

Potentiometric method for determination of hydraulic activity of quartz-containing powders

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ABSTRACT

Introduction. An important aspect of concrete mixture preparation technology is the exploration of methods to effectively utilize the properties of aggregates (fillers) in hardening multi-component systems. The most common binder composition is a mixture of a binder system with crushed quartz-containing polymineral sand. It is known that micro silica is classified as an active mineral additive (filler), the properties of which are characterized by the amount of Ca^{2+} ions absorbed from a saturated lime solution. Literature sources describe two types of analytical methods for determining pozzolanic activity. The first type that trace the change in the content of $\text{Ca}(\text{OH})_2$ over time during the pozzolanic reaction. The second type that aim to determine the physical and mechanical characteristics of the material under study. These characteristics reflect its ability to bind free calcium oxide into stable hydrate compounds. Previously applicability of the potentiometric method of analysis using an ion-selective electrode with pCa-function was demonstrated for the assessment of pozzolanic activity of highly dispersed materials. It should be noted to note that this electrochemical method of analysis which is functionally related to the concentration of the determined component in the tested solution, is very efficient in terms of expressiveness and labour intensity. The objective of the research is to validate the method for micro silica systems obtained by mechanical grinding of raw materials of polymineral sands from different deposits. The experiments were conducted using sands from the Arkhangelsk region deposits. The quartz sand (QS) was chosen as a reference object to establish the nature of change in the functional relationship of the measured potential of the electrode system from the volume of added $\text{Ca}(\text{OH})_2$ solution. **Methods and Materials.** The polymineral sand of the Krasnoflotsky-West deposit is categorised as alluvial-marine modern Quaternary sediments (am IV). The sand of the Kholmogorskoye deposit is quartz-feldspathic sand, which belongs to alluvial modern Quaternary sediments (a IV). The mineralogical composition of polymineral sands was determined by means of the semi-quantitative method, utilising the binocular microscope MBS-1. Fine sand powders were obtained by dry mechanical grinding in a Retsch PM100 planetary. The specific surface area of the obtained fine powders was measured by the Kozeny-Karman gas permeability method on a PSKh-10a apparatus. The potentiometric analysis was conducted using an apparatus comprising an electrode pair, consisting of a measuring electrode with pCa-function and a reference electrode connected to an Expert-001-3.0.1 ionometer. The reaction system was stirred using a magnetic stirrer. In order to ascertain the sorption capacity of silica-containing raw materials, a lime solution with a concentration and a suspension of fine sand powders were prepared in advance. Concurrently, the EMF (potential) of the system was measured, with constant stirring. The concentration of calcium ions, $C_{\text{act}'}$ was then calculated based on the previously established calibration dependence, using the potential values (mV) obtained. In order to determine the activity of fine mineral powders of silica, the dependence between the values of the given concentration of calcium ions in lime solution when adding a certain volume of lime to the suspension of the studied sands and the concentration values obtained by potentiometric measurements was plotted. **Results and Discussion.** The obtained powders of quartz-containing polymineral sands, which had been finely dispersed, had the following specific surface values: quartz sand – $1020 \pm 31 \text{ m}^2/\text{kg}$, Krasnoflotsky West – $465 \pm 14 \text{ m}^2/\text{kg}$ and Kholmogorskoye – $450 \pm 14 \text{ m}^2/\text{kg}$. The given data on the specific surface of powders of natural origin allow for a comparative analysis of experimental potentiometric measurements. Concurrently, the dependence of the measured potential on the concentration of calcium ions in the solution for quartz sand suspension can be utilised as a reference, given the significantly high specific surface of the powder, thereby resulting in a more pronounced dependence $E = f(V_{\text{add}'})$. Relationship obtained the dependence of the measured potential of the electrode system on the volume of added $\text{Ca}(\text{OH})_2$ solution in a suspension of quartz sand (as a reference sample) and distilled water (as an idle experiment) shows that the nature of the change in the functional relationship of the analysed two samples (QS and H_2O) is different. Concurrently, it can be observed that the incorporation of a lime solution into water (in accordance with the anticipated outcome) results in a nearly constant augmentation in the measured potential values, the magnitude of which is proportional to $-\lg C_{\text{Ca}}$. Change of potential of electrode pair in suspension of quartz sand powder has character different from that mentioned above for water. This functional dependency can be divided into three periods. The initial period is characterised by an induction phase, during which the electrode potential displays a linear increase in

