Effect of Pore Solution Composition on Zeta Potential and Superplasticizer Adsorption

by Dirk Lowke and Christoph Gehlen

The effect of pore solution composition on zeta potential and superplasticizer adsorption has been investigated experimentally. The investigations were conducted on highly concentrated suspensions, containing quartz flour, limestone flour, cement and combinations of these materials. Furthermore cement-limestone suspensions with different types of cements and a varying ratio of cement to limestone were investigated.

The results show that the zeta potential is significantly determined by pore solution. In a pore solution of highly concentrated cement suspensions the zeta potential can be characterized by the ratio of calcium to sulfate concentration. Furthermore it was shown that the superplasticizer adsorption is affected the zeta potential. At higher, more positive zeta potentials the superplasticizer molecules are more likely adsorbed onto the solid surfaces. Moreover, superplasticizer adsorption in limestone-cement suspensions is predominantly controlled by the composition of pore solution rather than the ratio of cement to limestone flour. If the ion concentration of the pore solution is artificially kept constant, the polymer adsorption is almost constant independent of the cement to limestone ratio in the suspension.

Keywords: zeta potential; pore solution; superplasticizer adsorption.

INTRODUCTION

Rheological properties of high performance concrete like SCC and UHPC are affected by the surface properties of the particles, the properties of the liquid phase and the adsorbed polymers. It is necessary to consider the interactions of the colloidal particles in the cement-based suspension to understand the effect of these parameters on the rheological properties. The present contribution focuses on the effect of pore solution composition on zeta potential and superplasticizer adsorption in highly concentrated cement-based suspensions.

The aim of the investigations was to provide a clear understanding of the mechanism of surface charge and zeta potential in cement suspensions with high solid fractions as well as the interactions between the composition of pore solution, zeta potential and superplasticizer adsorption onto surfaces of cement and mineral additions.

For this reason, the experimental program was divided into to three test series:

a) Zeta potential of quartz, limestone and cement in suspensions with high solid fractions - Effect of pore solution composition

b) Superplasticizer adsorption onto quartz, limestone and cement - Effect of zeta potential

c) Superplasticizer adsorption in limestone-cement suspensions - Effect of cement and limestone content

ELECTRIC DOUBLE LAYER AND ZETA POTENTIAL
Surface charge and Stern potential of oxides and carbonate minerals

As soon as a cement or mineral addition particle is exposed to water, its surface becomes electrically charged. The potential ψ_0 resulting from the surface charge is causing a predominant attraction of ions of opposite charge (counterions). As a result, an electrical double layer is formed between the charged particle surface and the liquid phase. From a historical point of view, the double layer model originates from the Helmholtz model (1879) and the Gouy-Chapman model (1910/13). Finally, both models were combined by Stern (1924).[1] The Stern model describes the interface as a combination of a rigid layer of adsorbed ions on the surface, the so called Stern layer, and a diffuse layer of mobile counterions.
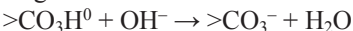
The mechanisms causing a surface charge are complex. According to the Surface Complexation Theory[2] surface charges are formed due to chemisorption and dissociation of water molecules onto unsaturated surface lattice ions. The oxygen atoms of chemisorbed water molecules fill the vacant cationic surface sites. Simultaneously, the anionic surface sites are stabilized by the transfer of dissociated protons from the chemisorbed water molecules. This hydration process leads to a surface composed of hydroxylated cationic sites ($>KatOH^0$) and protonated anionic sites ($>AnH^0$), where > represents the mineral lattice and Kat or An is the mineral cation or anion respectively.[2] A surface potential ψ_0 is finally formed by protonation ($>KatOH_2^+$) or deprotonation ($>KatO^-$, $>An^-$) of the hydration surface sites.

