

# On Understanding the Dispersion Behaviors of Cement Treated with Dispersants

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The dispersion and rheological performance of cement treated with different admixtures can be better understood by studying changes in the adsorption behaviors of the admixtures and changes in the ionic concentrations of cement pore water solutions. The subjects of this study are two poly(ethylene glycol) ethers (PEGs) and four polycarboxylate ethers (PCEs). Prior literature suggested that non-reactive dead-burnt magnesium oxide (MgO) could be a model surface for cement. In this investigation, the impact of using simulated pore solutions with a dead-burnt MgO was studied. Flow behaviors using two PCEs on three different cements and MgO suspensions made with simulated pore solutions were shown to give similar trends, thus confirming the validity of using MgO for the adsorption studies. The flow behavior of PCE was noted to begin low, gradually increase and then decrease again as a function of total alkali concentrations. Adsorption results showed no adsorption from the two PEGs, but significant amount with the PCEs. A PCE with shorter teeth and lower teeth densities was shown to adsorb more readily than that with longer teeth and higher teeth densities.

## 1. Introduction

Polymers have been used as dispersants to stabilize particulate slurries in many industries, such as in ceramics and mineral processing and in the formulation of ink and paints. Poly(ethylene oxide) (PEO), for example, has been used as dispersants for latex [1] and flocculants for clays [2]. It has been established that the adsorption of PEO on oxide surfaces is sensitive to the nature of surface hydroxyls present. In highly acidic oxide surfaces, such as MoO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> and SiO<sub>2</sub>, PEOs were found to strongly adsorb. In weaker acid oxides, such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO, no adsorption of PEO was observed [3]. PEOs are, therefore, not expected to adsorb on cement surfaces with weakly acidic surface hydroxyl groups. However, comb-type polycarboxylate ethers (PCE) have worked well as dispersants for cements. These PCEs are made of polymers with a backbone such as a carbon backbone to which are attached both pendant carboxylic acid groups and pendant polyalkylene oxide groups such as ethylene oxide (EO) groups, or propylene oxide (PO) groups, or a combination of EO and PO groups.

The mechanism of how PCEs and other dispersants work in cement has been studied for many years. It has been recognized that the interaction between naphthalene sulfonate formaldehyde condensate (NSFC) and the calcium aluminate phases is crucial in controlling the rheology of cement. It has been found that cements containing low amount of soluble alkali have tendencies to adsorb a high amount of NSFC by the aluminate phase. As a result, the effective dosage for dispersion is reduced, leading to a flow decrease. In cements with high amount of water-soluble alkalis, NSFC adsorption tendency is less. As a result, more NSFC is available in solution for dispersion and a better flow is noted [4-7]. Recently further investigations have been conducted on PCEs. Yamada *et al.* showed that competitive adsorption of alkali sulfates decreases adsorption of PCE on cement paste, thereby resulting in a flow decrease [8]. Magarotto *et al.* demonstrated that the flow of cement pastes treated with PCE is reduced by the addition of alkali sulfate. This decrease was, however, not observed with cement pastes treated with NSFC [9]. In this study, the flow behaviors of different PEGs and PCEs under different alkali conditions were investigated.

Because cement is a heterogeneous mixture where its surface area grows continuously as cement hydrates, mechanistic study poses a challenge. Flatt *et al.* proposed the use of a dead-burnt MgO as a model surface because the surface area of this powder does not increase with time and because its isoelectric point (IEP) is close to the average of IEPs of cements [10]. Another objective of this study is to determine if the suggested dead-burnt MgO is a good model system for understanding dispersion and adsorption mechanisms of admixture on cement.

## **2. Materials and Methods**

### **2.1 Materials**

#### **2.1.1 Cements**

Three different commercial cements were chosen for this study. Their total water-soluble alkali contents are 0.06, 0.20 and 0.78 as Na<sub>2</sub>O eq. The elemental analyses and other chemical information on the cements are given in Table 1.

#### **2.1.2 MgO**

A sample of MagChem P-98 pulverized dead burnt magnesium oxide was obtained from Martin Marietta Magnesia. As reported in datasheet provided by the supplier, this sample contains 98% magnesium oxide, 0.7% silicon oxide, 0.95% calcium oxide, 0.15% iron oxide and 0.19% aluminum oxide. The MagChem P-98 powder was sieved through a #50 sieve to obtain a powder with a particle size finer than 300µm.

