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Zeta potential study of paste blends with slag

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ABSTRACT

Electrokinetic studies of interfaces between solid phase and aqueous solution have most often been undertaken to elucidate the mechanism of adsorption and transport of different species into cementitious materials. The zeta potential is used to understand the electrokinetic properties of interfaces. In the present paper, zeta potential studies of cements and paste, with and without addition of slag, in different electrolyte solutions are carried out to understand the effect of the adsorption of charged species. The amounts of adsorbed ions are also measured to verify the results obtained by zeta potential measurement. This study shows that the cements and paste particles are negatively charged in water, sodium chloride solution, and at low concentration of calcium. At high concentration of calcium a charge inversion is observed. Thus, both calcium and chloride are potential determining ions, whereas sodium behaves as an indifferent ion. Moreover, slag particles strongly influence the surface chemistry not just of the slag but of the whole paste.

1. Introduction

When solid surfaces contact with aqueous solution the electric double layer develops at the interfaces. The electric double layer is generally viewed as consisting of two layers: an immobile layer of ions opposite in sign to that of the surface and a diffuse layer, which can be viewed as a cloud of hydrated ions that transition from the significant excess of counterions at the fixed charge layer to a balance of cations and anions in the bulk solution. The shear plane is located close to the boundary between the fixed and diffuse layer. The potential at the shear plane is called zeta potential. The change in zeta potential is due to either a change in surface charge or adsorption of ions to the surfaces. The surface charge of a hydrate phase depends on the chemical nature of the phase and ions in the pore solution. The main hydration product of cementitious materials is calcium silicate hydrates (C–S–H). It represents 40–60% in mass of cement and has a high specific surface area of 200 $m^2\,g^{-1}$ [1]. The surface of cements and their hydration products become charged either by dissociation of surface groups or adsorption of ions from the electrolyte solution. The surface charge of C–S–H is due to ionization of silanol sites. The dissociation equilibrium of silanol sites due to pH increase is given by [1,2]

$$> \mathrm{SiOH} \iff\ > \mathrm{SiO}^- + \mathrm{H}^+ \tag{1}$$

and by the adsorption of Ca^{2+} on the silanol sites, resulting in a positive charge:

$$> \mathrm{SiOH} + \mathrm{Ca}^{2+} \iff\ > \mathrm{SiOCa}^+ + \mathrm{H}^+ \tag{2}$$

The surface of C–S–H is mainly dominated by $>SiO^-$, $>SiOCa^+$, and SiOH surface groups. On the C–S–H surface, the mean surface charge is the sum of $>SiO^-$ and $>SiOCa^+$. The magnitude and sign of zeta potential depend on the above surface groups and the charges located within the shear plane.

During the past decade, much effort has been devoted to determine the zeta potential of cements and synthetic C–S–H [3–9]. In addition, much attention has been dedicated to the adsorption of potential determining calcium ions on to the surface of synthetic C–S–H [1,2,10]. However, much less attention has been paid to chloride adsorption on the surface of paste concerning electrokinetic study. The influence of binder on surface chemistry of cementitious materials is important to understand the many properties. There are several mineral admixtures which have been used as a replacement of cement for over many years, ground granulated blast furnace slag (GGBS) is one of those. Nowadays GGBS concrete is used in offshore construction. The performance of GGBS concretes depends on both the amount of GGBS used and other materials present in the mixture [11]. Authors have identified the surface charge of both hardened cement paste and slag cement paste by membrane potential mechanisms [12,13], and confirm that GGBS addition influences the pore surface properties of paste. In this paper, electrophoresis technique was used to study the evolution of the zeta potential of paste blended with GGBS to understand the surface properties of concrete. In addition, authors investigated the correlation between cements (both ordinary Portland cement (OPC) and GGBS), and paste properties and the adsorption of ions to the surface and its influence on the zeta potential.