accordance with the rising concentration of $\text{Ca}(\text{OH})_2$ within the solution. The presence of a second period of functional dependence, where stabilisation of potential values is observed when calcium hydroxide is added to the reaction system, is directly related to the adsorption (pozzolanic) effect of finely dispersed quartz. The third and final period is characterised by the growth of the electrode potential value due to the appearance of excess Ca^{2+} ions in the solution. The data presented demonstrate that the powder from the Krasnoflotsky-West deposit exhibits the highest pozzolanic and adsorption activity in relation to calcium ions. The dependence has a pronounced three-stage character, as determined by us through conducting a similar experiment with quartz sand powder. Given that quartz-containing powders with high dispersion exhibit sorbent properties discrepancy in the dependencies may signify a quantitative variation in the active adsorption centres of the studied powders, consequently resulting in a disparity in their degree of filling. This fact is a kinetic factor in the process of solid-phase concentration of the determined cations. The results obtained demonstrated that the sorption capacity of calcium oxide in the powders of the studied sand deposits was practically equivalent. However, the character of the functional dependence of the change in the determined concentration of calcium hydroxide in the solution relative to its added value was different. This observation suggests the potential for distinct mechanisms underlying the sorption processes. **Conclusion.** The paper demonstrates that the potentiometric method of determining the sorption capacity of calcium oxide can be used as an express method for powders of quartz-containing polymineral sands. It is demonstrated that to accurately calculate the specified parameters under experimental conditions that ensure full reproducibility, it is essential to conduct an experiment using a suspension of quartz sand (as a reference sample) alongside a comparative experiment in which the dissolution water serves as the measurement object. The functional dependence of the change in the determined concentration of calcium hydroxide in the solution relative to its added value can be used for comparative evaluation of the mechanism of sorption processes for powders of different material nature.

KEYWORDS: polymineral quartz sand, pozzolanic activity, calcium oxide, calcium hydroxide concentration, sorption capacity

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INTRODUCTION

In the domain of concrete mix preparation, a significant concern pertains to the exploration of methodologies for the effective utilization of the properties of aggregates (fillers) in multi-component systems [1]. It has been established that the most prevalent binder composition consists of a mixture of binder systems with minor (filler) fractions of natural and (or) man-made materials. Historically, crushed quartz-containing polymineral sands have been employed as fillers in concrete mixtures derived from natural materials. In such instances, it is imperative that the degree of silica fines does not decrease below the level commensurate with the particle size of the binder. Under these conditions, the filler grains will be encircled by cement hydration products, thereby accelerating the hydration process of cement grains. Consequently, the gel phase will compact and crystallize more intensively on the surface of the filler grains. Furthermore, in certain instances, the presence of the filler can exert a modifying influence on the hydration products of the cement grains, thereby contributing to the development of crystalline neoplasms.

As stated in [2], micro silica (finely ground quartz-containing sand) is classified as an active mineral additive (filler), the properties of which are characterized by

the amount of Ca^{2+} ions absorbed from a saturated lime solution.

Literature sources describe two types of analytical methods for determining pozzolanic activity. The first type are direct methods that trace the change in the content of $\text{Ca}(\text{OH})_2$ over time during the pozzolanic reaction. The second type are indirect methods that aim to determine the physical and mechanical characteristics of the material under study. These characteristics reflect its ability to bind free calcium oxide into stable hydrate compounds [3–7]. In [8], the applicability of the potentiometric method of analysis using an ion-selective electrode with pCa-function was demonstrated for the assessment of pozzolanic activity of highly dispersed materials. This was achieved through the use of clay soil models with different plasticity numbers as an exemplar. It is important to note that this electrochemical method of analysis, based on the measurement of the electrode potential, which is functionally related to the concentration of the determined component in the tested solution, is very efficient in terms of expressiveness and labour intensity. The objective of the research presented in this paper is to validate the method for micro silica systems obtained by mechanical grinding of raw materials of polymineral sands from different deposits. The experiments were conducted using sands from the Arkhangelsk region deposits (Fig. 1):

