions at different concentrations of acid and alkali, respectively. Acid-alkali treatment effects on physicochemical properties of clays that may eventually result in the transformation of protective properties of the electrokinetic barrier. Fig. 1 shows dependence of physicochemical parameters of clayey suspensions on concentration of added alkali and acid solutions. An addition of HCl decreases pH values (Fig. 1a) and increases reduction/oxidation potential (Fig. 1b), while the treatment of clayey suspension by $Ca(OH)_2$ solution leads to an opposite change of mentioned parameters (Fig. 1a,b). Increase in solution concentration causes a growth of total dissolved solids (TDS) and, therefore, of specific electrical conductivity, which is a linear function of TDS (Fig. 1c). Data for specific electrical conductivity is not given due to it shows similar trend as TDS.

In addition, Fig. 1 demonstrates a change in these parameters of blank acid and alkali solutions with the same concentrations as were used for suspensions. In general, pH values are higher and Eh meanings are lower for clayey suspensions in comparison with blank solutions. These trends change to opposite for $Ca(OH)_2$ concentration > 0.0005 M, i.e. suspensions medium is more acidic and oxidative than blank solutions medium. When an amount of H^+ or OH^- ions in pore solution grows, clay particles engages neutralization reactions by adsorption of H^+ ions or dissociation of surface OH-groups [2,9]. This is an acidic-alkaline buffering of clays [13]. In particular, this property is of importance for a usage of clays to treat mentioned acidic mine tailing solutions [1].

The clayey suspensions at HCl and $Ca(OH)_2$ concentrations < 0.001 M have TDS and therefore specific electrical conductivity values higher than those for the blank solutions, which is explained by surface electrical conductivity of double electrical layer ions at these concentrations. At higher concentrations, the clay particles adsorb ions from solution so electrical conductivity and TDS of suspensions are halved to those of blank solutions.

The suspension medium in the range 'Glukhovetsk kaolin/ Cambrian illite clay/ Makharadzian montmorillonite clay' at the same concentration of acid or alkali gets more alkaline and reductive, that accompanied with a growth of specific electrical conductivity and total dissolved solids values. This is due to increasing the specific surface area and, consequentially, quantity of reactive OH-groups in volume unit in this raw. Therefore montmorillonite clay barrier binds pollutants the most effectively.

The results of ζ-potential determination are given in Table 3 and Fig. 2. As it can be seen from Table 3, p.z.c. values of all presented clays except Polozhsk kaolin and Makharadzian clay lay at pH < 3. Polozhsk kaolin p.z.c. value lies in range of pH 3-7. Data obtained for Ca-form of Glukhovetsk kaolin, Cambrian illite and Makharadzian montmorillonite
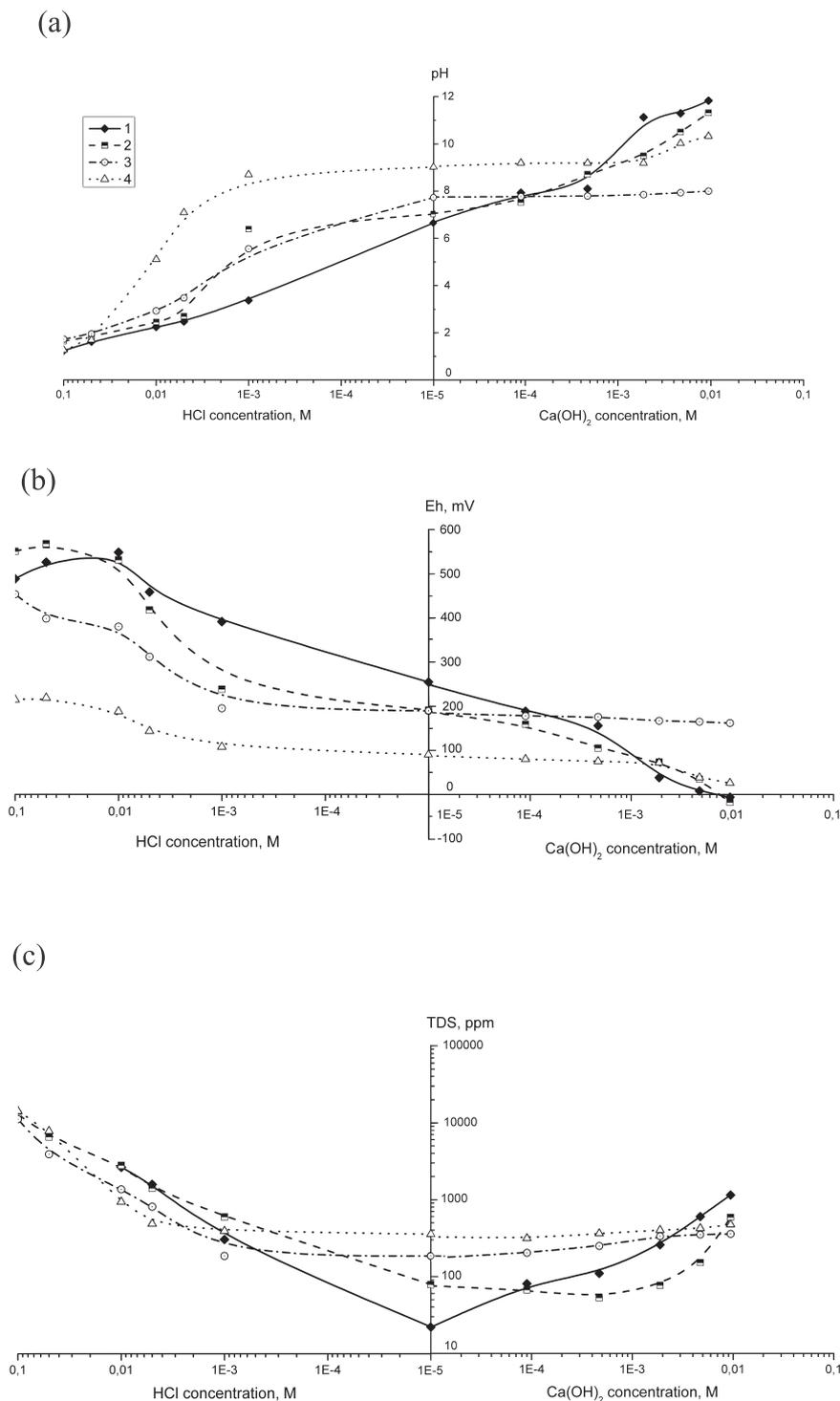
(a)

