

ELECTROKINETIC POTENTIAL MEASUREMENTS IN A SYSTEM OF SiO₂ - CaCl₂ - H₂O

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The aim of the presented work was to study the dependence of the SiO₂ sol zeta potential on the contents of calcium chloride. The sol contained 2.27 wt. % of SiO₂ and the content of anhydrous CaCl₂ varied between 0.126 and 13.0 wt.%. The experiments demonstrated an influence of calcium and chloride ions on the electrokinetic potential. Formation of gels based on calcium-silicate hydrates can be expected with an increasing content of calcium ions in the solution. On the other hand, increasing content of chloride ions brings about a lowering of the pH of the solution, thus slowing down the transport of the silicate components into the solution. These chloride effects are more apparent at higher CaCl₂ concentrations. The described phenomenon explains the behaviour of calcium chloride as an additive accelerating the hydration of the silicate components of clinker minerals.

INTRODUCTION

Measurement of the zeta potential of high-dispersion silicate systems in the presence of additives provides a better insight into the origin of electrical double layer on the particles of silicon oxide sol, facilitates a theoretical evaluation of the process of gel system formation, and contributes to understanding of the effects of additives on the kinetics of hydration of the silicate phases of Portland cement [1]. Provided that the starting point is a pure sol with particle size in range from 7 to 25 nm, a layer characterized by an electric charge is formed as a consequence of a reaction of the surface of the present SiO₂ aggregates with the dispersed medium [2]. The size and polarity of the charge determines the chances of mutual particle interactions. If the charges have identical sign, which occurs in systems with a single solid high-dispersion phase, an electrostatic barrier retarding the formation of larger aggregates will exist and such conditions can be expected to lead to temporarily stable high-dispersion solidus-liquidus systems. In course of time, the metastable equilibrium becomes disturbed by processes occurring within the dispersed medium and liquid aqueous solution whose composition will vary as a result of reactions proceeding in the solution [3]. The change of the composition of the solution leads to variations in surface charges, which can be associated for example with particle approximation, which in turn facilitates a polymerization of the silicate systems and the formation of larger SiO₂ aggregates. Characterization of the influence of a particular additive based on calcium chloride on the development of the electrokinetic potential is essential for understanding the mechanisms of the accelerating effect of CaCl₂ in the hydration of calcium-silicate clinker phases [3, 4] and/or defining the conditions of optimal hydrate synthesis.

EXPERIMENTAL PART

The dependence of zeta potential on the amount of added CaCl₂ was evaluated on the basis of results obtained by using Zeta Potential Analyzer type 1202 made by Micromeritics. The principle of the measurements in the mentioned type of zetameter lies in evaluating differences in the suspension mass resulting from the transport of high-dispersion particles in an electrical field. The calculation is then based on differences in the mass of the sample cell with the studied suspension recorded before and after the experiment. Zeta potential is calculated according to Helmholtz - Smoluchowski equation [5]:

$$\zeta = 1.13 \times 10^6 v_c \left(\frac{\mu}{D} \right), \quad (1)$$

where μ is viscosity and D dielectric constant of water. The velocity of particles [6] moving in the electric field is represented by the value of electrophoretic mobility v_c

$$v_c = \frac{\Delta w k}{Rt\phi(1-\phi)(\rho_p - \rho_l)}, \quad (2)$$

where Δw is mass difference, k the conductivity cell constant, I is the applied current, ρ_p the density of the dispersed phase, and ρ_l is the density of the liquid phase. For the parameter ϕ representing the volume ratio of the components it holds that

$$\phi = \frac{[w_{dp}/\rho_p]}{[w_{dp}/\rho_p] + [w_l/\rho_l]}, \quad (3)$$

where w_{dp} is the mass concentration of the dispersed phase, w_l the mass concentration of the liquid phase, ρ_p

the density of the dispersed phase, and ρ_l the density of the liquid phase.