For oxide minerals like SiO_2, the anionic crystal lattice sites are formed by an oxygen atom of the mineral. Thus the primary hydration surface sites are described as hydroxylated surface cations ($>SiOH_0$). By protonation or deprotonation of the hydroxyl groups surface charges are formed as follows:

Positive surface sites: $>SiOH^0 + H_3O^+ \rightarrow >SiOH_2^+ + H_2O$

Negative surface sites: $>SiOH^0 + OH^- \rightarrow >SiO^- + H_2O$

Hence, the surface charge of oxides in water is controlled by the pH-value of the solution. At high pH-values, as usual in cement-based suspensions, a negative surface potential ψ_0 is formed.

For carbonate minerals like $CaCO_3$, the surface consists of hydroxylated cationic sites ($>CaOH^0$) as well as protonated anionic sites ($>CO_3H^0$). By protonation or deprotonation surface charges are formed, again depending on solution pH.

Positive surface sites: $>CaOH^0 + H_3O^+ \rightarrow >CaOH_2^+ + H_2O$

Negative surface sites: $>CaOH^0 + OH^- \rightarrow >CaO^- + H_2O$

$>CO_3H^0 + OH^- \rightarrow >CO_3^- + H_2O$

In addition, the charge of a $CaCO_3$-particle is determined by the adsorption of calcium ions (Ca^{2+}), hydrogen carbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}). These ions

originate from carbonic acid (H_2CO_3) as well as marginal dissolved amounts of calcium carbonate (14 mg/l at 20°C).

Calcium ions: ($CaCO_{3(s)}$ + H_2O $\rightleftarrows$ Ca^{2+} + HCO_3^- + OH^-)

>CO_3-Ca^+, >CaO-Ca^+, >Ca-HCO_3^0

Carbonate ions: (CO_2 + $3H_2O$ $\rightleftarrows$ H_2CO_3 + $2H_2O$ $\rightleftarrows$ HCO_3^- + H_3O^+ + H_2O $\rightleftarrows$ CO_3^{2-} + $2H_3O^+$)

>Ca-HCO_3^0, >Ca-CO_3^-

The solubility of these ion species is controlled by the *pH*-value of the solution. Mainly hydrogen carbonate ions as well as calcium ion are existent in neutral *pH*-range. Providing a sufficient calcium concentration, $CaCO_3$–particles dispersed in water in contact with atmospheric air therefore can have a positive Stern potential. With increasing *pH*-value, the number of dissolved carbonate ions increases. Due to adsorption of the divalent carbonate ions onto cationic surface sites, an increasingly number of negative charges are formed in the stern layer (>Ca-CO_3^-). Simultaneously, the concentration of dissolved calcium ions is decreasing, resulting in a reduction of positive sites like >CO_3-Ca^+ or >CaO-Ca^+. Furthermore, negative surface charges are formed by deprotonation of the hydroxylated calcium sites or carbonate sites of the surface (>CaO^-, >CO_3^-). Thus, the Stern potential of calcium carbonate in alkaline milieu becomes progressively negative.

The role of ion adsorption in cement-based suspension

The pore solution of cement-based suspensions is typically characterized by a high pH > 12 as well as a high ionic strength > 100 mmol/l. A considerable difference compared to the mechanism described before is the high concentration of dissolved ions in pore solution. Furthermore, besides dissolved ions from the crystal lattice of the particle surface, there are additional ion species, originated from readily soluble cement components. During the first minutes after water addition alkali sulfates (Na_2SO_4, K_2SO_4), free lime (CaO) and parts of the setting regulator ($CaSO_4$•xH_2O) are dissolved. Besides *pH*-controlling hydroxide anions, the pore solution contains further anions like sulfate and chloride as well as cations like calcium, potassium and sodium. Further Ca^{2+}-ions and OH^--ions results from the hydrolysis of tricalcium aluminate and tricalcium silicate.