(b)

(c)

Fig. 1. Dependence of physicochemical parameters of clayey suspensions and blank solutions on concentration of HCl and Ca(OH)$_2$ solutions: a – pH, b –oxidation/ reduction potential (Eh, mV), c – total dissolved solids (TDS, ppm); 1 – blank solutions; suspensions: 2 – Ca-form of Glukhovetsk kaolin, 3 – Cambrian illite clay, 4 – Makharadzian montmorillonite clay.

clays are more specific. P.z.c. value of Ca-form of Glukhovetsk kaolin lies in the interval 2.5–2.7 for average values of ζ-potential (Fig. 2). The maximum of ζ-potential average values (+ 114.5 mV) was at pH = 1.7 whilst the minimum (-83.5 mV) was at pH = 9.8. Cambrian illite clay p.z.c. value for ζ-potential average values lays in range 2.8–3.2 pH units. The maximum of ζ-potential average values (+ 83.4 mV) is observed at pH = 2.0 and the minimum (-61.1 mV) – at pH = 7.8. For suspensions of this clay pH values larger than 8.0 cannot be obtained by using Ca(OH)$_2$ solution due to a high absorptivity of this clay toward

alkali. P.z.c. value of Makharadzian montmorillonite lies in interval 5.0–5.2 pH units for average ζ-potential values. The maximum of ζ-potential average values (+ 35.9 mV) is observed at pH = 1.6 and the minimum (-103.7 mV) – at pH = 11.4 (Fig. 2). The suspension of this clay prepared in distilled water has value of pH = 9.5. For these three studied samples, p.z.c. value shifts to alkaline area of pH from Ca-form of Glukhovetsk kaolin to Makharadzian montmorillonite clay. The dependence of electrokinetic potential on pH for other clays was studied only at three pH values so more data is required to find p.z.c. value of

Table 3
ζ-potential values (mV) of studied clayey suspensions particles at different pH values [18].

