

ELECTROKINETIC POTENTIAL MEASUREMENTS IN SiO_2 - H_2O SYSTEM IN THE PRESENCE OF CALCIUM SULPHATE DIHYDRATE

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The nature of the hydration, or gelation processes in SiO_2 - H_2O system in the presence of calcium sulphate dihydrate was studied by electrokinetic potential measurements. SiO_2 sol contained 31.47 wt.% of silicon dioxide and the concentration of the calcium sulphate dihydrate was varied between 0.2 and 10.0 mass %. Calcium ions presumably tend to become incorporated in the surface layer and form a new type of particles composed of a nucleus SiO_2 and a surface layer C-S-H whose significance will increase with increasing amounts of Ca^{2+} ions. Increasing amount of calcium sulphate dihydrate causes the lowering of pH value and rate of gelation of individual SiO_2 is higher. In these condition, calcium ions cannot form surface layer of C-S-H gel.

INTRODUCTION

Gypsum is used in the hydration [1, 2] of Portland cement as a setting regulator. It blocks the reactions of alumina phases, whereby favoring the hydration of silicate phases, especially that of tricalcium silicate (alite). A suitable quantity of gypsum in the cement is given by its C_3A contents which is usually defined by a standard [3].

It retards tricalcium aluminate hydration by forming microcrystalline, colloid-like ettringite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 30\text{-}32\text{H}_2\text{O}$. Excessive sulphates lead to a recrystallization of the formed ettringite and the delayed enlargement in the crystal volume increases the probability of deterioration in mechanical properties, or even a destruction of the cement composite. Ordinary Portland cement contains 55 - 60 % of alite (C_3S), 10 - 15 % of tricalcium aluminate (C_3A), 20 - 30 % of dicalcium silicate (C_2S) and 8 - 15 % of aluminate ferrite phase (C_4AF). The greatest effect on the final strength of the cement is exerted by tricalcium silicate, namely by the firm Si-O bonds. The presence of sulphates in the system can, in theory, also affects the structure development and hydration kinetics of the silicates.

The objective of this work is determination of the influence of calcium sulphate on the hydration of silicate components. Hydration of a model SiO_2 sol leads to a gelation of the system where a hydrosilicate gel is formed under the influence of a particular calcium sulphate concentration, and the incorporation of calcium ions in the gel structure should result in a transition to calcium hydrosilicate gel C-S-H. The course of gelation in the presence of CaSO_4 can be influenced in two ways. By the actual transport of calcium ions across the gel layer formed on the alite surface, or it can be conditioned

by lowering the pH of the system as a result of increasing sulphate concentration in the solution. The nature of the hydration, or gelation processes can be studied by the surface charge measurements. Reactions taking place in the system result in changes in the electrokinetic potential, thus making it possible to determine conditions leading to an acceleration (at $\zeta \approx 0$), or retardation of the gelation ($\zeta \neq 0$), and therefore, the kinetics of the hydration process [4].

EXPERIMENTAL PART

The work was designed to examine the effect of calcium cations and the role of sulphate anions in the formation of hydrosilicate gel and the values of zeta potential. The sol was prepared from a commercial product Tosil (Tonaso a.s.) which was checked for its chemical composition employing by ICP (Thermo Jarrel Ash instrument, type Iris AP), using anorganic elementary analysis. The sol contained 31.47 wt.% of silicon dioxide, the density being 1.22 g cm^{-3} , and the pH value was 9.10. The solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ at 25°C is tabulated [5] as $0.26 \text{ g} / 100 \text{ g H}_2\text{O}$. Samples were prepared from a 10 % solution of the sol and a solution of calcium sulphate dihydrate (Lachema a.s.) in concentration range from 0.2 to 10 wt.%. The molar ratio

$$r = x (\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) / x (\text{SiO}_2) \quad (1)$$

thus varied between 0.02 and 1.11 at a molar concentration 0.52 mol l^{-1} of SiO_2 .

In this paper usual chemistry cement notation is used in which: C = CaO, S = SiO_2 , A = Al_2O_3 , F = Fe_2O_3 , H = H_2O .

The binary system of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ - H_2O was also studied in connection with the electrokinetic potential measurements of the ternary system. The electrokinetic potential of both the reacting and the non-reacting samples was measured after 15 minutes from beginning of the sample preparation. Perfect homogenization of the system was thus achieved.

Zeta potential was measured using a Zeta Potential Analyzer type 1202 (Micromeritics). While evaluating electrokinetic potential, other parameters were also studied. Electrical conductance was determined by means of a conductance cell, pH values were obtained with the use of a glass and a reference argentochloride electrodes using a Gryf instrument, type 208 with an accuracy of ± 0.01 units of pH , temperature was recorded using a mercury thermometer with a precision of ± 0.05 °C, and sample densities were determined with a pycnometer.