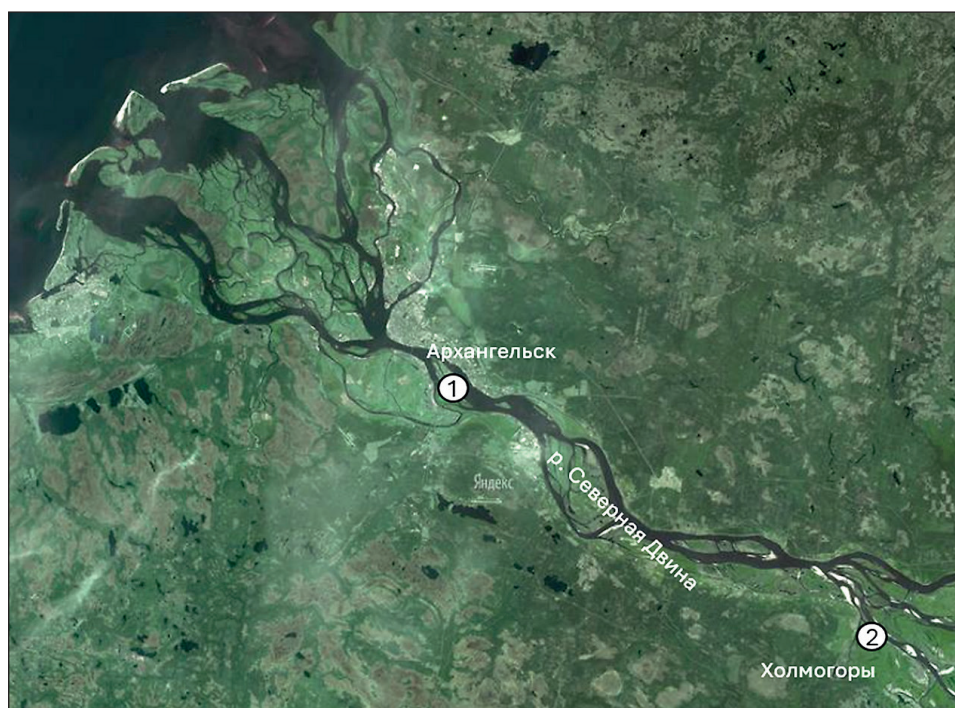


Fig. 1. Deposits of polymineral sands in the Arkhangelsk region: 1 – Krasnoflotsky-West deposit (KW); 2 – Kholmogorskoye deposit (Kh)

Krasnoflotsky-West (KW) and Kholmogorskoye (Kh) [9, 10]. The quartz sand (QS) (Volsky monofractional sand according to GOST 6139-2003), fraction 0.1–0.2 mm, containing not less than 98% SiO_2 and density 2610 kg/m^3 was chosen as a reference object to establish the nature of change in the functional relationship of the measured potential of the electrode system from the volume of added $\text{Ca}(\text{OH})_2$ solution.

METHODS AND MATERIALS

The polymineral sand of the Krasnoflotsky-West deposit is categorized as alluvial-marine modern Quaternary sediments (am IV). The name of the deposit is predicated on its territorial affiliation, specifically the shoreline of Krasnoflotsky Island. The modulus of coarseness, M_k , is 1.7, which corresponds to the classification of fine sand. The true density of the sand is measured at 2710 kg/m^3 .

The sand of the Kholmogorskoye deposit is quartzfeldspathic sand, which belongs to alluvial modern Qua-

ternary sediments (a IV). The sand deposit is located within 2 km of Kholmogory village. The modulus of coarseness, M_k , is 1.5, which corresponds to the classification of fine sand. The true density of the sand is 2230 kg/m^3 .

The elemental composition of the experimental samples in terms of oxides is presented in Table 1.

The mineralogical composition of polymineral sands was determined by means of the semi-quantitative method, utilizing the binocular microscope MBS-1. The results of the mineralogical analysis are presented in Table 2.

Fine sand powders were obtained by dry mechanical grinding in a Retsch PM100 planetary ball mill (rotor speed 420 rpm) for 40 minutes. The specific surface area of the obtained fine powders was measured by the Kozeny-Karman gas permeability method on a PSKh-10a apparatus.

The potentiometric analysis was conducted using an apparatus comprising an electrode pair, consisting of

Table 1. The elemental composition (%) of the polymineral sands [11]

Sample	SiO_2	Al_2O_3	MgO	Fe_2O_3	CaO	K_2O	Na_2O	l.a.i.*
KW	91.35	5.06	0.74	0.65	0.26	0.36	1.37	0.21
Kh	77.48	12.13	1.80	1.61	1.45	2.09	2.76	0.68

* loss after ignition

Table 2. The results of the mineralogical analysis of sands

Sample	Description
KW	The fine-grained sand is light grey with a brown tinge, consisting of rounded and angular grains (grains of sand) of various minerals and rocks. The mineral composition is dominated by quartz (approximately 90%), with a subordinate amount of grey and pink feldspars (5–7%), ore opaque minerals of black and dark brown colour, garnets, and fragments of rocks (granite-gneisses, quartzites).
Kh	The fine-grained sand is light grey with a brown tinge, consisting of rounded and angular grains (grains of sand) of various minerals and rocks. The mineral composition is dominated by quartz (approximately 80%), with subordinate amounts of grey and pink feldspars (5–8%), ore opaque minerals of black and dark brown colour, garnets, magnetite, mica, and fragments of rocks (granite-gneisses, quartzites).

a measuring electrode with pCa-function and a reference electrode connected to an Expert-001-3.0.1 ionometer. The electrode pair was immersed in a glass beaker with a capacity of 100 ml. The reaction system was stirred using a magnetic stirrer. The experiments were conducted at a temperature of 20 ± 2 °C. Prior to the commencement of the experiment, the calcium-selective electrode XC-Ca-001 was subjected to an incubation period of three days in a 0.01 mol/l calcium chloride solution. Thereafter, the electrode was meticulously rinsed with distilled water to ensure the establishment of a stable and minimal electrical signal (electrode potential). The calibration of the electrode was then undertaken using standard calcium chloride solutions (prepared in advance) with concentrations (C_{Ca}) ranging from 10^{-1} to 10^{-5} mol/l. It is acknowledged that the EMF exhibited by the mounted electrode pair is governed by the classical equation (under the assumption that the activity coefficient of Ca^{+2} ions for the areas of working concentrations of calcium ions 10^{-2} – 10^{-4} mol/l approximates unity in value) [12]:

$$E = E_0 + \frac{2,303RT}{nF} \lg C_{Ca} = E_0 - a \cdot pCa, \quad (1)$$

where E and E_0 – measured EMF value and standard, constant value (depends on solution temperature), mV, respectively;

