PSC as well as a decrease in the permeability against water and different types of ions.³⁻⁶ It has also been reported that compared to the non-blended portland cement, dispersants show higher fluidizing properties in PSC.⁷

Polycarboxylate (PCE) based superplasticizers are applied in the construction industry to produce highly flowable concrete possessing a low water-to-cement ratio (w/c). Generally, PCEs are comb-shaped copolymers which consist of a negatively charged backbone comprised of carboxylate groups, and uncharged graft chains, mainly polyethylene glycols. The charged backbone of PCE can adsorb onto the surface of hydrated cement particles in three different possible conformations (train, loop or tail), while the non-adsorbed side chains freely protrude from the cement surface into the pore solution.⁸ Therefore, the anionic charge amount of a PCE polymer presents a main factor guiding its adsorption behavior and thus its dispersing performance. The higher the anionic charge amount of a PCE molecule, the higher its adsorbed amount. The mechanism behind the dispersing effect of a PCE is based on a combination of steric hindrance and electrostatic repulsive forces between the cementitious particles.⁹⁻¹¹

In previous works by the authors, the surface chemistry of slag dispersed in deionized water and synthetic cement pore solution (SCPS) has been studied extensively.^{12,13} The major observation was that in slag suspensions, strong interaction occurs between the surface of slag and the ions present in the cement pore solution. First, at the high pH value of the suspension, the surface of slag becomes negatively charged as a result of deprotonation of silanol groups. This negatively charged surface then adsorbs calcium ions, thus forming a layer of Ca^{2+} on the surface of slag which in turn attracts sulfate ions present in the pore solution, hence forming a second ion layer consisting of sulfate ions. Therefore, when slag is dispersed in SCPS, the apparent surface charge of slag is negative, because of the high sulfate content. Further deprotonation of silanol groups present on slag occurs over time, and more calcium and sulfate ions are adsorbed. These processes alter the zeta potential of slag slurries after a certain time period (~ 3 h) until a stable state of equilibrium is reached.

Furthermore, interaction between slag and PCE superplasticizers was studied as well.¹³ It was found that a competitive adsorption between the polymers and sulfate ions for positively charged sites present on the slag surface occurs. Sufficiently anionic PCE molecules occupy adsorption sites on slag while PCEs of low anionic character cannot compete with $SO_4^{2^2}$ and hence do not adsorb in large amounts on the surface of slag.

The study here continues the previous work from the authors on pure slags and now investigates the interaction between PCEs and different portland slag cements (PSCs). At first, the electrical surface charge of PSC samples dispersed in water was determined using a zeta potential instrument. Next, the concentrations of Ca^{2+} and SO_4^{2-} ions contained in the pore solutions were determined and compared with those occurring in neat cement pore solutions. Furthermore, the physico-chemical interactions between PCE and PSC were studied *via* adsorption and zeta potential measurements. Based on these experimental results, the mechanism behind the different dispersing effect of two chemically different PCE polymers added to PSC pastes comprised of slags from different sources will be discussed.

RESEARCH SIGNIFICANCE

Previous studies on the interaction between slag cements and polycarboxylates have considered slag as an inert component which has no influence on this interaction. There-

Oxide content (wt. %)	CEM I 52.5N	Slag S1	Slag S2	Slag S3			
SiO ₂	23.56	35.9	36.3	38.6			
CaO	67.76	42.8	36.4	38.6			
Al ₂ O ₃	3.58	11.4	11.5	12.4			
MgO	0.53	6.44	11.50	6.40			
TiO ₂	0.24	0.82	0.78	0.82			
K ₂ O	0.73	0.33	0.66	0.53			
Na ₂ O	0.02	0.27	0.34	0.45			
Fe ₂ O ₃	1.29	0.45	0.26	0.46			
Mn ₃ O ₄	0.04	0.28	0.22	0.26			
SO ₃	2.61	2.40	2.57	1.55			
SrO	0.20	0.09	0.09	0.09			
ZrO ₂	0.00	0.03	0.03	0.03			
BaO	0.05	0.13	0.19	0.00			
P ₂ O ₅	0.18	0.00	0.00	0.00			
Spec. surface area (<i>Blaine</i>) [cm ² /g (ft ² /oz)]	3400 (102)	4000 (120)	3480 (104.4)	4080 (122.4)			
d ₅₀ value [µm]*	11.52	9.53	10.19	9.25			
Density [g/cm ³ (oz/in ³)]	3.16 (1.83)	2.86 (1.65)	2.91 (1.68)	2.91 (1.68)			
*conversion factor: 1 μ m = 3.937 × 10 ⁻⁶ in							