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2. Materials and methods

OPC, GGBS, and the pulverized powders of HCP (hardened cement paste) and SCP (slag cement paste, GGBS blended with OPC at 55% in weight) were used in this study. The chemical composition and physical properties of OPC and GGBS are given in Table 1. A water to binder ratio (W/B, by weight) of 0.5 was used for HCP and SCP. The samples were cured in saturated calcium hydroxide for 91 days. The cured samples were grounded by ball mill. The fraction of particles having diameter less than 45 μm was separated by sieving and used for zeta potential measurement. De-ionic water was used as mixing water throughout the whole experiment. Different concentrations of calcium hydroxide, calcium chloride, and sodium chloride solutions were used to prepare the suspensions. Suspensions with 0.1 g/l solid to water ratio were used for zeta potential and ionic adsorption measurements. The suspensions were kept for 2 h, and then dispersed by ultrasonic waves for one minute before the measurement. Average particle size in the suspensions was measured with Zetasizer Nano series and it is in the range of 1.4–1.7 μm.

The zeta potential measurement was performed with Zetasizer Nano series. This apparatus calculates the zeta potential by determining electrophoretic mobility and then applying Henry equation. The electrophoretic mobility is obtained by performing an electrophoresis experiment on the sample and measuring the velocity of particles using laser Doppler velocimetry (LDV). The Smoluchowski approximation was made during the measurement. Therefore, calculation of zeta potential from the mobility is straightforward for systems which fit the Smoluchowski model, i.e. particles larger than about 0.2 μm dispersed in electrolyte containing more than that 0.001 molar salt. Electrolyte concentration for the zeta potential measurement was limited in this study. The calcium hydroxide concentration was 0.01–10 mmol/l and the chloride concentration was 1–100 mmol/l.

The amounts of adsorbed chloride and sodium ions on the paste in sodium chloride solution were determined from the ionic concentration measurements. The suspensions were centrifuged for 1 min and then filtered by using filter of 0.45 μm. The concentration of sodium and chloride ions in the filtered sample was measured by ion chromatography.

3. Results and discussion

In the present research, zeta potential of OPC, GGBS, HCP, and SCP particles in various electrolyte solutions was measured to better understand their surface properties. The measured value of zeta potential results from the contribution of all hydrated and unhydrated phases of cementitious materials such as C–S–H, portlandite, AFm, unhydrated cement and slag. The surface chemistry of each phase might be different when it contacts with electrolyte solution.

3.1. Influence of pH of aqueous phase on zeta potential

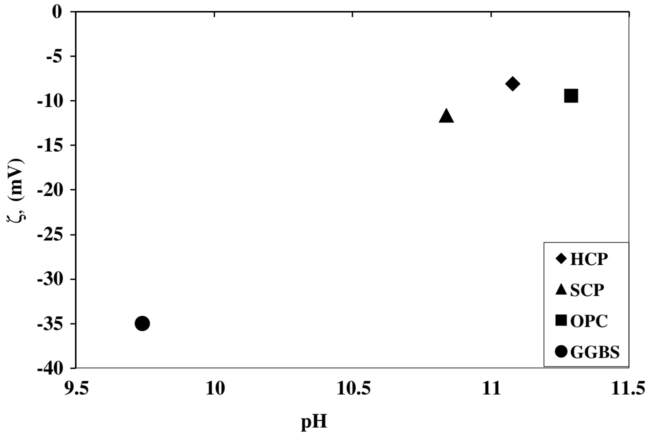

Fig. 1. Zeta potential of suspension in water.

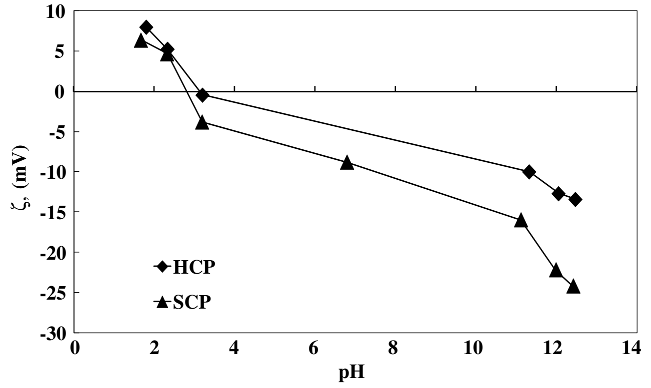

Fig. 2. Zeta potential of paste as a function of pH. HNO_3 and NaOH solutions were used to adjust the pH.