Electrophoretic mobility and zeta potential values were calculated from the mass difference of the cuvette with a sample in an electrical field during an experiment using Helmholtz-Smoluchowski relation [6, 7].

RESULTS AND DISCUSSION

The mean value of zeta potential of the SiO_2 sol with contents of 0.52 mol l^{-1} fluctuated around $\zeta = -50.93 \text{ mV}$ at $pH = 9.05$.

The recorded dependence of zeta potential on molar ratio r is plotted in the diagram in figure 1, and the development of surface charge is illustratively represented in particular steps in figures 2a - 2g.

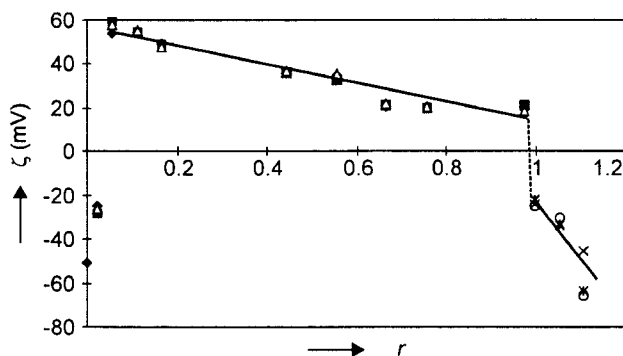


Figure 1. The dependence of zeta potential values on molar ratio $x(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) / x(\text{SiO}_2)$.

It follows from the results that at low molar ratio values r the zeta potential is negative, which indicates the fact that the surface of SiO_2 particles is likely to be formed by silicate anions (figure 2a). In the next phase, represented in figure 2b, the sol particle surface charge is compensated by the charge of calcium cations whose concentration increases, while the total surface charge still remains negative. Calcium ions presumably tend to

become incorporated in the surface layer and form a new type of particles composed of a nucleus SiO_2 and a surface layer C-S-H whose significance will increase with increasing amounts of Ca^{2+} ions.

Within the molar ratio r range of 0.03 to 0.05 the value of $\zeta = 0$ is exceeded (isoelectric point). At a zero surface charge the conditions favor interactions between individual particles and gelation can occur at this point. Negative surface of the particles is thoroughly compensated by positive ions and the total charge is zero (figure 2c). At a value of $r = 0.02$, which is in the vicinity of the isoelectric point, the concentration corresponds to the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in water (in binary system with water). From this point onwards the presence of undissolved matter in suspension should be taken into account.

Above the isoelectric point at $r = 0.03$, the zeta potential value is positive. In this case, the chemical equilibrium at the surface is shifted in favor of C-S-H, thus giving rise to positively charged aggregates, as illustrated in figure 2d.

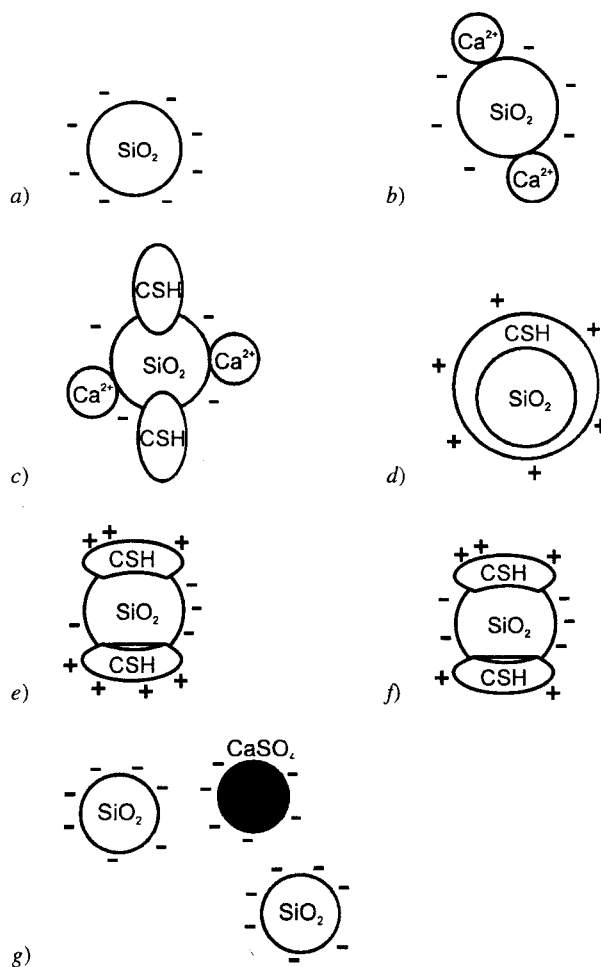


Figure 2. The formation of surface charge in SiO_2 - H_2O - CaSO_4 system.