 Table 1 – Oxide compositions and properties of cement and GGBFS

 samples studied

fore, the impact of different types of slag on this interaction was ignored. Various slags can result in considerable differences in workability when incorporated into cement. This effect is due to the disparity in the surface chemistry of different slag samples which results from their different ability to adsorb calcium ions. The anionic charge amount of a PCE polymer and the thickness of the calcium layer present the key factors for the dispersing effect of PCE in PSC.

EXPERIMENTAL INVESTIGATION

Materials

A commercial portland cement sample (CEM I 52.5 N) was used as base cement to prepare a total of six blends whereby 30 or 70 wt.% of the cement were replaced with either slag S1, slag S2 or slag S3. The three ground granulated blast furnace slag (GGBFS) samples were from different sources in Germany. **Table 1** lists the oxide composition (XRF), specific surface area (*Blaine* instrument) and particle size distribution (d_{50} value; laser granulometer) of the neat cement sample and the three slag samples.

Two PCE superplasticizers (denominated as 45PC1.5 and 45PC6) were synthesized and used in the tests. Free aqueous radical copolymerization was employed to synthesize the copolymers using sodium peroxodisulfate as initiator and methallyl sulfonic acid as chain transfer agent. A detailed description of the synthesis process has been published in previous work.¹⁴ These PCEs are based on a copolymer of methacrylic acid and ω -methoxy poly(ethylene glycol) methacrylate ester (so-called MPEG type PCE). Their general chemical structure is displayed in **Fig. 1**. In the designations 45PC1.5 and 45PC6, "45" refers to



Fig. 1 – Chemical structure of the synthesized PCE samples

Table 2 – Characteristic	properties	of the s	ynthesized	PCE polyme	ers
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	Molar ratio	Side			Polydispersity	Hydrodynamic	
	methacrylic	chain			index	radius R _{h(avg)}	
Copolymer	acid:ester	$n_{\rm EO}$	M _W (g/mol)*	M _n (g/mol)*	(M_W/M_n)	(nm)**	
45PC1.5	1.5	45	196,300	51,900	3.8	8.7	
45PC6	6.0	45	222,300	52,340	4.2	10.4	
*conversion factor: 1 g/mol = 0.035 oz/mol; **conversion factor: 1 nm = 3.937×10^{-8} in							

the number of ethylene oxide units ($n_{\rm EO}$) present in the side chain, whereas "1.5" and "6" refer to the molar ratio between methacrylic acid and the MPEG methacrylate ester. The characteristic properties of the PCE polymers are presented in **Table 2**.

Methods

Rheological properties – Cement pastes were prepared and their flow properties were determined using a '*mini slump*' test according to DIN EN 1015. The w/c ratios of the cement pastes were selected such as to produce a flow value (spread) of 18 ± 0.5 cm (7.1 ± 0.2 in) in the absence of PCE polymer (**Table 3**). In measurements incorporating PCE, the polymer was added to the mixing water, and its dosage was adjusted to produce a flow value of 26 ± 0.5 cm (10.2 ± 0.2 in). The test was carried out as follows: In a porcelain cup, over 1 min 300 g (10.58 oz) of PSC were added to the specific amount of mixing water as given in **Table 3**, then left to soak for 1 min which was followed by manual stirring with a spoon for 2 min. Immediately after the end of stirring, the slurry was poured into a *Vicat* cone [height 40 mm (1.57 in), top diameter 70 mm (2.76 in), bottom diameter 80 mm (3.15 in)] placed on a glass plate and filled to the brim. The cone was removed vertically and the resulting spread of the paste (= diameter of slurry cake) was taken as flow value of the slurry. The diameter was measured twice perpendicularly, and the two values were aver-