These ions affect the charge of the dispersed particle significantly by adsorbing to the stern layer. In this context, the adsorption of divalent calcium cations and sulfate anions are of particular importance for the formation of the Stern potential. Surface charge equalization increases with increasing adsorption of ions to the Stern layer. Furthermore, in case of the adsorption of divalent ions a charge reversal is possible.[1] For calcium carbonate suspensions, it could be experimentally confirmed that the effect of calcium ion concentration is of more importance than the effect of *pH*-value.[3] Similarly, a positive charge reversal of an initially negative surface charge due to adsorption of cations was verified in experiment.[4,5]

Zeta Potential

While the surface potential ψ_0 in a cement-based suspension is - owing to ion adsorption - experimentally not accessible, the determination of the zeta potential ψ_Z allows the conclusions to the Stern potential ψ_S. The zeta potential ψ_Z of a particle surface is defined as the potential at a shear plane that arises from particle motion. The exact location of this shear plane is a matter of controversial discussions in the literature. While in various

Table 1 – Characteristics of powder materials

	ρ [g/cm³]	A_s [m²/cm³]		ρ [lb/yd³]	ρ [oz/in³]	A_s [ft²/in³]
Cement (C(a))	3.1	3.3		5225	1.79	582
Cement (C(b))	3.1	3.7		5225	1.79	653
Cement (C(c))	3.1	3.0		5225	1.79	529
Quartz flour (Q)	2.7	3.0		4550	1.56	529
Limestone flour (L)	2.8	4.1		4720	1.62	723

Table 2 – Pore solution composition of suspension L.C(a)

Ion species	Ca^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	OH^-
Concentration [mmol/l]	16.9	27.8	198.9	33.6	88.0	50.9

hypothesizes, the shear plane is within the diffuse layer, investigations done by Lyklema,[6] Smith[7] or Sprycha[8] show that the shear plane is located directly at the interface between the Stern plane and the bulk electrolyte. Thus, the zeta potential can be used as a direct measure of the Stern potential depending on the measurement technique, compare.[9]

According to the manifold of influencing factors, the zeta potential of cement and mineral additions given in the literature vary over a wide range. A detailed overview is available in.[10] In the subsequent investigations, the effect of pore solution on zeta potential and superplasticizer adsorption is discussed in detail.

MATERIALS AND METHODS
Mixture proportions

Three Portland cements (C(a) - C(c)) as well as quartz flour (Q) and ground limestone (L) as mineral additions were used in the investigations. The density of the materials was determined by helium pycnometry and the surface area by nitrogen adsorption, Table 1. The mixes were prepared with a commercial polycarboxylate ether based superplasticizer (SP) with 35% solids in aqueous solution and a number average molecular weight of 69.000 g/mol.

Three kinds of pastes were prepared for the investigations.

L, Q, C(a) using 100 l/m³ (0.1 yd³/yd³) of water and 100 l/m³ (0.1 yd³/yd³) of ground limestone (L), quartz flour (Q) or cement (C)

L*, Q* using 100 l/m³ (0.1 yd³/yd³) of artificial pore solution and 100 l/m³ (0.1 yd³/yd³) of ground limestone (L) or quartz flour (Q)

L.C(a), Q.C(a) using 100 l/m³ (0.1 yd³/yd³) of water, 50 l/m³ (0.05 yd³/yd³) of ground limestone (L) or quartz flour (Q) and 50 l/m³ (0.05 yd³/yd³) of cement (C)

The volumetric water-to-powder ratio V_w/V_p of all pastes was 1.0. The superplasticizer dosage was kept constant at 2.9 mg per cm³ of solids ($1.7 \cdot 10^{-3}$ oz per in³ of solids). The composition of the artificial pore solution was equivalent to the pore solution of paste containing 100 l/m³ (0.1 yd³/yd³) of water, 50 l/m³ (0.05 yd³/yd³) of cement C(a) and 50 l/m³ (0.05 yd³/yd³) of ground limestone (L), Table 2.

Zeta Potential

The zeta potential was determined using electro-acoustic spectroscopy (*Quantachrome Dispersion Technology, Electroacoustic Spectrometer, DT 1200*) 15 min after water addition. Electro-acoustic spectroscopy allows measurements of undiluted pastes with w/c-ratios in a range of 0.3 to 0.8.