Suspensions	Values of ζ-potential, mV at pH:		
	3.0	7.0	11.0
Na-sample of Glukhovetsk kaolin	−30.8	−14.0	−55.0
Ca-sample of Glukhovetsk kaolin	−15.0	−40.0	−60.0
Polozhsk kaolin	+14.9	−11.3	−103.4
Cambrian illite clay	−10.0	−40.0	No data
Biyasalin's illite clay	−54.1	−13.2	−57.0
Kil smectite clay	−41.7	−47.4	−108.3
Oglanly montmorillonite clay	−12.5	−67.0	−115.7
Makharadzian montmorillonite clay	+ 25.0	−20.0	−75.0
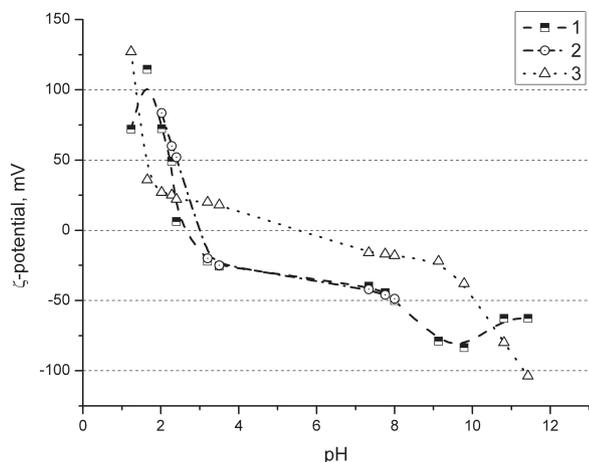
Fig. 2. Dependence of ζ-potential values (mV) of clayey particles on pH: 1 — Ca-Glukhovetsk kaolin, 2 – Cambrian illite clay, 3 – Makharadzian montmorillonite clay.
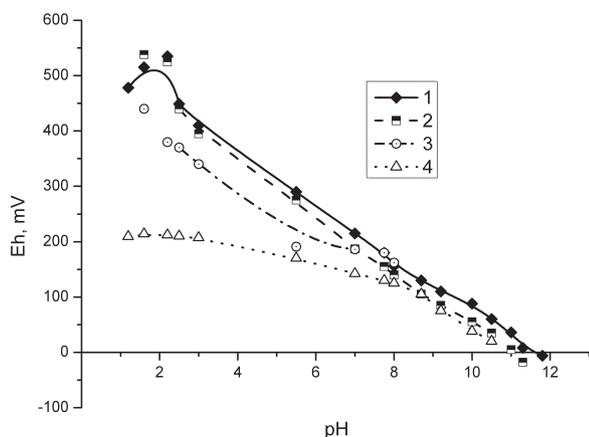

Fig. 3. Dependence of oxidation/reduction potential (Eh, mV) of clayey suspensions on pH: 1 – blank solutions; suspensions: 2 – Ca-Glukhovetsk kaolin, 3 – Cambrian illite clay, 4 – Makharadzian montmorillonite clay.

each clay and to draw certain conclusions.

In general, clay particles are negatively charged at pH > p.z.c., so clay barrier will adsorb predominantly positively charged pollutants, i.e. cations like Zn^{2+}, Pb^{2+} and Rb^{+}. At pH < p.z.c. clay particles are positively charged, and in this case the barrier will adsorb anionic toxicants such as CrO_4^{2-}, SO_4^{2-}, AsO_3^{-}. For this reason, most of the studied clays can be effectively used against cationic toxicants at pH > 3 and against anionic toxicants at pH < 3. Makharadzian montmorillonite clay particles change a sign of their electrical charge and adsorptive parameters at pH ≈ 5.

Table 4
The effect of ionic strength of $NaNO_3$ buffer solution on p.z.n.p.c. values of the studied clayey suspensions [18].

Ionic strength of $NaNO_3$ solution, $mol \cdot L^{-1}$	P.z.n.p.c. values:				
	Polozhsk kaolin	Glukhovetsk kaolin (Na-sample)	Biyasalin's illite clay	Kil smectite clay	Oglanly montmorillonite clay
0.1	7.3	7.2	8.0	4.6	8.0
0.01	7.5	7.2	8.5	4.8	8.9
0.001	7.8	7.5	9.1	4.8	9.5

Table 5
The effect of ionic strength of $CaCl_2$ buffer solution on p.z.n.p.c. values of the studied clayey suspensions [18].

Ionic strength of $CaCl_2$ solution, $mol \cdot L^{-1}$	P.z.n.p.c. values:		
	Glukhovetsk kaolin (Ca-sample)	Cambrian illite clay	Makharadzian montmorillonite clay
0.3	7.0	7.0	7.9
0.03	7.6	7.2	9.6
0.003	7.8	7.3	10.0

Oxidation/reduction potential (Eh) of the clayey suspensions versus pH is given at Fig. 3. As it can be seen, the suspensions of clays have positive values of Eh in neutral medium. Eh values increase in acidic and decrease in alkaline medium. In some cases, Eh values change their sign in an alkaline medium. The maximum of Eh values of Glukhovetsk kaolin (+ 540 mV) is at pH = 2.1 whereas the minimum (−10 mV) is at pH = 11.9. The change of Eh sign takes place at pH = 11.8. For Cambrian clay the maximum of Eh (+ 450 mV) was reached at pH = 1.6 and the minimum (+ 130 mV) was at pH = 7.8. The change of Eh values sign does not occur in pH interval 1–9 for Cambrian clay. Oxidation/reduction potential of Makharadzian montmorillonite clay suspensions is maximum at pH = 1.7 (+ 220 mV), and minimum at pH = 10.5 (+ 20 mV).

Generally speaking, clays studied in a wide range of pH may be effectively used against reductional pollutants. However, some kaolinite and, possibly, montmorillonite clays have negative values of Eh in high-alkali medium, therefore they can be used to treat ground water from some oxidative toxicants.