The experiments were based on the commercially supplied sol of silicic acid Tosil (produced by Tonaso Neštemice a.s.). Analysis of the composition of the aqueous sol by the ICP technique using instrument Thermo Jarrel Ash, type Iris AP showed the SiO_2 concentration to be 22.75 wt.%, and among the other components the content of Na_2O was 0.35 wt.%. The density of the sol used was 1.21 g cm^{-3} and the pH value at 25°C was 9.51. The measurements were performed in 10 % solution of sol with addition of calcium chloride. Suspensions contained between 0.126 - 13.0 wt.% of CaCl_2 and the molar ratio of CaCl_2 to SiO_2 varied within a range 0.009 - 3.09.

RESULTS AND DISCUSSION

Unlike other studies dealing with zeta potential, our experiments were focused on unstable systems and their objective was to evaluate the development of zeta potential of a dynamic system prior to gelation or during its course. The employed technique evaluates zeta potential from time integral values. The dispersion variance of the obtained values indicates the variability of the system, where the particle size distribution and the velocities of the processes taking place change in the given time interval. As seen in the diagram of zeta potential dependence on the molar ratio in figure 1, the value of zeta potential for the low value range of the ratio

$$r = x(\text{CaCl}_2) / x(\text{SiO}_2) \quad (4)$$

is clearly negative, which is evidence for the active centres formed by unsaturated oxygen bonds in the surface layer of the Si_nO_m aggregates of the sols. At a low molar ratio of the components the results of the measurements are characterized by a high dispersion variance. With increasing the CaCl_2 contents we can expect charge compensation as well as blocking the surface as a result of interactions with calcium ions. These phenomena are documented by increasing zeta potential values. The value characterizing the isoelectric point, i.e. $\zeta = 0$, is exceeded within a range of the r ratio values r_{crit} of 0.713 - 0.915. Under these conditions the dispersion variance is apparently reduced indicating the achievement of a stable state. Visual observations of the reacting system prove the close vicinity of the isoelectric point to be the value where gelation occurs. Apparent discontinuity seen in the diagram of figure 1 characterizes these conditions. A removal of the energetic barrier in the form of a negatively charged layer can be expected at $\zeta = 0$, so that fast particle interactions can occur. Our idea is that a change in the surface charge contributes significantly to the gelation of the system.

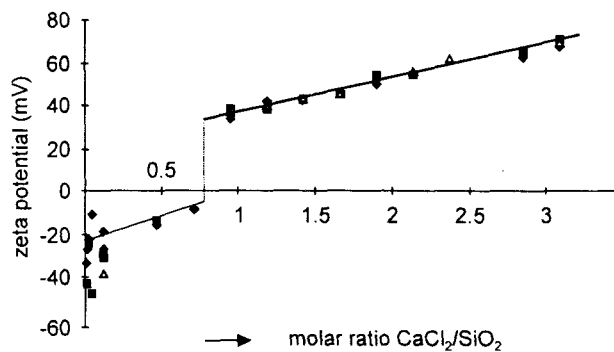


Figure 1. The dependence of zeta potential on molar ratio $\text{CaCl}_2 / \text{SiO}_2$.

The hypothesis of electric field affecting gel stability and gelation velocity is proved by the so-called reversible gelation in the electric field. At low values of the molar ratio r a formation of larger aggregates was observed, which are stable in a rotating vessel only when voltage is applied. Reversible gelation thus takes place as a consequence of an electric potential gradient dU / dx on the individual particles when surface charge can be temporarily polarized at distance dx . At the same time, a linear chaining of aggregates is likely to occur, because only the ends of the aggregates are temporarily available for approximation and interaction. From an energetic point of view, this interaction can be even more favourable near zero charged particles at $\zeta = 0$. Discontinuation of the current results again in disjoining the aggregates and clearing the solution.