For the determination of the zeta potential a relative motion between the charged particles and the surrounding fluid is necessary. As soon as the particle or the surrounding fluid is moving, a part of the diffuse layer is slipping off. The higher the velocity, the larger is the part of the diffuse layer that is slipped off. As a result, the particle appears no longer electrically neutral. The electrical potential at the shear plane characterizes the zeta potential.

For the electroacoustic zeta potential measurement, a high frequency acoustic wave ($\approx$ 1 MHz) induces an oscillating motion of particles and ions. Due to the lower inertia, there is a larger movement of the ions in the double layer. This generates dipoles, creating a macroscopic detectable electrical field. Due to the high ion concentration of the pore solution of cement-based suspensions the measured electroacoustic signal *TVI* (total vibration current) contains a signal contribution from the colloidal particles *CVI* (colloid vibration current) and a signal contribution from the ionic background *IVI* (ion vibration current). Therefore, for the determination of the *CVI*, two measurements have to be performed: a) a separate measurement of the extracted pore solution for the determination of the *IVI* and b) a measurement of the suspension for the determination of the *TVI*.

De-ionized water was used for the preparation of suspensions of cement and mineral additions. Water and solids were manually mixed for 3 min. 15 min after water addition pore solution was extracted from the pastes by means of a vacuum pump. Subsequently the *IVI* of the pore solution (15 ml / 0.5 fl oz) was determined. The determination of the *TVI* of a separately prepared suspension (500 ml / 16.7 fl oz) was again carried out 15 min after water addition. To prevent particle sedimentation the suspension was gently stirred during the measurement.

Ion concentration of pore solution and Superplasticizer Adsorption

In addition, 500 ml (16.7 fl oz) of suspensions were prepared to determine *pH*-value and ion concentration of pore solution as well as superplasticizer adsorption. Pore solution was extracted from the pastes 15 min after water addition by means of a cylindrical pressure device, see.[1] The pH-value was determined by potentiostatic titration. Furthermore, the concentration of anions and cations was determined using ion chromatography and inductively coupled plasma optical emission spectrometry (ICP-OES) respectively.

The total organic carbon (TOC) content of the pore solution and the superplasticizer solution were determined by high-temperature oxidation of the organic ingredients. The amount of adsorbed superplasticizer was calculated as the difference between the TOC of the added superplasticizer solution and the pore solution of the mortar.

RESULTS AND DISCUSSION

Zeta potential of quartz, limestone and cement - Effect of pore solution composition

The zeta potential of mineral additions, cement and mixtures of mineral additions and cement dispersed in water or artificial pore solution is shown in Figure 1. For quartz in
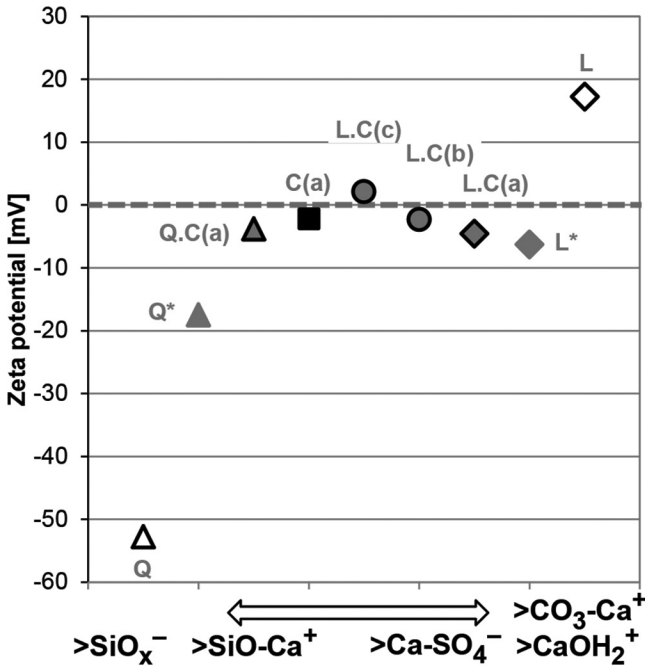
Figure 1 – Zeta potential of quartz, limestone and cement

water (Q) the zeta potential is strongly negative at -52.8 mV. As there are almost no ions dissolved from the SiO_2^-particles, the zeta potential of quartz-water suspensions represents the charge conditions at the surface. The negative characteristic of the zeta potential is caused by the deprotonation of the hydroxyl groups $>SiOH^0 + OH^- \rightarrow >SiO^- + H_2O$.