Like most silicates, C–S–H shows a negative surface charge at high pH (as given in Eq. (1)) and it will change due to adsorption of ions on to the surface. The zeta potential of the suspension tested in water is shown in Fig. 1. All suspensions show a negative zeta potential. In particular, GGBS shows the most negative. Furthermore, SCP particle shows a slightly more negative zeta potential value compared to HCP in water. The zeta potential of both pastes is plotted in Fig. 2 as a function of pH. The pH value was adjusted by addition of sodium hydroxide or nitric acid solutions. The sign of zeta potential is positive at high concentration of nitric acid (10 mmol/l or more). The reversal of zeta potential is obtained when the hydroxyl concentration in the paste suspensions is increased. Thus, the surface charge of hardened paste particles shows the same tendency with pH as C–S–H. The change of zeta potential for both HCP and SCP particles with pH is quite similar. Moreover, it is found that SCP particles give a more negative zeta potential than HCP particles when the value of pH increases. The isoelectric point is situated at pH around 3 for HCP and 2.6 for SCP. This is almost consistent with the results obtained by Nagele [6]. He found the isoelectric points for OPC and GGBS to be at 2.2 and 2.3, respectively. The difference between the results obtained in this study and his results might be derived from different methods used to

Table 1
Physical properties and chemical composition of OPC and GGBS

	Density (kg m^{-3})	Blain surface area (m^2 kg^{-1})	LOI (%)	Chemical composition (wt%)						
				SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Cl^-
OPC	3160	325	0.072	21.5	5.5	2.9	64.3	1.9	1.8	–
GGBS	2890	573	0.001	32.3	15.5	0.43	41.7	5.6	3.3	0.003

adjust the pH; he adjusted the pH value by preparing suspensions in HCl or NaOH and zeta potential value was measured after 15 min.

Fig. 3 represents the change of zeta potential of HCP particles in calcium hydroxide solution with pH. The isoelectric point is dramatically shifted towards around 11.15 of pH. In the presence of calcium, the value of zeta potential increases with pH. This represents a different trend compared with the results shown in Fig. 2. It means that the zeta potential of paste particles in suspension not just depends on pH, but also on the specific absorption of ions on the surface.

3.2. Influence of adsorption of ions on zeta potential

3.2.1. Adsorption of calcium ion

The zeta potential of suspensions is very dependent on the kind of contact solution because adsorption of ions is a determining factor on zeta potential. Figs. 4 and 5 show the zeta potentials as a function of calcium hydroxide concentration for OPC and GGBS, and those for paste particles, respectively. As shown in Fig. 3, calcium hydroxide influences both pH and adsorption of calcium onto the surface of the suspended particles. When lowering the calcium concentration under 0.4 mmol/l, the zeta potential values for both OPC and GGBS become negative. The positive zeta potential values found at higher concentration of calcium. In particular, for the GGBS suspensions a decrease in calcium concentration is results in a remarkable decrease of zeta potential, resulting in a more and more negative zeta potential. In contrast, for OPC suspension, the value of zeta potential is almost the same at calcium concentration less than 0.1 mmol/l. Particles of both HCP and SCP show the same tendency as OPC particles and there is little difference between the zeta potential values of particles for HCP and SCP; that is, SCP particles show more negative or less positive value of zeta potential than HCP particles. The isoelectric point for particles of hardened paste and cement lies at $Ca(OH)_2$ concentration from 0.4 to 0.8 mmol/l. This is different from the results reported for synthetic C–S–H (1–4 mmol/l) [2,4]. A major difference with respect to sign and absolute value of zeta potential is observed in calcium hydroxide solution. These results confirm that the concentration of divalent cations calcium in the solution dominates the zeta potential. At higher calcium concentration of around 1 mmol/l, calcium ions are adsorbed onto the surface, resulting in lower zeta potential by compensating the negative charge (i.e. $[SiO^-] = [SiOCa^+]$). With further increase of the calcium concentration in the solution, the zeta potential of the suspensions will increase due to large amount of calcium adsorption on the surface.