R – universal gas constant, 8.314 J/K;

F – Faraday constant, 96500 C/mol;

$n = 2$ – number of electrons involved in an electrode reaction is usually numerically equal to the charge of the ion;

$a = 0.029$ – constant for $T=293$ K;

$pCa = -\lg C_{Ca}$.

In order to ascertain the sorption capacity of silica-containing raw materials, a lime solution with a concentration of 0.015 mol/l (saturated solution at 20 °C) and a suspension of fine sand powders (0.5 g in 80 ml of distilled water) were prepared in advance. To the obtained suspension, the lime solution was added in volumes ranging from 0.2 to 0.8 ml, successively, using a laboratory pipette. Concurrently, the EMF

(potential) of the system was measured, with constant stirring. The concentration of calcium ions, C_{act} , was then calculated based on the previously established calibration dependence, using the potential values (mV) obtained.

In order to determine the activity of fine mineral powders of silica, the dependence between the values of the given concentration of calcium ions in lime solution C_{theor} when adding a certain volume of lime to the suspension of the studied sands and the concentration values obtained by potentiometric measurements C_{act} was plotted. The concentration of calcium ions in the lime solution, taking into account dilution of the solution (C_{theor}), was determined by the formula:

$$C_{theor} = C_0 \frac{V_{add}}{V_{total}}, \quad (2)$$

where C_0 – initial concentration of saturated lime solution, 0.015 mol/l;

V_{add} – total volume of added lime solution, ml;

V_{total} – total system volume, $(80 + V_{add})$ ml.

RESULTS AND DISCUSSION

The obtained powders of quartz-containing poly-mineral sands, which had been finely dispersed, had the following specific surface (S_{spec} , m^2/kg) values: quartz sand – 1020 ± 31 , Krasnoflotsky West – 465 ± 14 and Kholmogorskoye – 450 ± 14 . It is the opinion of the authors that the given data on the specific surface of powders of natural origin allow for a comparative analysis of experimental potentiometric measurements. Concurrently, the dependence of the measured potential on the concentration of calcium ions in the solution for quartz sand suspension can be utilised as a reference, given the significantly higher S_{spec} of the powder, thereby resulting in a more pronounced dependence $E = f(V_{add})$.

As demonstrated in Figure 2, the calibration dependence $E = f(pCa)$ is characterised by a straight line with a mathematical equation $E = -28.2pCa + 309$ (approximation reliability coefficient $R^2 = 0.99$). The angular coefficient $2.303RT/nF$ of the experimentally obtained

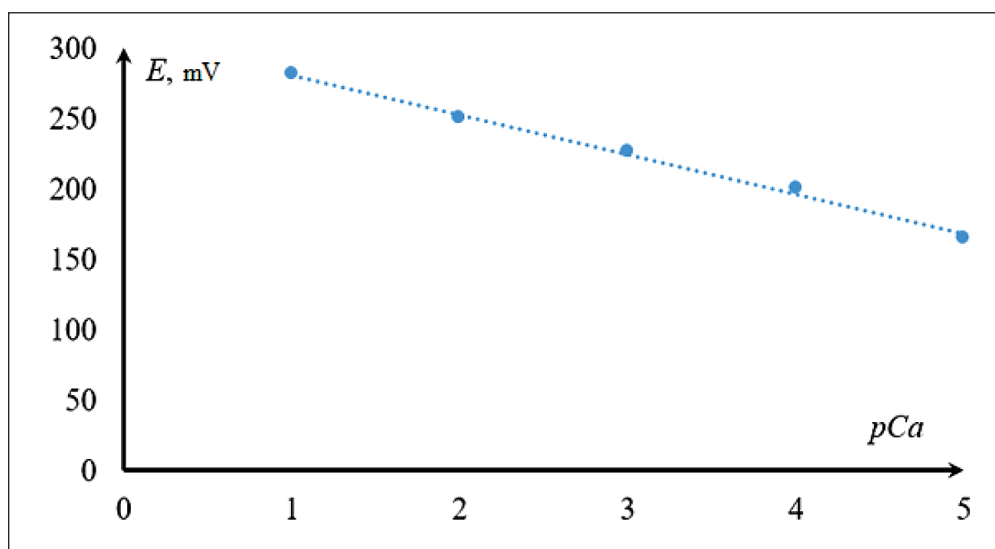


Fig. 2. Calibration curve of the dependence $E = f(pCa)$.

dependence is close to the theoretical one, with a discrepancy between these values of 2.8%. This observation is indicative of the validity of the laboratory setup employed to measure the electrode potential in aqueous lime-containing solutions within the selected range of concentrations of $\text{Ca}(\text{OH})_2$.