In contrast, for limestone in water (L) the zeta potential is positive at + 17.3 mV. The positive zeta potential is primarily attributed to the adsorption of monovalent hydrogen carbonate anions as well as divalent calcium cations, which are the predominantly dissolved ion species in pore solution of limestone suspensions at neutral *pH*-range. While the adsorption of monovalent hydrogen carbonate ions induces a neutralization of the cationic calcium sites of the surface ($>Ca-HCO_3^0$), the adsorption of divalent calcium ions causes a positive charge reversal of the anionic carbonate surface sites ($>CO_3-Ca^+$). In total, this results in a larger number of positive charges, i.e. a positive zeta potential.

The zeta potential of the investigated cement (C(a)) and cement-addition mixtures (Q.C(a), L.C(a-c)) varies between -4.6 and +2.1. Thus, the absolute value of the zeta potential of the cement-based suspensions is significantly lower than for quartz or limestone dispersed in water, Figure 1. The main reason for the decrease is the high concentration of ions in the pore solution of cement-based suspensions. Immediately after water addition, ions are dissolved from the readily soluble compounds of the cement. The adsorption of counterions from the solution to the Stern plane causes a charge equalization, which is reflected in a significantly reduction of the absolute zeta potential value.
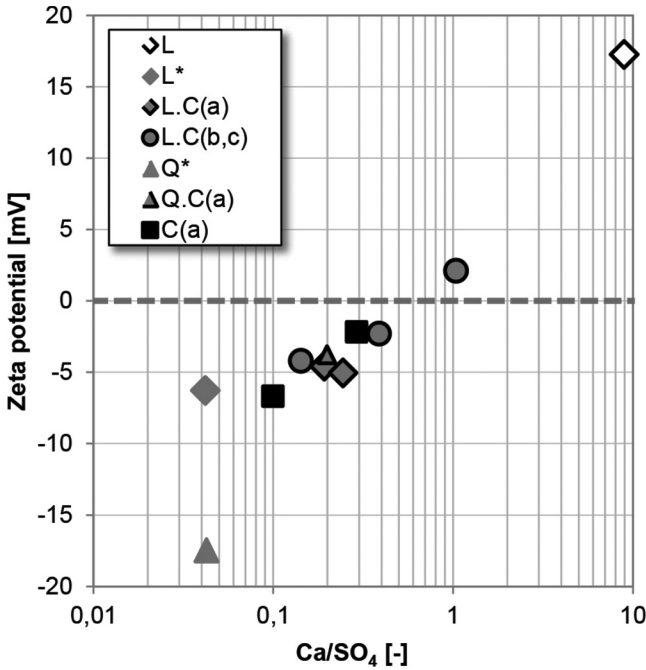
Figure 2 – Effect of Ca/SO₄-ratio on zeta potential of cement and mineral additions

To illustrate the mechanism of counter ion adsorption, the mineral additions were dispersed in an artificial pore solution. The composition of the artificial pore solution is equivalent to the pore solution of the limestone-cement suspension L.C(a), Table 2. It was apparent that the absolute value of zeta potential of quartz and limestone dispersed in the artificial pore solution (Q* and L*) significantly decreases to -17.5 mV and -6.3 mV, respectively, Figure 1. Analogous to the cement-based suspensions, the ions dissolved in the artificial pore solution adsorb to the Stern layer of quartz or limestone, resulting in a charge equalization or even in a charge reversal, like in the case of limestone. The charge reversal of the limestone surface is attributed to two mechanisms: a) With increasing *pH*-value (increasing OH⁻-concentration) the number of negative surface sites increases (>CaO⁻, >CO₃⁻) and b) the divalent sulfate anions (SO₄²⁻), which are dissolved in high concentration in the artificial pore solution, adsorb onto the remaining cationic surface sites. As a result, the zeta potential of the limestone particles in artificial pore solution is similar to the zeta potential of cement and cement-addition mixtures.