Increasing contents of calcium ions in the solution bring about an increase in the zeta potential, which can be explained by a build-up of the calcium chloride concentration in the solution. An increase in Ca^{2+} content takes place on the surface or in the vicinity of the surface of colloidal particles, and the equilibrium is shifted in favour of increasing chloride ion contents in the solution. Compilation of the obtained results enabled the formulation of a linear expression for the dependence of zeta potential on the molar ratio r

$$\zeta = 15.69r + 21.13 \quad (5)$$

whereby it follows that increasing calcium chloride contents in the range of the molar ratio r from 0.915 towards higher values leads to an increase in the positive charge near the gel particles. From a practical point of view, it is important that an increase in the concentration of calcium chloride in the solution will increase calcium ion capacity in the surface layer, which is significant during antiparallel transport of Ca^{2+} and water in the gel packing of the hydrating calcium-silicate. The mechanism of calcium chloride effect on the acceleration of the hydration process can thus be explained.

It is also interesting to follow the course of pH dependence on increasing calcium chloride concentration in the diagram of figure 2. It shows gelation to divide the course into two areas within the coordinate system of $pH = f(\log r)$ differing in their slope characteristics. At a lower molar ratio r the dependence can be described by the relation

$$pH = - 0.17 \times 2.30 \times \ln(r) + 7.86 \quad (6)$$

while at a higher ratio has the form:

$$pH = - 0.38 \times 2.30 \times \ln(r) + 7.98 \quad .$$

The discontinuity is caused by a change in the consistency of the mixture as an effect of gelation, and especially by decreasing the contents of the available liquid phase. The relationship between volume and concentration can be derived from the volume and mass balance. The mass balance of CaCl_2 can be expressed by summing

$$m_1 + \Delta m = m \quad , \quad (7)$$

where m_1 is the amount in the original volume, Δm an increase in the amount, and m being the final amount of CaCl_2 in the solution. When considering volumes and concentrations, the relation (7) can be rewritten as

$$V_1 c + \Delta V c_0 = V c_1 \quad , \quad (8)$$

where V_1 is the volume of the original solution, c its concentration, ΔV the volume of the additive, c_0 its concentration, V the final volume, and c_1 the final concentration. Volume balance is

$$V_1 + \Delta V = V$$

and after substituting for V we obtain:

$$V_1 c + \Delta V c_0 = (V_1 + \Delta V) c_1 \quad (9)$$

$$V_1 (c - c_1) = \Delta V (c_0 - c_1) \quad . \quad (10)$$

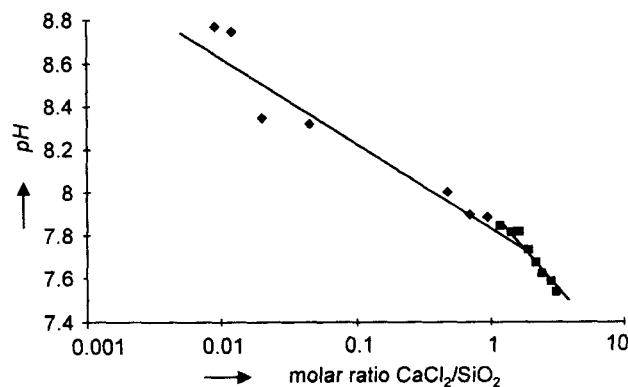


Figure 2. The dependence of pH value on molar ratio $\text{CaCl}_2 / \text{SiO}_2$.

For an infinitesimal increase of dV the expression can be written in the following differential form:

$$V_1 dc = dV (c_0 - c_1) \quad (11)$$

or

$$dV / V_1 = dc / (c_0 - c_1) \quad (12)$$

or

$$dV = V_1 d \ln(c_0 - c_1) \quad . \quad (13)$$

For a constant increase, in the case of two solutions characterized by indexes 1 and 2, we can write the equality

$$V_1 d \ln(c_0 - c_1) = V_2 d \ln(c_0 - c_2) \quad (14)$$

and compare changes in the composition or the logarithms of the differences $(c_0 - c_i)$ as follows:

$$d \ln(c_0 - c_1) / d \ln(c_0 - c_2) = V_2 / V_1 \quad . \quad (15)$$

It follows from the expression (15) that for an identical addition dV the change in concentration is inversely proportional to the actual total volume of the solution. In our case, the slope change brought about by gelation enables us to evaluate the reduction of the actual available volume of liquid phase for "CaCl₂ titration". If the ratio of the slopes is 0.38 : 0.17, it means that the volume of the available liquid phase was reduced in the ratio of 1/2.23, that is 0.45. The unavailable volume is 55.1 %. It is not only the question of water bound in the originating hydrosilicate, but also that of the solution in closed or poorly available capillaries, and a condensation of the $\text{SiO}_2 - \text{CaO} - \text{H}_2\text{O}$ system will also contribute to the decrease in the available volume.