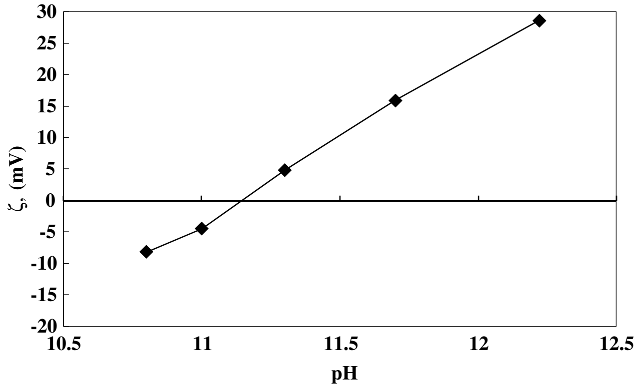

Fig. 3. Zeta potential vs. pH for HCP in $Ca(OH)_2$ solution.

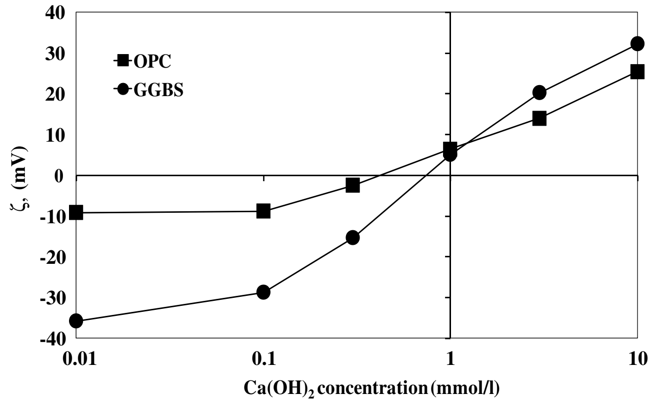

Fig. 4. Dependence of zeta potential on $Ca(OH)_2$ concentration for OPC and GGBS.

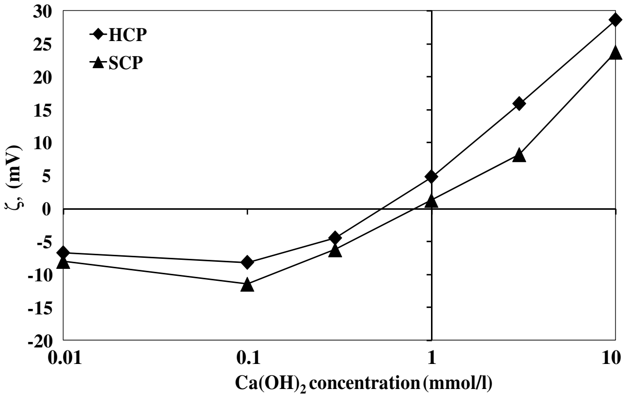

Fig. 5. Dependence of zeta potential on $Ca(OH)_2$ concentration for paste.

The zeta potentials for SCP suspensions in calcium hydroxide and calcium chloride solutions are illustrated in Fig. 6. In the calcium chloride solution, the isoelectric point was around 2 mmol/l of calcium and the SCP suspensions showed the same tendency as in calcium hydroxide solution. However, at calcium concentration greater than 1 mmol/l, there is a significant difference in the zeta potential at the same concentration of calcium. Hence, the mono-valent anions (OH^- and Cl^-) also influence the zeta potential of hardened paste particles.