In the case of quartz flour, again the high *pH* of the artificial pore solution causes an increase of negative surface sites (SiO⁻). Additionally, due to the adsorption of the divalent calcium ions, dissolved in the artificial pore solution as well, the number of negative charges decreases, resulting in a substantial decrease of the zeta potential absolute value. However, owing to the low solubility of calcium in water, the number of calcium ions dissolved in the artificial pore solution is limited. By contrast, in a real cement-based

suspension, calcium ions can be dissolved constantly, causing a further reduction of the zeta potential, compare Q.C(a).

According to the previous results and discussions, the ion concentration of the pore solution affects the zeta potential significantly. In principle all ion species in pore solution are able to adsorb to the Stern layer. However, the adsorption capacity is controlled by sign of charge, charge density (valence and ion size) and the size of the ionic hydration shell. Various investigations of ion adsorption onto mineral surfaces demonstrate that the adsorption capacity increases with increasing valence of the ions. Thus, with regard to ions dissolved in cement-based suspensions, divalent calcium cations as well as divalent sulfate anions can be classified as potential determining ions.

For this reason the Ca/SO_4-ratio was used to describe the effect of ion concentration on zeta potential quantitatively. The zeta potential of the investigated mineral additions, cements and addition-cement mixtures depending on the Ca/SO_4-ratio of the pore solution is shown in Figure 2. It is apparent that the zeta potential increases with increasing Ca/SO_4-ratio. A Ca/SO_4-ratio of about 0.4 to 0.6 characterizes the point of zero charge (*pzc*).

Another important conclusion can be derived from the interrelation between Ca/SO_4-ratio and zeta potential ψ_z. Interestingly, the mineral additions dispersed in water or artificial pore solution (Q*, L*, L) as well as the cement-based suspensions (C(a), Q.C(a), L.C(a,b,c)) are within the same - almost material non-specific - functional correlation. For this reason, it seems reasonable to assume that all particles dispersed in cement-based suspensions exhibit comparable low Stern potentials. The sign and value of the Stern potential is primarily controlled by the adsorption of inorganic ions and can be described by the Ca/SO_4-ratio.

Superplasticizer adsorption onto quartz, limestone and cement – Effect of zeta potential

From the point of view of thermodynamics, the adsorption of superplasticizer polymers onto a particle surface is associated with a heat release (enthalpy loss) and/or an entropy increase of the total system. An entropy increase results for example from a release of adsorbed ions or water molecules from the surface during polymer adsorption. On the other hand, enthalpic adsorption is caused by attractive electrostatic as well as van der Waals interactions.

Adsorption due to electrostatic forces requires both a charge at the surface and a polymer bearing dissociated ionic groups. Polycarboxylate superplasticizers are polyanions containing carboxylate groups COO^-. The adsorption of the negatively charged carboxylate groups can occur either directly onto cationic surface sites or indirectly onto cations, adsorbed to the Stern layer. In the latter case, owing the high charge density, mainly calcium ions are suitable as adsorption sites for the carboxylate groups. Thus, provided a sufficient high calcium concentration, superplasticizer adsorption is possible even in domains of initial negative surface charge.