In addition, the decrease of the liquid phase volume is obtained when monitoring the sample density. Figure 3 shows that the decrease in basicity (below $pH = 8$) brings about increase in the sample density. The discontinuity in the course of the curve corresponds to the moment where gelation of the system occurs. Density measurements thus provide data for a description of the coexistence of solid and liquid phases. The dependence of sample density on molar ratio r (figure 4) illustrates formation of more dense structure of the gel.

It is also interesting to follow the course of the dependence of sample electric conductivity on the molar ratio r (figure 5), where an increase in electric conductivity is associated with an increasing concentration of the electrolyte in aqueous solution, as expected. It is apparent from the course of the curve that until a molar ratio of around 1 (that is near the isoelectric point) or r_{crit} is reached, there exists a plateau representing stagnation in the growth. After overcoming this

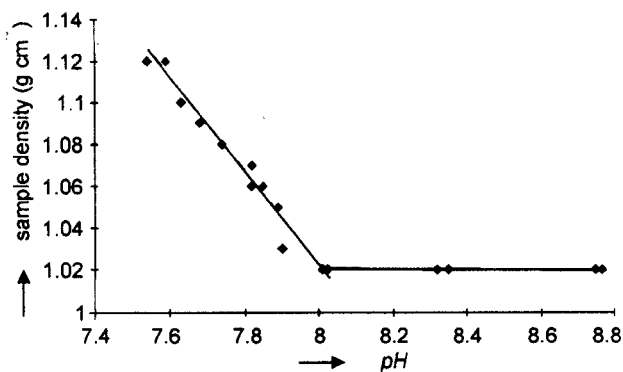


Figure 3. The dependence of sample density on pH values.

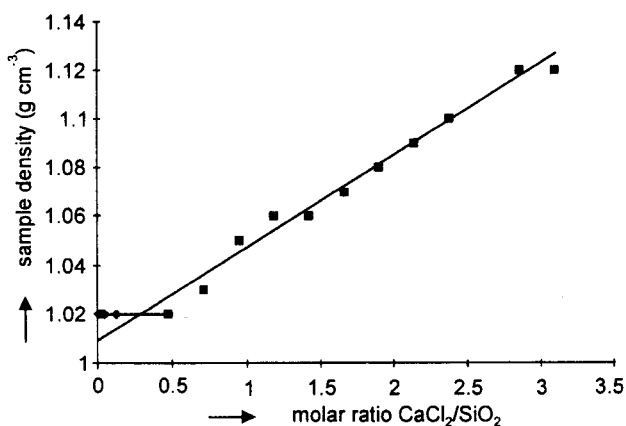


Figure 4. The dependence of sample density on molar ratio $\text{CaCl}_2 / \text{SiO}_2$.

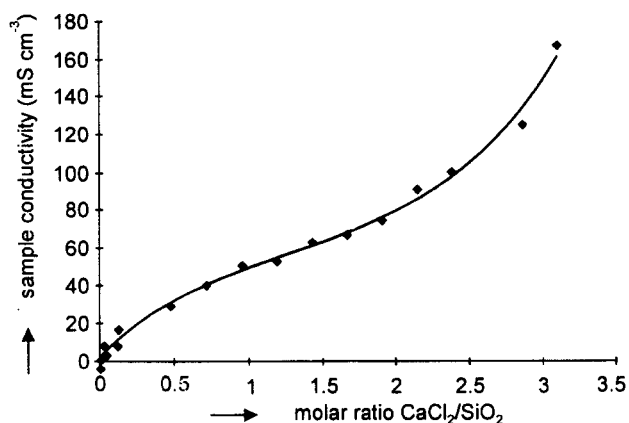


Figure 5. The dependence of sample conductivity on molar ratio $\text{CaCl}_2 / \text{SiO}_2$.

boundary, there is a faster increase in conductivity. This phenomenon can be explained by an increased resistance accompanying gelation as a consequence of necks formation among the gel particles. The polymerization reaction, or the formation of a larger aggregate is then accompanied by a more intensive connection of the

individual particles, which results in better contacts and improved conductivity. Increasing amounts of the electrolyte brings larger amounts of ions to the surface, thus facilitating the transport of charge.