As demonstrated in Figure 3, the dependence of the measured potential of the electrode system on the volume of added $\text{Ca}(\text{OH})_2$ solution in a suspension of quartz sand (as a reference sample) and distilled water (as an idle experiment) shows that the nature of the change in the functional relationship of the analysed two samples (QS and H_2O) is different. This indicates that the used ion-

selective electrode is sufficiently sensitive to the level of given concentrations of lime in the solution.

Concurrently, it can be observed that the incorporation of a lime solution into water (in accordance with the anticipated outcome) results in a nearly constant augmentation in the measured potential values, the magnitude of which is proportional to $-\lg C_{Ca}$. The initial potential of the electrode pair (prior to the introduction of the lime solution) corresponds to the value of the background concentration of calcium ions in the solution. Consequently, the dependence $E = f(V)$ for an idle experiment (Fig. 3) is described by a polynomial equation of the second degree:

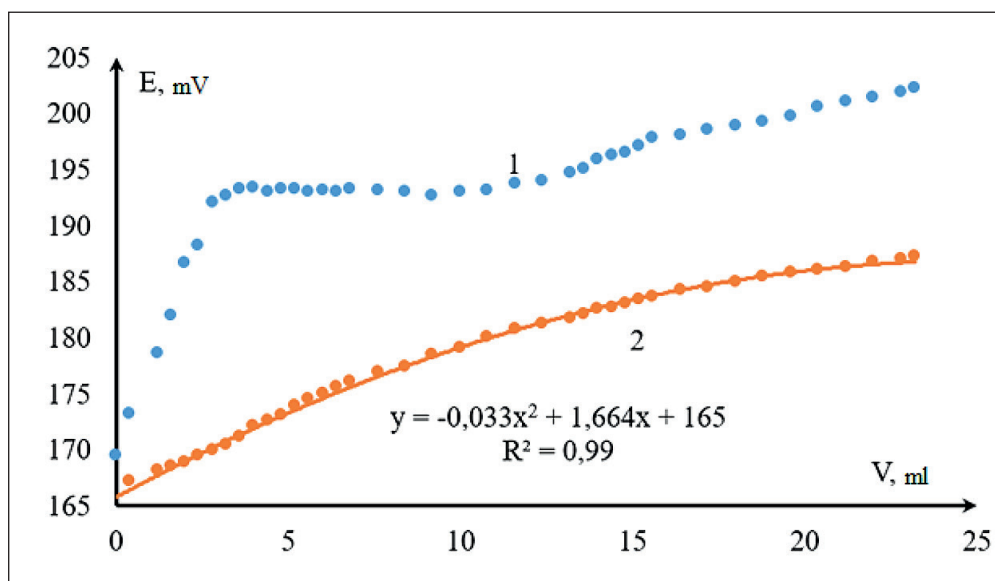


Fig. 3. Potential of an electrode pair when adding a $\text{Ca}(\text{OH})_2$ solution: 1 – to a suspension of quartz sand powder; 2 – to distilled water

$$E = -0,030V^2 + 1,664V + 165. \quad (3)$$

The background concentration of calcium ions in the solution is thus 10^{-5} mol/l. This value is incorporated in the calculations of the current concentration of calcium ions in the reaction medium during the analysis of the experimental results obtained for the studied samples of mineral sands.

The alteration in the electrode pair potential within the silica sand powder suspension exhibits a distinct character compared to that previously observed in water. Consequently, this functional dependence can be subdivided into three periods. The initial period is characterised by an induction phase, during which the electrode potential displays a linear increase in

accordance with the rising concentration of $\text{Ca}(\text{OH})_2$ within the solution. This phenomenon, it is hypothesised, is attributable to the restructuring of the double electric layer of particles, resulting in the compensation of the negative charge of the quartz surface by positively charged Ca^{2+} ions. The presence of a second period of functional dependence, where stabilisation of potential values is observed when calcium hydroxide is added to the reaction system, is directly related to the adsorption (pozzolanic) effect of finely dispersed quartz. The third and final period is characterised by the growth of the electrode potential value due to the appearance of excess Ca^{2+} ions in the solution.