Sample	CEM I 52.5 N	30% S1	30% S2	30% S3	70% S1	70% S2	70% S3	
w/c ratio	0.505	0.57	0.55	0.52	0.60	0.60	0.55	
Cal. w/c*	0.505	0.81	0.79	0.74	2.00	2.00	1.83	
* calculated as a ratio between the cement part present in PSC and water								

 Table 3 – Water to cement ratios determined via "mini slump test" to achieve

 18±0.5 cm spread

aged to give the slump spread value. Each test was repeated three times, and the average was reported as slump flow value (the margin of error was \pm 3%). Generally, the amount of water introduced with the PCE solution was subtracted from the amount of mixing water to maintain comparable w/c ratios. The dosage of PCEs is expressed on a dry mass basis and is stated in % by weight of cement (% bwoc).

Ion concentrations in pore solutions – From these cement pastes, 10 mL (0.338 fl oz) were taken in 20 min intervals over a total period of 180 min, and then were centrifuged for 10 min (8,500 rpm) and diluted with 0.1N HCl to avoid precipitation of calcium carbonate. The ion concentrations were obtained from an atomic absorption spectroscope. Additionally, sulfate concentrations were quantified by utilizing ion chromatography.

Electrokinetic properties of blended cements – Electrokinetic properties were measured using Electroacoustic Spectrometer. The highly solids loaded suspensions used in this work require an electroacoustic instrument to obtain zeta potential values which are representative of the conditions occurring in actual concrete.¹⁵ Zeta potential values were measured during the dropwise addition of aqueous solutions of the copolymers (concentration 10 wt. %, pH=7) to the cement pastes, and the zeta potentials of the slurries were recorded as a function of PCE concentration.

PCE adsorption on PSC – Polymer adsorption was determined according to the depletion method. Different dosages of PCE copolymer were added to the individual cement pastes (w/c ratios as listed in **Table 3**), stirred for 2 min, centrifuged for 10 min (8,500 rpm) and then diluted with 0.1 N HCl to remove inorganic carbonates and to prevent dissolution of carbon dioxide in the alkaline solution. A High TOC II apparatus was employed to determine the total organic carbon content in the supernatants. The adsorbed amount of PCE was calculated by subtracting the concentration of PCE found in the supernatant from the initial PCE concentration used prior to contact with PSC.

EXPERIMENTAL RESULTS AND DISCUSSION Zeta potential of PSC pastes

In previous publications where the authors studied neat slag suspensions, it was found that in alkaline solution the surface of slag is generally negatively charged as a result of deprotonation of the silanol groups present on the surface.^{12,13} This charged surface attracts counter ions from the pore solution which then adsorb and form an electrical double layer on the surface of slag. The thickness of this layer mainly depends on two parameters: the type of slag (*i.e.* the number of silanol groups) and the ionic strength of the pore solution. Therefore, different slag samples exhibit different zeta potential values. Over time, the zeta potential values change due to partial hydration of the slag whereby some ions are released into the pore solution. These results explain the fundamental behavior of slag in cement pore solution and were taken as basis for the following experiments with the slag cement samples.



Fig. 2 – Time-dependent zeta potential of CEM I 52.5 N and PSC paste (w/c ratios as shown in Table 3)

For all 30% PSC samples (*i.e.* cement containing 30% slag), the initial zeta potential values were negative (~ - 4.5 mV), as is shown in **Fig. 2**, while the 70% PSC samples consistently exhibited positive initial zeta potential values (*e.g.* +3.5, +1.6 and +1.5 mV for 70% S1, 70% S2 and 70% S3, respectively). When considering the initial zeta potential value for the neat cement slurry (- 6 mV), it seems that the addition of slag to cement changes the zeta potential to less negative or even positive values, depending on the amount of slag added. Furthermore, the PSC samples containing the same amount of slag (30% or 70%) still exhibit slightly different initial zeta potential values, signifying that variations in the chemical composition of the slags cause different behaviors. For the slag samples studied here, the zeta potential values of the resulting PSC blends follow the trend S1 > S2 ~ S3 which infers a higher positive charge to the blend incorporating S1 than S2 or S3. These results are in agreement with previous results on pure slag.^{12,13} Over time, the surface charges of the PSCs increased to more positive values and stabilized after ~ 3 h (**Fig. 2**). The results indicate that the zeta potential values of PSCs are strongly related to the amount and type of slag added.