The electrostatically caused adsorption of superplasticizer polymers should therefore be directly depending on the charge conditions of the particle surface. For this reason, the effect of zeta potential on the superplasticizer adsorption was investigated. Therefore suspensions of water or artificial pore solution, superplasticizer and quartz flour, limestone flour, cement or mixtures of quartz, limestone and cement were prepared. The superplasti-
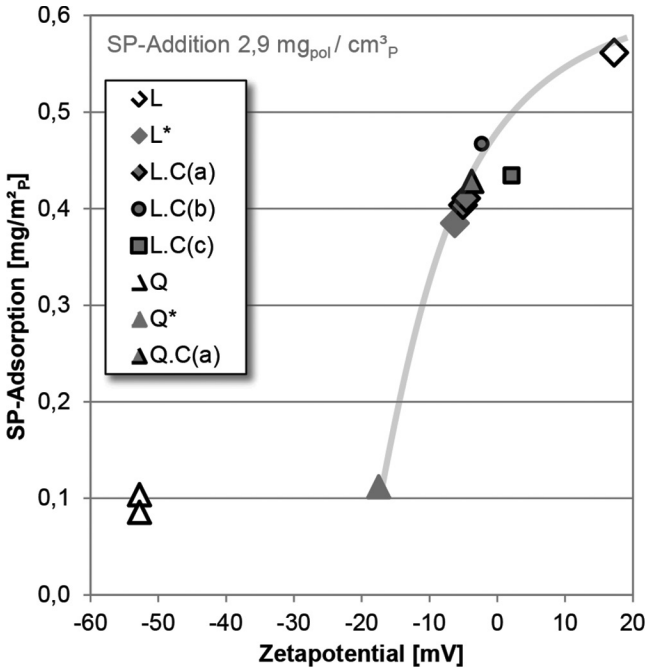
Figure 3 – Effect of zeta potential on superplasticizer adsorption (Note: $1mg/m^2 = 3.3 \cdot 10^{-6} oz/ft^2$)

cizer content of all suspensions was kept constant at 2.9 mg_{pol}/cm^3_P (in relation to the solid content = $1.7 \cdot 10^{-3}$ oz per in^3 of solids). The fraction of adsorbed superplasticizer molecules was determined 15 min after addition of water and superplasticizer. After that time the cement hydration changes from the dissolution period to the induction period, characterized by a slowdown of the reaction kinetics.[10,11] Thus almost equilibrium conditions of superplasticizer adsorption and desorption can be assumed.

The effect of zeta potential on superplasticizer adsorption is shown in Figure 3. It is apparent that for strong negative zeta potentials < 15 mV only minor polymer adsorption of about 0.1 mg_{Pol}/m^2_P occurs (Note: $1mg/m^2 = 3.3 \cdot 10^{-6} oz/ft^2$). At higher zeta potentials between -6.3 and +17.3 mV the superplasticizer adsorption increases by trend with increasing zeta potential from 0.39 to 0.56 mg_{pol}/m^2_P. However, not every influence on superplasticizer adsorption is captured by this trend. In spite of a higher zeta potential at +2.1 mV for the limestone-cement mixture L.C(c) compared to the mixture L.C(b) at -2.3 mV, there is a lower superplasticizer adsorption for the mixture L.C(c). This is mainly attributed to lower hydration kinetics of cement C during the first 15 min after water addition. Thus, measurements using a heat flow calorimeter show a significantly lower maximum heat flow for the suspension L.C(c) at 1.3 mW/g than for the suspension L.C(b) at 8.1 mW/g, compare.[10]
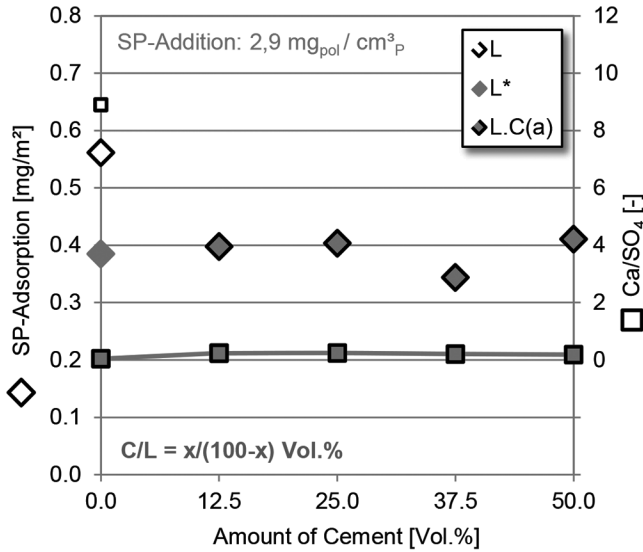
Figure 4 – Effect of cement and limestone content on super-
plasticizer adsorption (Note: $1mg/m^2 = 3.3 \cdot 10^{-6} \ oz/ft^2$)

Superplasticizer adsorption in limestone-cement suspensions – Effect of cement and limestone content

The previous results show clearly that superplasticizer polymers adsorb onto cement as well as onto mineral addition particle surfaces. At this point, the question of selective polymer adsorption arises: In which amount does the polymer adsorb onto the different particle surfaces in suspensions containing both cement and mineral addition particles?