As illustrated in Figure 4, the functional dependences $C_{\text{fact}} = f(C_{\text{theor}})$ for the powders of natural sands under

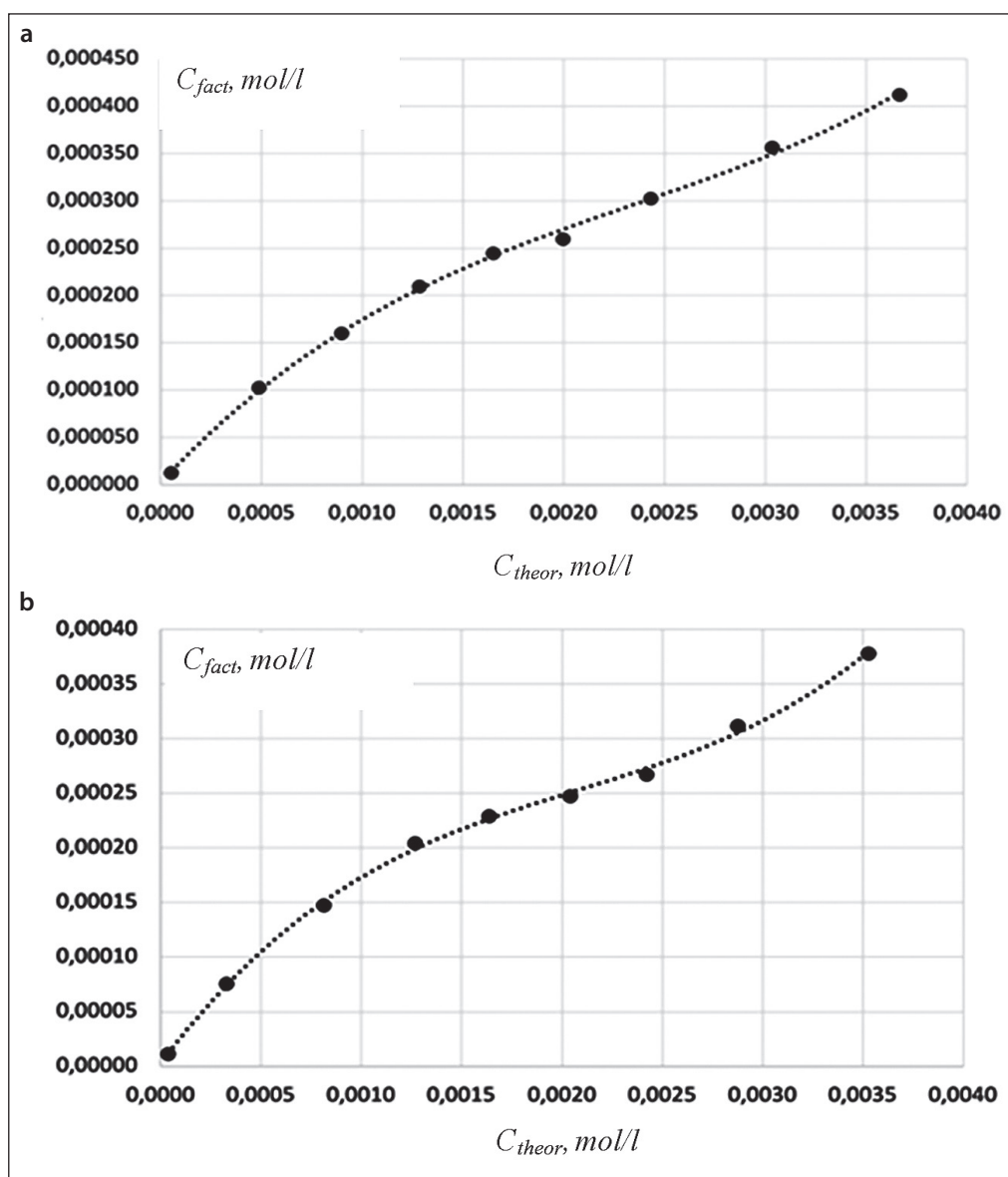


Fig. 4. Concentration dependences $C_{\text{fact}} = f(C_{\text{theor}})$ for powders: a – "Kholmogorskoye"; b – "Krasnoflotsky Zapad"

Table 3. Characteristics of powder activity

Powder	C_{theor} , mol/l	C_{fact} , mol/l	$\Delta C_{Ca(OH)_2}$, mol/l	$\Delta C_{Ca(OH)_2}$, ml/g	α_{CaO} , ml/g	Γ_a
Kh	$2.50 \cdot 10^{-3}$	$0.29 \cdot 10^{-3}$	$2.21 \cdot 10^{-3}$	26.2	19.83	0.99
KZ		$0.19 \cdot 10^{-3}$	$2.31 \cdot 10^{-3}$	26.6	20.13	1.00

study were calculated from the data of potentiometric measurements.

The data presented demonstrate that the powder from the Krasnoflotsky-West deposit (Fig. 4b) exhibits the highest pozzolanic and adsorption activity in relation to calcium ions. The dependence (Fig. 4b) has a pronounced three-stage character, as determined by us through conducting a similar experiment with quartz sand powder.