Apparently, at a molar ratio $r = 0.055$, maximal possible binding of calcium cations to the sol surface occurs. With any further enrichment in calcium sulphate contents the value of zeta potential decreases down to $r = 0.98$. Explanation of the zeta potential values presumably lies in the changing composition of the solution. In case of SiO_2 sol, an important role is played by the pH value. This is, in our case, significantly influenced by adding the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ solution. Decreasing pH (increasing r values) obviously results in relatively stable SiO_2 colloid particles of SiO_2 with a lower reactivity. These no longer react so intensively towards C-S-H formation, and the contribution of positively charged Ca^{2+} particles will be lower. The dependence pattern during this stage is described by a linear equation

$$\zeta = -5.06 \times r + 57.84 \quad (2)$$

and a schematic representation of this step is seen in figure 2e.

At a molar ratio value $r = 0.98$, which corresponds to 8.9 wt.% of added $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, the electrokinetic potential dropped to a value of $\zeta = 0$ (figure 2f). At this second isoelectric point the situation somewhat differs from the conditions at $r = 0.03$. No surface layer of C-S-H particles is possible to arise here and the zeta potential will be determined by an interaction of the SiO_2 surface with positive ions occurring in the solution (Ca^{2+} or H^+).

Above the molar ratio value of $r = 0.98$, significant influence is likely to be exerted by sulphate anions in the solution, or by undissolved particles of calcium sulphate (figure 2g). Experiments with pure $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ demonstrated a negative value of the electrokinetic potential in the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{H}_2\text{O}$ system. Apparently, the surface charge will be changed in this more complicated system of $\text{SiO}_2 - \text{H}_2\text{O} - \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and the value of zeta potential will tend to become negative with the increasing contents of calcium sulphate dihydrate. C-S-H particles will migrate towards the cathode, undissolved calcium sulphate will be drawn by their charge towards the anode.

The patterns of the values obtained during zeta potential measurements are shown in the diagrams in figures 3 - 5.

The dependence of sample density on the molar ratio r (diagram in figure 3) shows an apparent linear increase that can be described by the following equation

$$\rho = 0.04 r + 1.02 \quad (3)$$

The intercept on the ordinate axis (density) of 1.02 follows the extrapolated value for diluted SiO_2 sol. In the measured interval of molar ratio values, the maximum density was $\rho = 1.06 \text{ g cm}^{-3}$ at $r = 1.1$.

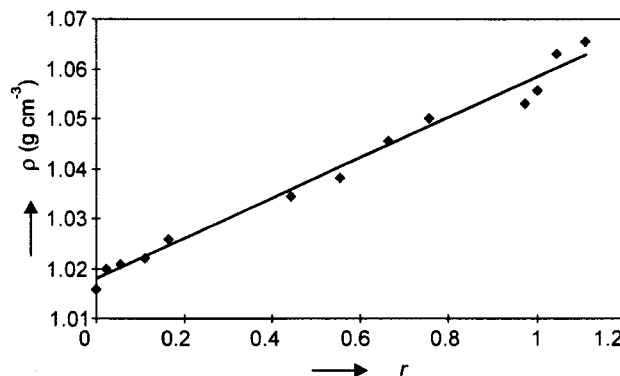


Figure 3. The dependence of sample density on molar ratio x ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) / x (SiO_2).

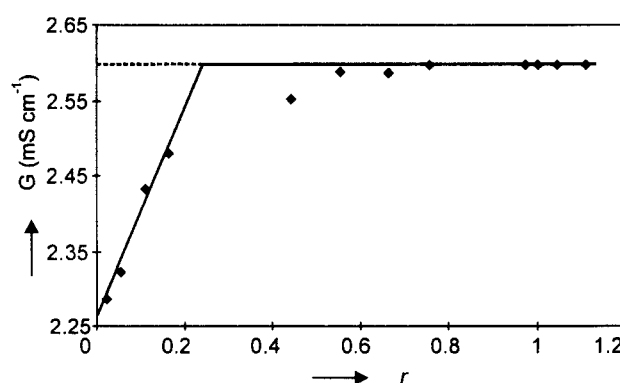


Figure 4. The dependence of sample conductivity on molar ratio x ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) / x (SiO_2).