In the case of zeta potential, it was shown that, due to the high concentration of divalent ions in pore solution and adsorption of these ions to the Stern layer, the charge conditions of different materials in a cement-based suspension are equalized. Furthermore it was discussed that superplasticizer polymers adsorb onto calcium ions of the Stern layer. Thus, it seems reasonable to assume that despite different material properties of cement and mineral additions, there is an equalization of the superplasticizer adsorption characteristics, as soon as these materials are present together in a cement-based suspension.

To clarify this question, adsorption measurements of limestone-cement suspensions L.C(a) were carried out at different cement contents (0,0/12,5/25,0/37,5/50,0 Vol.%). Owing to the difference in specific surface of cement (S_v = 3,3 m²/cm³ = 582 ft²/in³) and limestone flour (S_v = 4,1 m²/cm³ = 723 ft²/in³) the total surface area of the solids is decreasing slightly with increasing cement content from 4.1 m²/cm³ to 3.7 m²/cm³ (723 ft²/in³ to 653 ft²/in³). The volumetric water/powder ratio V_w / V_p of the suspensions was kept constant at 1.0. Furthermore, the composition of the pore solution was kept constant at the same level as the pore solution at a cement content of 50 Vol.%. To compensate the decreasing ion concentration at decreasing cement contents, water was substituted by artificial pore solution according to Table 2 from 0% at a cement content of 50 Vol.% to 100% at

a cement content of 0 Vol.%. In all cases, the dosage of superplasticizer was constant at 2.9 mg_{pol}/cm^3_p (mass of polymer m_{pol} in relation to total volume of cement and limestone V_p).

Figure 4 shows the amount of adsorbed superplasticizer polymers in dependence of the cement content. The results indicate that the adsorbed amount of superplasticizer in relation to the specific surface of the solids is almost constant, independent of the cement content. Even for the limestone suspension without cement but artificial pore solution is the amount of adsorbed polymers at the same level as for the suspension containing 50 Vol.% of cement. According to these results, provided a constant composition of the pore solution, superplasticizer adsorbs in the same order onto cement and limestone. Thus, the adsorption characteristics of superplasticizer of the investigated limestone-cement suspensions, is preponderantly controlled by the composition of the pore solution rather than the kind of solids dispersed in the suspension.

CONCLUSIONS

The effect of pore solution composition on zeta potential and superplasticizer adsorption has been investigated experimentally. The investigations were conducted on highly concentrated suspensions, containing quartz flour, limestone flour, cement and combinations of these materials. Furthermore cement-limestone suspensions with different types of cements and a varying ratio of cement to limestone were investigated.

The results show that the zeta potential of cement and mineral additions is significantly determined by the composition of pore solution. It seems reasonable to assume that all particles dispersed in cement-based suspensions exhibit comparable low Stern potentials. The sign and value of the potential is primarily controlled by the adsorption of inorganic ions. Moreover, the zeta potential cement-based suspensions can be characterized by the ratio of calcium to sulfate dissolved in the pore solution.

Furthermore it was shown that the superplasticizer adsorption is affected by zeta potential. At higher more positive zeta potentials the superplasticizer molecules are more likely adsorbed onto the solid surfaces. Moreover, the superplasticizer adsorption in limestone-cement suspensions is predominantly controlled by the composition of pore solution rather than the ratio of cement to limestone flour. If the ion concentration of the pore solution is artificially kept constant the polymer adsorption is almost constant independent of the cement to limestone ratio in the suspension.

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