Ion Concentrations in PSC Pore Solution

The time - dependent evolution of Ca^{2+} and SO_4^{2-} concentrations present in the pore solutions of all PSC slurries was measured. These measurements were performed to determine the impact of each slag on the ionic strength of the pore solutions. For comparison, neat portland cement slurries prepared at the same w/c ratios as the PSCs (see **Table 3**) were also analyzed. Their w/c ratios were calculated assuming that slag constitutes an inert component in the PSC samples.

When compared with the neat portland cement slurries, lower concentrations of Ca^{2+} and SO_4^{2-} ions in the pore solutions were observed for all PSC samples. For the 30% PSC samples, the slags seem to consume significant amounts of Ca^{2+} (**Fig. 3** –top). This trend was even stronger for PSCs possessing high slag contents (70% PSC) (**Fig. 3** – bottom). In all PSC pastes the changes in Ca^{2+} concentrations over time followed almost the same

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Fig. 3 – Time-dependent evolution of Ca^{2+} concentrations in CEM I 52.5 N and PSC pore solutions (conversion factor: l g/L = 0.001 oz/fl oz)

trend found for neat portland cement pastes. This effect is due to the continuous release of Ca^{2+} ions from the cement at the same rate as the slag consumes Ca^{2+} .

On the other hand, the 30% PSCs consume considerable amounts of sulfate ions from the pore solution, compared to the related neat portland cement samples (**Fig. 4** – top). The sulfate ions released from the slag samples were not significant because of the substantially higher concentration of sulfate present in cement. Contrary to this, the sulfate concentrations occurring in the pore solutions of 70% PSCs are lower or comparable to those from the neat cement (**Fig. 4** – bottom). According to these data, slag S2 releases the highest amount of SO₄²⁻ ions into the pore solution while slag S3 produces a medium and slag S1 the lowest concentration of sulfate ions in the pore solution. The same trend was observed before for the pure slag samples.¹³ Note that the concentrations of SO₄²⁻ ions in the pore solutions of the 30% PSCs. This signifies that in the 30% PSC samples, the negative sulfate layer adsorbed onto the positive sites of the slag surface is thicker. It explains why the 30% PSCs exhibit negative zeta potential values while the 70% PSCs show positive zeta potentials (see **Fig. 2**).

In general, the presence of slag in blended cements significantly changes the ionic strength of the pore solution, compared to the neat cement. Furthermore, the pore solution compositions of PSC samples containing the same amount of different slags can differ considerably as a result of variations in the chemical composition of the slags. This finding confirms that in such composite cements, slag is not an inert constituent.



Fig. 4 – Time-dependent evolution of SO_4^{2-} concentrations in CEM I 52.5 N and PSC pore solutions (conversion factor: l g/L = 0.001 oz/fl oz)

Dispersing effectiveness of PCEs in PSC

Similar to what has been reported before from another research group,⁷ PCEs show higher fluidizing effect in PSC compared to the non-blended portland cement. Here, for the 70% PSC pastes, enhanced flow properties were recorded compared to the 30% PSCs. However, the dosage of PCEs required to achieve the same paste spread of PSC samples incorporating the same amount of different slags varied significantly.

Generally, in CEM I 52.5 N as well as PSC pastes significantly lower dosages of PCE polymer 45PC6 (0.012 - 0.06% bwos) were required to achieve the same paste spread than with 45PC1.5 (0.09 - 0.55% bwos), as is shown in **Fig. 5**. The reason behind this result is the high anionic charge amount of polymer 45PC6 [~ 1200 µeq/g (34286 µeq/oz)]. Obviously, PCE polymer 45PC1.5 which is a polycarboxylate typically used in ready-mix concrete to provide extended slump life presents a less effective dispersant. To clarify the mechanism behind this effect, the adsorption of both polymers on the PSCs was compared.

Adsorption of PCE on PSC

For the polymers 45PC1.5 and 45PC6, adsorption isotherms in PSC pastes were produced using TOC measurement. In general, for both PCEs the adsorbed amounts increase with dosage until they reach a saturation point (*Langmuir* type isotherm; see **Fig. 6**). The saturated adsorbed amounts are the lowest for the cement blended with slag S3 and the highest for cements which contain slag S1.