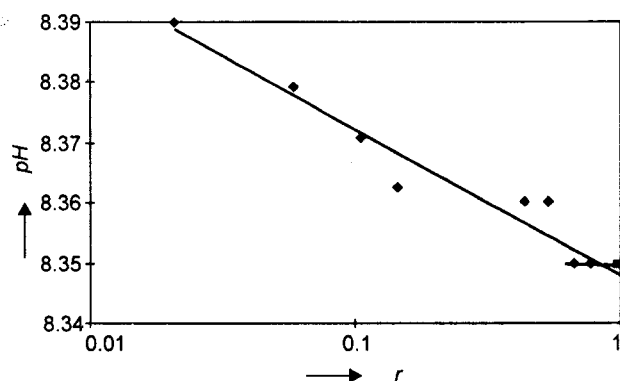


Figure 5. The dependence of pH values on molar ratio x ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) / x (SiO_2).

The dependence of sample conductivity on molar ratio, which is divided in two stages, is plotted in figure 4. The first stage shows a sharp increase in the system conductivity, which is caused by the onset of the gelation process according to the relation

$$G = 1.31 r + 2.26 \quad (4)$$

The region where r is between 0.3 and 0.98 represents a transition from one type to the other one. At high r values conductivity of sample becomes stabilized at a maximum value of 2.6 mS cm^{-1} .

The dependence of pH on molar ratio is illustrated in figure 5 where pH decreases with increasing molar ratio r . Lowering the pH of the system supports the process of gelation. The pH of a sample decreases according to the relation

$$pH = -0.01 \log r + 8.35 \quad (5)$$

Figure 6 then illustrates the dependence $\zeta = f(pH)$ which documents decreasing zeta potential values with increasing pH . Figure 5 documents graphically the limiting pH value near $pH = 8.35$.

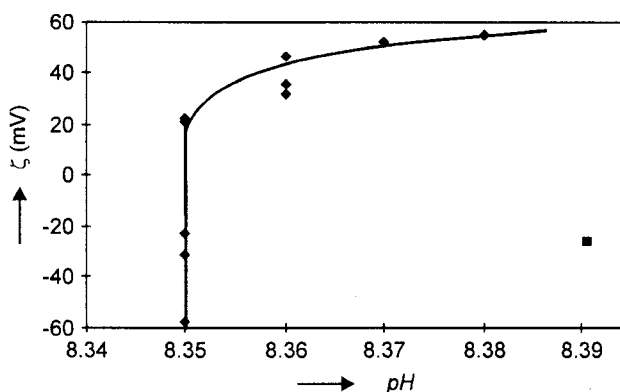


Figure 6. The dependence of zeta potential values on pH .

CONCLUSION

Electrokinetic potential measurement in a system of SiO_2 - H_2O in the presence of calcium sulphate dihydrate provides information on the process of gelation in the course of increasing contents of Ca^{2+} and SO_4^{2-} ions. The studied system was found to possess two isoelectric points. Interactions between Ca^{2+} ions and the sol particles result in the formation of a surface layer of the CSH gel with a positive charge. These reactions take place preferably in the region of higher pH values. On the contrary, lower pH values will favor the gelation of SiO_2 particles alone, and the formation of CSH gell will not be so possible. Besides the gel SiO_2 particles the zeta potential values of the system of SiO_2 - H_2O - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ will also be influenced by the electrokinetic potential of the undissolved particles of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

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MĚŘENÍ ELEKTROKINETICKÉHO POTENCIÁLU V SOUSTAVĚ SiO_2 - H_2O V PŘÍTOMNOSTI DIHYDRÁTU SÍRANU VÁPENATÉHO

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Práce byla orientovaná na sledování vlivu dihydrátu síranu vápenatého na hydrataci a gelaci modelového solu oxidu křemičitého měřením změn elektrokinetického potenciálu. Měření zeta potenciálu a vyhodnocení hmotnostního transportu bylo realizováno na přístroji Zeta potential analyzer typ 1202 firmy Micromeritics. Hodnoty elektroforetické pohyblivosti a zeta potenciálu byly vypočítány na základě Helmholtz-Smoluchowského vztahu [6, 7].

Molární poměr dihydrátu síranu vápenatého a oxidu křemičitého ve formě solu (r) se pohyboval v rozmezí od 0.02 do 1.11. V systému SiO_2 - H_2O - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ hraje důležitou úlohu vznik povrchové vrstvy C-S-H gelu. Z tohoto důvodu jsou závislosti $\zeta = f(r)$ charakterizované dvěma izoelektrickými body. Se stoupající koncentrací přidaného $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ dochází současně ke snižování pH systému, což má za následek zrychlení procesu gelace samotných částic SiO_2 a vznik C-S-H gelu není již tak pravděpodobný.