It is acknowledged that quartz-containing powders with high dispersion exhibit sorbent properties [13]. The observed discrepancy in the dependencies depicted in Fig. 4 (a and b) may signify a quantitative variation in the active adsorption centres of the studied powders, consequently resulting in a disparity in their degree of filling. This observation, as posited by the authors [13], is a kinetic factor in the process of solid-phase concentration of the determined cations.

The activity parameters of powders were calculated from potentiometric data, as presented in [8]. The absorption capacity of calcium oxide ($\alpha_{CaO} = \Delta C_{CaO} = (\Delta C_{Ca(OH)_2} / M_{Ca(OH)_2}) \cdot M_{CaO}$) and the hydraulic activity coefficient ($H = \ln^3 \sqrt{\alpha_{CaO}}$) were determined as a characteristic of absorption by the studied quartz-containing disperse systems. The results obtained are presented in Table 3.

The results obtained (Table 3) demonstrated that the sorption capacity of calcium oxide in the powders

of the studied sand deposits was practically equivalent. However, the character of the functional dependence of the change in the determined concentration of calcium hydroxide in the solution relative to its added value was different. This observation suggests the potential for distinct mechanisms underlying the sorption processes.

CONCLUSION

In conclusion, the following observations can be made:

1. The paper demonstrates that the potentiometric method of determining the sorption capacity of calcium oxide can be used as an express method for powders of quartz-containing polymineral sands.

2. It is demonstrated that for accurate calculation of the determined parameters under conditions of experiments that ensure full reproducibility, it is necessary to carry out an experiment with a suspension of quartz sand (as a reference sample) and a comparison experiment in which dissolution water is used as the object of measurement.

3. The functional dependence of the change in the determined concentration of calcium hydroxide in the solution relative to its added value can be used for comparative evaluation of the mechanism of sorption processes for powders of different material nature.

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ADDITIONAL INFORMATION

The authors declare that generative artificial intelligence technologies and technologies based on artificial intelligence were not used in the preparation of the article.

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CONTRIBUTION OF THE AUTHORS

Maria A. Frolova – conducting research, collecting, analyzing and processing the results obtained, writing an article.

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Marina V. Morozova – conducting research, collecting, analyzing and processing the results obtained, writing an article.

Tatyana N. Orekhova – conducting research, collecting, analyzing and processing the results obtained, writing an article.

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Потенциометрический метод определения гидравлической активности кварцсодержащих порошков

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АННОТАЦИЯ

Введение. Важным вопросом в технологии приготовления бетонной смеси является поиск путей эффективного использования свойств заполнителей (наполнителей) в твердеющих поликомпонентных системах. Самой распространенной вяжущей композицией является смесь вяжущей системы с измельченным кварцсодержащим полиминеральным песком. Известно, что микрокремнезем относится к активным минеральным добавкам (наполнителям), свойства которых принято характеризовать по количеству поглощенных из насыщенного известкового раствора ионов Ca^{2+} . Сейчас известны прямые аналитические методы определения пуццолановой активности, которые отслеживают изменение содержания $\text{Ca}(\text{OH})_2$ во времени в ходе протекания пуццолановой реакции, и косвенные, которые направлены на определение физико-механических характеристик, отражающих способность исследуемого материала связывать свободный оксид кальция в устойчивые гидратные соединения. Ранее была подтверждена применимость потенциометрического метода анализа с использованием ион-селективного электрода с rCa -функцией для оценки пуццолановой активности высокодисперсных материалов. Следует отметить, что этот метод, функционально связанный с концентрацией определяемого компонента в испытуемом растворе, является весьма эффективным с точки зрения экспрессности и трудоемкости. Поэтому целью исследований является апробация метода для микрокремнеземных систем, полученных способом механического помола полиминеральных песков различных месторождений. Для выполнения экспериментов были использованы пески месторождений Архангельской области. В качестве эталонного объекта для установления характера изменения функциональной взаимосвязи измеряемого потенциала электродной системы от объема добавляемого раствора $\text{Ca}(\text{OH})_2$ был выбран кварцевый песок (КП). **Методы и материалы.** Полиминеральный песок месторождения «Краснофлотский-Запад» относится к аллювиально-морским современным четвертичным отложениям (am IV). Песок месторождения «Холмогорское» – это кварцево-полевошпатовый песок, который относится к аллювиальным современным четвертичным отложениям (a IV). Минералогический состав полиминеральных песков определен полуколичественным методом с помощью бинокулярного микроскопа МБС-1. Тонкодисперсные порошки песков получали методом сухого механического помола на планетарной шаровой мельнице Retsch PM100. Удельную поверхность порошков определяли методом газопроницаемости Козени-Кармана на установке ПСХ-10а. Для проведения потенциометрического анализа была собрана установка, представляющая собой электродную пару из измерительного электрода с rCa -функцией и электрода сравнения, подключенных к иономеру Эксперт-001-3.0.1 и погруженных в стеклянный стаканчик вместимостью 100 мл. Перемешивание реакционной системы осуществлялось с помощью магнитной мешалки. Калибровку электрода проводили по стандартным растворам хлорида кальция с разной концентрацией. Для определения сорбционной способности кремнеземсодержащего сырья предварительно готовили раствор извести и суспензию из проб тонкодисперсных порошков песков. В полученную суспензию последовательно добавляли известковый раствор и проводили измерение ЭДС (потенциал) системы при постоянном перемешивании. Далее рассчитывали концентрацию ионов кальция C_{ϕ} по предварительно установленной калибровочной зависимости. Для определения активности строили зависимость между значениями задаваемой концентрации ионов кальция в растворе извести при добавлении ее определенного объема в суспензию исследуемых песков и значениями концентрации, полученными потенциометрическими измерениями. **Результаты и обсуждение.** Полученные тонкодисперсные порошки кварцсодержащих полиминеральных песков имели следующие значения удельной поверхности: кварцевый песок – $1020 \pm 31 \text{ м}^2/\text{кг}$, Краснофлотский Запад – 465 ± 14 и «Холмогорское» – $450 \pm 14 \text{ м}^2/\text{кг}$. Приведенные данные позволяют проводить сравнительный анализ экспериментальных потенциометрических измерений. Вместе с тем зависимость измеряемого потенциала от концентрации ионов кальция в растворе для суспензии кварцевого песка может быть использована в качестве некоторого эталона в связи с значительно более высокой удельной поверхностью порошка, а следовательно, более ярко выраженной зависимостью $E = f(V_{\text{доп}})$. Полученная зависимость измеряемого потенциала электродной системы от объема добавляемого раствора $\text{Ca}(\text{OH})_2$ в суспензию кварцевого песка