Fig. 5 – Dosages of polycarboxylate superplasticizers required to obtain a target slump flow of 26 ± 0.5 cm (10.2 ± 0.2 in) for PSC pastes (w/c ratios as shown in Table 3)

Comparable adsorbed amounts of PCE 45PC1.5 were found for all 30% PSCs (see **Fig. 6** – top left). The same trend has been observed before for the pure slags dispersed in SCPS.¹³ Apparently, adsorption of 45PC1.5 is driven by a gain in entropy and not by electrostatic attractive forces, as in 30% blended slag systems its adsorption is independent of the different positive surface charges of the slag.¹⁶ Furthermore, the low adsorbed amount explains why 45PC1.5 is not an effective dispersant, as was shown in **Fig. 5**. In general, for the 70% PSCs the adsorbed amounts of 45PC6 and 45PC1.5 follow the order: Slag S1 > S2 > S3. This trend correlates well with the zeta potential results presented in **Fig. 2**: PSCs containing slag S1 exhibit the most positive surface charge while those blended with slag S3 show the lowest.

The adsorbed amounts of PCE polymer 45PC6 on the blended cements were consistently lower than those on the neat cement (**Fig. 6**). This explains why sample CEM I 52.5 N required a higher dosage of this polymer to achieve the 26 cm (10.2 in) spread compared to the same cement blended with slag (**Fig. 5**). The reason behind this effect is that cement particles adsorb higher amounts of this polymer [3 mg/g (21 gr/lb)] than pure slag [0.4 – 1.8 mg/g (2.8 – 12.6 gr/lb)].^{12,13} Apparently, PCE polymer 45PC6 exhibits a higher affinity for cement than for slag.

Influence of PCE on Zeta potential of PSC slurry

The evolution of zeta potential during dropwise addition of the PCE solutions to the PSC pastes is shown in **Fig. 7**. When PCE is added to the PSC slurries, a shift in zeta potential values towards the isoelectric point (IEP) occurs which confirms that adsorption of PCE does indeed take place. The reason behind such shift to the IEP is the steric effect of the polyethylene oxide (PEO) side chains contained in the PCEs. They move the shear plane of the zeta potential further away from the particle surface. At such distance, the zeta potential approaches a value close to zero.¹⁷



Fig. 6 – Adsorption isotherms for PCE polymer 45PC1.5 (top) and 45PC6 (bottom) on PSC (w/c ratios as shown in Table 3) (conversion factor: 1 mg/g = 7.015 gr/lb)



Fig. 7 – *Effect of dosage of PCE polymers* 45PC1.5 (*left*) *and* 45PC6 (*right*) *on zeta potential of PSC pastes* (*w/c ratios as shown in Table 3*)

CONCLUSIONS

When blended with cement, various slags are known to produce different results with respect to workability of the concrete or mortar. This is due to the disparity in the surface chemistry of the slag samples which results from their dissimilar ability to sequester calcium and sulfate ions from the pore solution. Partial replacement of cement by slag alters the ionic strength of the pore solution, and this change varies depending on the composition of the slag. In PSC pastes, at first significant amounts of calcium ions are

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Fig. 8 – Schematic illustration of the electrochemical double layer existing in the equilibrium state on the surface of the slag samples in PSC suspension, and the consequences for the adsorption behavior of PCE polymers on these slags

released from the cement into the pore solution which are partially taken up by the negatively charged slag surface. The amount of calcium consumed by a slag sample depends on the absolute value of its negative surface charge which can vary. Slags having thick layers of Ca^{2+} ions on their surface adsorb higher quantities of PCE and thus require increased dosages of superplasticizers to achieve the same fluidity as slags possessing a thin Ca^{2+} ion layer. This mechanism is schematically summarized in **Fig. 8**.

This study demonstrates that in blended cements, strong interaction between polycarboxylate superplasticizers and the surfaces of both slag and portland cement occurs. Apparently, slag is not inert towards PCE. In portland slag cements, normally lower polycarboxylate dosages are required compared to the pure cement. Furthermore, when using slags from different sources, the dosages of superplasticizer required to establish comparable