3.2.2. Adsorption of chloride ion

From the results shown in Figs. 7 and 8, it is evident that the particles of hardened paste, OPC, and GGBS in sodium chloride solution show a negative zeta potential due to partially ionized silanol sites $[SiO^-]$ and adsorption of chloride ions. Chloride ion plays an important role on zeta potential of the particles of hardened

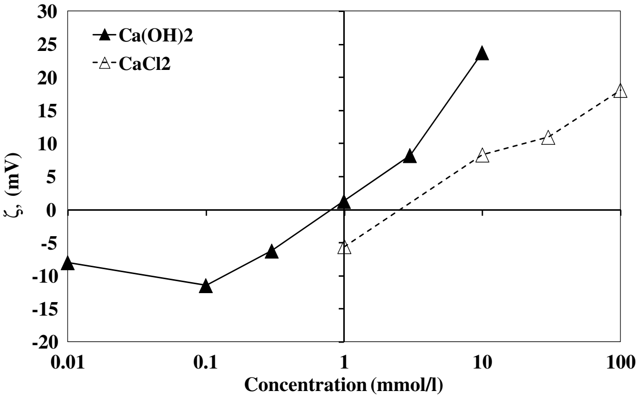

Fig. 6. Zeta potential of SCP in $Ca(OH)_2$ and $CaCl_2$ solution.

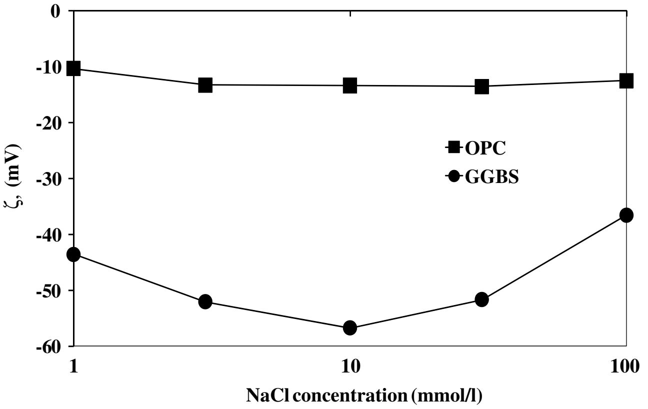

Fig. 7. Zeta potential of OPC and GGBS as a function of NaCl concentration.

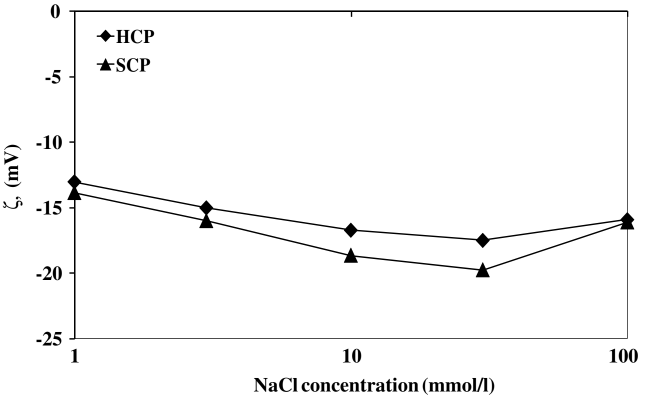

Fig. 8. Zeta potential of paste as a function of NaCl concentration.

paste, OPC, and GGBS; the higher the concentration of chloride ion, the higher the negative value of zeta potential. The absolute value of zeta potential for GGBS increases with chloride concentration up to 10 mmol/l. At higher chloride concentration, it becomes less negative. In comparison, the absolute value of zeta potential for OPC does not change significantly with sodium chloride concentration. The SCP particles give slightly more negative zeta potential than HCP particles in sodium chloride solution, as shown in Fig. 8. This can be explained by adsorption of chloride ion on to the surface of paste and cement suspensions. Both chemical and physical adsorptions are believed to occur in hydrated paste. The amount of adsorbed chloride depends on several parameters such as the concentration of chlorides, the type of binder and its composition, and the specific surface area. The aluminate phases in cement are responsible for binding most of the chloride. At low concentration of chloride, i.e. below 5 mmol/l, chloride does not interact significantly with cement. But once the chloride concentration exceeds 5 mmol/l and ranges up to around 15 mmol/l, the chloride ions replace the hydroxyl ions in AFm (AFm may be viewed as built of sheet-like layers of net composition, $[Ca_2(Al,Fe)(OH)_6]^+$) to Friedel's salt, the AFm-type phase containing chloride [14]. In the present investigation, the adsorption of chloride and sodium ions was examined by ion chromatography. The amounts of adsorbed chloride and sodium ions on the surface of particles for hardened paste are shown in Figs. 9 and 10; these results verify the conclusions obtained from Figs. 7 and 8. SCP particles adsorb more chloride ions on its surface, while sodium ions behave indifferent as shown in Fig. 9. This is consistent with the results of a previous study made by Laurent Nachbaur, concluding that sodium and potassium ions are indifferent ions for synthetic C–S–H [4]. The higher the chloride concentrations, the more chloride ions are adsorbed. Furthermore, the adsorption of chloride ions on SCP is significantly higher than on HCP, shown in Fig. 10. Upon contact with aqueous solution, the hardened cementitious paste is well known to leach some ions (calcium leaching is very high compared to other ions). The leached calcium is again adsorbing to the surface of C–S–H with chloride. The reactions of sodium and chloride ions adsorption on the surface of C–S–H are shown below:

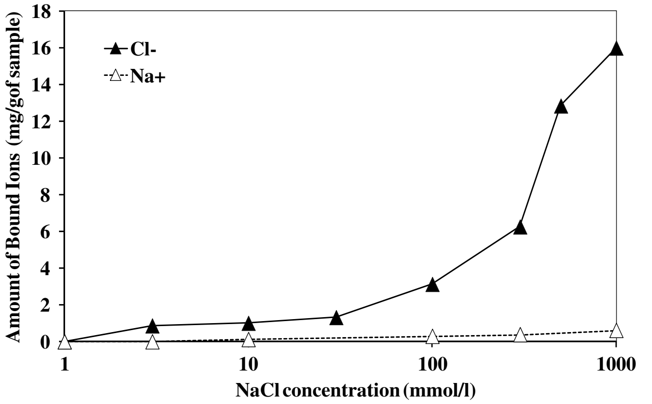

Fig. 9. Amount of Na^+ and Cl^- bound on SCP as a function of NaCl concentration.

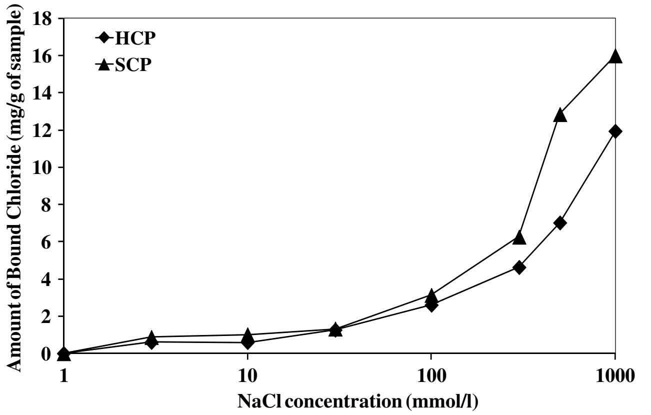

Fig. 10. Amount of chloride ions bound on paste as a function of NaCl concentration.

$$> SiOH + Na^+ \Longleftrightarrow\ > SiONa + H^+ \tag{3}$$

$$> SiOH + Ca^{2+} + Cl^- \Longleftrightarrow\ > SiOCaCl + H^+ \tag{4}$$

Beaudoin has pointed out that in tricalcium silicate, chloride can occur in three states such as free, adsorbed, and interlayer chloride [15]. Moreover, the amount of chemisorbed chloride held by C–S–H is dependent on the H/S, C/S, and nitrogen surface area. In addition, Hosokawa investigated the reaction of C–S–H and AFm phase concerning the chloride ion binding in hardened cement paste [16]. Obviously, an ion exchange reaction occurs in AFm by reaction between monosulfate and Friedel's salt. The amount of chloride bound in AFm decreases whereas the amount of chloride bound by C–S–H increases [16]. It is suggested that more chloride can physically adsorb to the surface of C–S–H by strong Van der Walls forces.

From the previous discussions, it can be concluded that the adsorption mechanism of ions is different for each cementitious material. In other words, the properties of cementitious materials affect adsorption mechanism of different ions in a different way, providing the change in zeta potential.