P.z.n.p.c. values for studied clays are given in Tables 4 and 5. P.z.n.p.c. values of kaolin shift to alkaline area from Na-form of Glukhovetsk kaolin to Polozhsk kaolin. In this raw, Hinkley and Sherer indexes of kaolin crystallinity degree decrease and, accordingly, its physicochemical activity parameters (CEC and SSA) increase. Physicochemical activity of illite clays, as was estimated by SSA and CEC values, increases from Cambrian to Biyasalin's clay. P.z.n.p.c. values of these clays follow the same trend as for kaolins, i.e. p.z.n.p.c. shifts to alkaline area with the increase in clay physicochemical activity. Oglanly and Makharadzian clays have p.z.n.p.c. values in alkaline area, whereas kil clay has p.z.n.p.c. values in acidic area. Therefore, p.z.n.p.c. values of montmorillonite clays are not in accordance with their physicochemical parameters like CEC and SSA. They may depend on other crystal structure parameters that were not considered in the present study. In general, it is difficult to compare p.z.n.p.c. values in the range of one clay type, because p.z.n.p.c. measurements were carried out on various clay forms (Na- or Ca-) with different buffer solutions at variable ionic strength values. P.z.n.p.c. values for Ca- и Na-forms of Glukhovetsk kaolin are different but comparable generally. P.z.n.p.c. values of kaolins are higher in comparison with that presented in literature [14]. Results obtained for Biyasalin's illite clay are comparable to data reported by Kriaa and coauthors for illite sample from Gafsa It(Ga) [15]. P.z.n.p.c. values of Oglanly clay are comparable to

Avena and De Pauli data [16].

Hydroxylation surface charge σ_H is the most sensitive surface charge characteristic of clay particles that depends on the change of medium conditions. Change in the sign of clay particle charge occurs due to change of σ_H charge sign. Clay particles have negative structural charge, so condition p.z.c. < p.z.n.p.c. is true. Therefore, the clay barrier will be the most effective against cationic pollutants at pH > p.z.n.p.c. and it will be the most efficient against anionic pollutants at pH < p.z.c. At p.z.c. < pH < p.z.n.p.c. barrier will have intermediate adsorptive properties.

5. Conclusions

The data of present study can be used for a design of protective electrokinetic PRB. Generally speaking, clay particles are negatively charged at pH > p.z.c., and they are positively charged at pH < p.z.c. In the first case, clay barrier will adsorb predominantly cationic toxicants, such as Zn^{2+}, Pb^{2+}, Cs^+, whereas in the second case – anionic ones, e.g. CrO_4^{2-}, SO_4^{2-}, AsO_3^-. Clay barrier neutralizes at pH > p.z.n.p.c. acidic toxicants like H_2SO_4 or complex acidic wastewater (with pH < 7), and at pH < p.z.n.p.c. alkaline toxicants like NaOH or complex alkaline wastewater (with pH > 7). So, potentiometric titration data demonstrates that Makharadzian, Oglanly and Biyasalin's clays are the most effective against alkaline toxicants, while kil clay is efficient to neutralize acidic pollutants. Cambrian clay may be used effectively for reduction of alkaline pollution according to the results of determination of suspensions' pH. It follows from the fact that increasing of alkali concentration in certain interval leads to negligible increase of pH. Makharadzian montmorillonite is effective for protection from alkaline pollutants too.

Many heavy metals are soluble in their cationic forms in acidic solutions, particularly at pH < 3, and their anionic forms are soluble in alkaline solutions especially at pH > 11. So, clay barriers can neutralize in appropriate conditions acidic or alkaline solutions, thereby preventing the distribution of heavy metals in cationic or anionic forms, respectively.

In general, at pH > p.z.n.p.c. clay barrier will be the most effective against cationic pollutants, at pH < p.z.c. – against anionic toxicants. In a borderline case, at p.z.c. < pH < p.z.n.p.c., the barrier will be the least effective against pollutions. Thus, the treatment of barrier by acidic or alkaline solutions changes surface charge characteristics of clay used as a protective media. Accordingly, the change of clay surface charge properties results in a change of adsorptive properties of the barrier that make possible to adjust it for specific pollutant. Eh-determination data shows that studied clays demonstrate oxidative properties in a wide range of pH, so that they can be effectively used against some reductional pollutants. The treatment of kaolinite clays by high-concentrate alkaline solutions creates a residual medium in their suspensions, and these clays may be applied against some oxidative pollutants.

Based on physicochemical characteristics of clays and results of the study, the most appropriate materials for barriers are monmorillonite and illite clays such as Oglanly, kil, Makharadzian and Cambrian clays. It should be noted that all these conclusions are applicable for clayey suspensions. Nevertheless, one can suppose that the values of ζ-potential and points of zero charge of a clay in the barrier's body should be the same as in a clayey suspension and depend only on the composition of a clay and its pore solution.

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