The particle-size distributions (PSD) of the sieved and hydrated powders were measured using laser diffraction (Horiba, LA-910). The reactivity of the MgO powder was evaluated by mixing 1 g of MgO powder with 0.5 mL of water. After given times, the powder was centrifuged and the entire paste was placed in a 250 mL container. Isopropyl alcohol was then added into the container to fill the container. The container was placed in a shaker for 6 minutes before being introduced into in the Horiba LA-910 light scattering apparatus for analysis. Figure 1 shows no increase in specific surface areas and a slight change in PSD between the un-hydrated and hydrated samples. No significant difference was noted among the hydrated samples. Surface areas varied from 290 to 310 m<sup>2</sup>/kg.

Figure 2 shows the x-ray diffraction pattern of a hydrated MgO taken after 30 minutes of hydration. The diffraction showed no presence of magnesium hydroxide (brucite), but only the appearance of magnesium oxide (periklase) and calcium carbonate (calcite).

Table I: Chemical Analysis of Cements

	Cement I	Cement II	Cement III
SiO <sub>2</sub> (%)	20.50	20.08	18.87
Al <sub>2</sub> O <sub>3</sub> (%)	4.66	5.11	6.15
Fe <sub>2</sub> O <sub>3</sub> (%)	2.14	3.39	2.09
CaO (%)	64.19	63.99	61.85
MgO (%)	3.06	1.61	2.61
SO <sub>3</sub> (%)	3.04	3.36	4.05
Na <sub>2</sub> O (%)	0.12	0.26	0.30
K <sub>2</sub> O (%)	0.09	0.32	1.23
TiO <sub>2</sub> (%)	0.31	0.23	0.25
P <sub>2</sub> O <sub>5</sub> (%)	0.10	0.18	0.29
Mn <sub>2</sub> O <sub>3</sub> (%)	0.15	0.03	0.06
SrO (%)	0.05	0.08	0.26
<b>Compounds (C150):</b>			
C <sub>3</sub> S (%)	62	59	53
C <sub>2</sub> S (%)	12	13	14
C <sub>3</sub> A (%)	9	8	13
C <sub>4</sub> AF (%)	7	10	6
Total alkali Na <sub>2</sub> O eq. (%)	0.18	0.47	1.11
Water sol. Na <sub>2</sub> O (%)	0.02	0.07	0.15
Water sol. K <sub>2</sub> O (%)	0.06	0.19	0.94
Total water sol. Na <sub>2</sub> O eq (%)	0.06	0.20	0.78
Total water sol. CaO eq (%)	0.08	0.06	0.05
Free Lime (%)	0.48	1.20	0.45

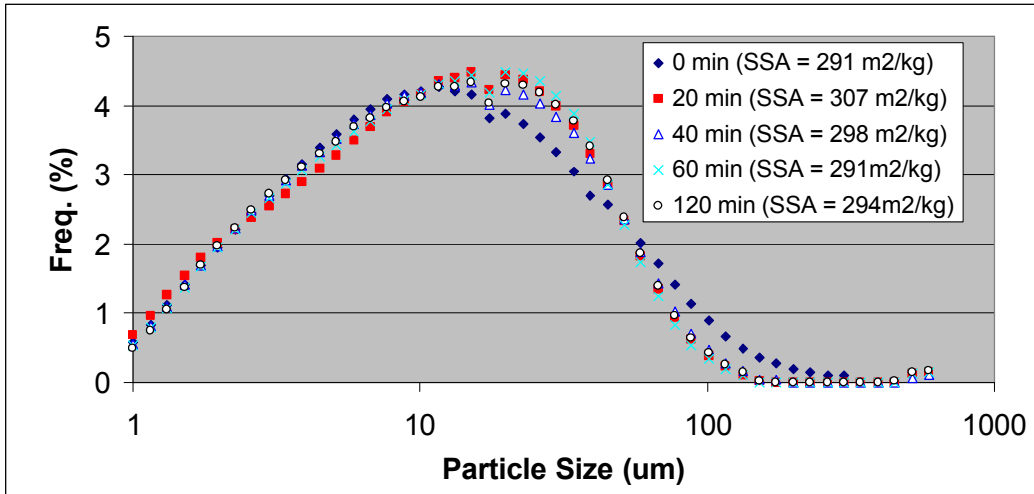


Fig. 1: Particle size distribution of MgO taken after 0, 20, 40, 60 and 120 minutes of hydration