3.3. Influence of slag properties on zeta potential

The zeta potential values of GGBS and SCP particles strongly depend on the properties of the slag. Physical properties and chemical composition of GGBS are quite different from that of OPC and its effect on zeta potential is more significant. GGBS contains much silica than OPC and thus produces a large amount of dissociated silanol sites [SiO^-]. Further, Taylor mentions that the mean Ca/Si ratio of the C–S–H produced in SCP is lower than that found in pastes of plain Portland cements [17]. From Fig. 1, GGBS has the highest negative value of zeta potential because it produces the highest amount of [SiO^-] in water. The absolute value of zeta potential of SCP is higher than of HCP due to differences in the amount of silica in the C–S–H of both pastes. The surface area correlates with the adsorption of ions to the surface. At higher calcium hydroxide concentration (higher than 1 mmol/l), the adsorption of calcium ions on the surface of GGBS is higher than for OPC, shown in Fig. 4. This could be due to the higher Blaine surface area of GGBS which is almost two times higher than for OPC, as given in Table 1. At low concentrations of calcium ions, the [SiO^-] groups dominate the surface charge of GGBS rather than [$SiOCa^+$], resulting in a more negative value of zeta potential. As shown in Fig. 7, more chloride binds on GGBS than on OPC. As mentioned previously, higher aluminum oxide content allows more chloride binding. Its amount in GGBS is almost three times higher than in OPC. Thus, the high Blaine surface area and the large amount of aluminum oxide content are responsible for chloride adsorption on to the surface of GGBS.

From the results of Figs. 2, 5 and 8, it is obvious that SCP particles have more negative zeta potential at high pH and low concentration of calcium ions as well as in the sodium chloride solution. This behavior is derived from several causes. First, each hydration product has a different surface charge and shows different adsorption behavior. The hydration product of slag is quite different from OPC [18,19]. Two distinct morphologies of OPC hydration products develop, namely inner and outer hydrates. GGBS also has high-density regions such as inner hydrate and low-density regions such as outer hydrates. However, the inner slag hydrates (ISH) within high-density regions are chemically different from OPC inner hydrates. Further, a large amount of C–S–H is formed in SCP by reaction of dissolved calcium hydroxide with silica. Second, there is a possibility that unhydrated slag makes contact with electrolyte solution or water. The unhydrated slag may come to the surface during sample preparation by milling. In SCP, much unhydrated slag remains and it is covered with ISH and C–S–H. Feng has pointed out that 0.28 g of unhydrated slag remained in every one gram sample of SCP determined at water to binder ratio of 0.5 and after 180 days aging [19]. However, no unhydrated cement is left in HCP at age of 91 days.

A solid to water ratio can greatly influence the electrochemical double layer and thus the zeta potential. However, this study is limited to highly dilute systems and therefore pertains to the adsorption phenomena of ions on charged surfaces in a general way. In addition, the paste consists of different kinds of phases and each phase influences the overall zeta potential. The data in this study does not allow the determination of the contribution of each phase separately. It would be of great interest to study the role of different phases with respect to zeta potential and adsorption mechanism separately. There might be an effect of the milling process also on the zeta potential. More research needs to be carried out to in order to solve these problems.

4. Concluding remarks

In the present investigation, the zeta potential of cements and paste suspensions was measured by an electrophoresis technique. Based on the results obtained in this research, the following conclusions can be drawn:

1. In suspensions containing pulverized paste, OPC and GGBS, the particles show negative zeta potential in water. The larger amount of silica in GGBS is responsible for its more negative value of zeta potential.
2. The zeta potential of suspensions is strongly influenced by adsorbed ions. The divalent cation calcium and mono-valent anion chloride have the ability to change the zeta potential of pulverized paste, OPC and GGBS particles, but sodium ions do not affect the zeta potential.
3. The slag properties influence the adsorption of both calcium and chloride ions on to the surface, resulting in a change of the zeta potential. In comparison to OPC, large amount of calcium and chloride ions are adsorbed on the surface of GGBS. Furthermore, SCP gives more negative or less positive zeta potential values compared to HCP in both sodium chloride and calcium hydroxide solutions.

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