(в качестве эталонного образца) и дистиллированную воду (в качестве холостого опыта) показали, что характер изменения функциональной взаимосвязи анализируемых двух образцов (КП и H_2O) различен, что свидетельствует о достаточной чувствительности используемого ион-селективного электрода к уровню задаваемых концентраций извести в растворе. Вместе с тем, можно отметить, что добавление раствора извести в воду приводит к практически постоянному росту значений измеряемого потенциала, величина которого пропорциональна $-lgC_{Ca}$, при этом начальный потенциал электродной пары (до ввода раствора извести) соответствует значению фоновой концентрации ионов кальция в растворе. Изменение потенциала электродной пары в суспензии порошка кварцевого песка имеет характер, отличный от вышеотмеченного для воды. Данную функциональную зависимость можно разделить на три периода. Первый – индукционный период, когда электродный потенциал линейно возрастает с увеличением концентрации $Ca(OH)_2$ в растворе. Наличие второго периода функциональной зависимости, на котором наблюдается стабилизация значений потенциала при добавлении в реакцию систему гидроксида кальция, связан непосредственно с адсорбционным (пуццолановым) эффектом тонкодисперсного кварца. Третий заключительный период характеризуется ростом величины потенциала электродов за счет появления избытка ионов Ca^{2+} в растворе. Полученные данные показывают, что наибольшую пуццолановую и адсорбционную активность по отношению к ионам кальция проявляет порошок месторождения «Краснофлотский Запад». Такая зависимость имеет ярко выраженный трехстадийный характер, фиксируемый нами при проведении аналогичного эксперимента с порошком кварцевого песка. Учитывая, что высокодисперсные кварцсодержащие порошки проявляют свойства сорбентов, разница в зависимостях может указывать также на количественное отличие в активных центрах адсорбции у исследуемых порошков и, как следствие, на разницу в их степени заполнения. Данный факт является кинетическим фактором процесса твердофазного концентрирования определяемых катионов. Используя алгоритм расчета параметров активности порошков по данным потенциометрии, были определены емкость поглощения оксида кальция и коэффициент гидравлической активности. Полученные результаты показали, что сорбционная емкость по отношению к оксиду кальция у полученных порошков исследуемых месторождений песков практически одинакова, однако характер функциональной зависимости изменения определяемой концентрации гидроксида кальция в растворе относительно добавляемого ее значения различается. Данный факт может свидетельствовать о разном механизме сорбционных процессов. **Заключение.** Показано, что потенциометрический метод определения сорбционной емкости по отношению к оксиду кальция может быть использован в качестве экспресс-способа для порошков кварцсодержащих полиминеральных песков. Для корректного расчета определяемых параметров при полностью повторяющихся условиях опытов необходимо проведение эксперимента с суспензией кварцевого песка и эксперимента сравнения, в котором в качестве объекта измерений используется вода растворения. Функциональную зависимость изменения определяемой концентрации гидроксида кальция в растворе относительно добавляемого ее значения можно использовать для сравнительной оценки механизма сорбционных процессов для порошков различной вещественной природы.

КЛЮЧЕВЫЕ СЛОВА: полиминеральный кварцевый песок, пуццолановая активность, оксид кальция, концентрация гидроксида кальция, сорбционная емкость

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