CONCLUSION

The dependence of zeta potential of the sol of SiO_2 on the content of calcium chloride was studied. The sol contained 2.27 wt.% of SiO_2 and the contents of CaCl_2 varied within the range of 0.126 - 13.0 wt.%. The maximum of gelation rate can be expected in the isoelectric point within the molar ratio range of 0.71 - 0.95 at 0.38 mol l⁻¹ SiO_2 , which corresponds to the contents of 3.0 - 4.0 wt.% of CaCl_2 and $pH \approx 8.0$. In lower molar rates r , an adsorption of Na^+ cations, which are present in the sol, takes place. However, these ions are present only in small amounts, so that their depletion and binding to the surface will be followed by an absorption of Ca^{2+} ions and their reaction with the hydrated surface of SiO_2 along with a fast formation of calcium hydrosilicates. Next, after a certain time period, the reaction rate will be held up until we come nearer to the isoelectric point where the reactions will be restored to a condition where the surface is active, steric barriers are absent, and water seeps to the surface. At a certain stage another layer compensating for the charge will be formed, namely of the Cl^- anions, which will impart a negative charge to the surface.

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MĚŘENÍ ELEKTROKINETICKÉHO POTENCIÁLU
V SOUSTAVĚ SiO₂ - CaCl₂ - H₂O

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Závislost zeta potenciálu na množství přidaného CaCl₂ byla vyhodnocována na základě výsledků získaných přístrojem Zeta Potential Analyzer typ 1202 firmy Micromeritics.

Na rozdíl od jiných prací zabývajících se studiem zeta potenciálů byly experimenty zaměřeny na neustálené systémy a jejich cílem bylo hodnocení vývoje zeta potenciálu dynamického systému před gelací nebo v průběhu gelace. Použitá technika vyhodnocuje zeta potenciál z časového integrálu a rozptyl naměřených hodnot je mírou variability systému, ve kterém se v daném časovém intervalu mění rozdělení velikostí částic a rychlost probíhajících procesů. Jak ilustruje diagram závislosti zeta potenciálu na molárním poměru na obr. 1., lze jednoznačně

konstatovat, že hodnota zeta potenciálu je při nízkých hodnotách poměru

$$r = x(\text{CaCl}_2) / x(\text{SiO}_2)$$

záporná, což je svědectvím, že aktivními centry jsou nenasyčené vazby kyslíku v povrchové vrstvě Si_nO_m agregátů solí. Výsledky měření při nízkém molárním poměru složek jsou charakterizovány velkým rozptylem. Dá se předpokládat, že při rostoucím obsahu CaCl₂ dochází jednak ke kompenzování náboje a jednak k blokování povrchu interakcí s vápenatými ionty. Tyto jevy jsou dokumentovány růstem zeta potenciálu. K překročení hodnoty charakterizující izoelektrický bod t.j. $\zeta = 0$ dochází v rozmezí hodnot poměru r (r_{krit}) od 0,713 do 0,915. Za těchto podmínek zjevně klesá rozptyl, což signalizuje dosažení ustáleného stavu. Vizualní pozorování reagujícího systému dokazují, že právě v blízkosti izoelektrického bodu dochází ke gelaci. V diagramu na obr.1 jsou tyto podmínky charakterizovány zjevnou diskontinuitou. Dá se očekávat, že při $\zeta = 0 \pm \epsilon$ byla odstraněna energetická bariéra ve formě záporně nabitě vrstvy a byly vytvořeny předpoklady pro rychlou interakci částic. Podle našich představ změna povrchového náboje významně přispívá ke gelaci soustavy.