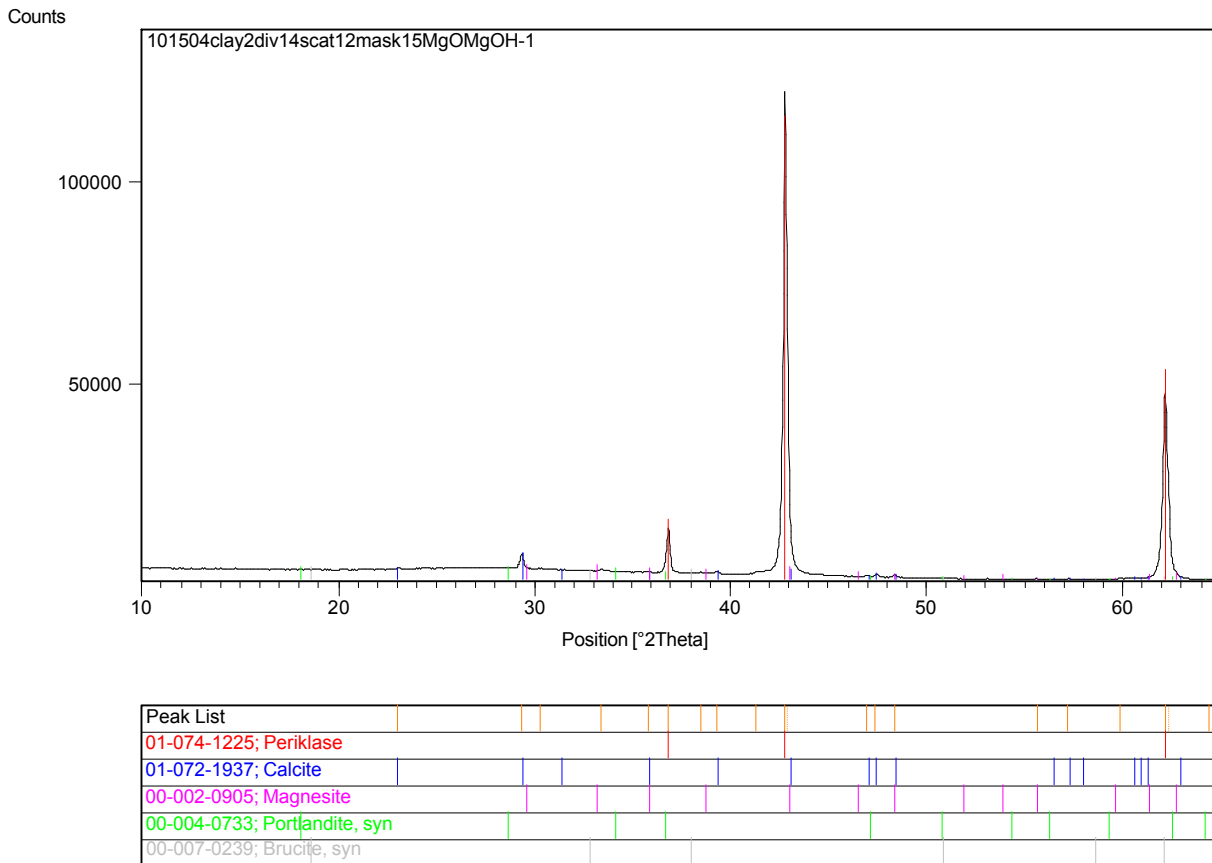


Fig. 2: X-ray diffraction pattern of MgO hydrated for 30 minutes

### 2.1.3 Electrolyte

In order to simulate the cement pore water, different ratios of NaOH, KOH and Ca(OH)<sub>2</sub> were dissolved in de-ionized water. The amount of calcium hydroxide was kept constant at 0.005 M while the ratios and concentration of Na/K varied according to Table II. The hydroxides were stirred in a flask at 200 rpm for two hours. The electrolyte solutions were then suction filtered through a 45µm paper. The pH was then measured and recorded.

Table II: Concentrations of alkali in cement paste (w/c=0.45)

	Cement I	Cement II	Cement III
Water Sol. Na (M)	0.014	0.050	0.108
Water Sol. K (M)	0.028	0.090	0.444
K/Na	2.0	1.8	4.1

### 2.1.4 Chemicals

A sample of PEG dimethyl ether (Mn~500) and PEG methyl ether (Mn~550) were obtained from Aldrich. Four PCEs used in the present study have a general structure shown in Figure 3. PCE 1 and PCE 2 were synthesized in our laboratory using a conventional fed-batch radical copolymerization process (Figure 4). PCE 3 and PCE 4 are commercially available concrete admixture polymer. The samples characteristics are summarized in Table III.

Table III: Characterization of PCE polymers

POLYMER	COOH/PEG molar ratio	PEG pendant average molecular weight (a.m.u)	Backbone polymethacrylic acid average molecular weight
PCE 1	3.0**	2,000***	4,500*
PCE 2	5.0**	2,000***	4,600*
PCE 3	5.5*	1,500*	5,500*
PCE 4	3.4*	3,600*	5,600*

\*: Numbers based on GPC and NMR measurements

\*\*: Based on the ratio of the monomers used

\*\*\*: Based on the PEG methacrylate monomer's nominal number

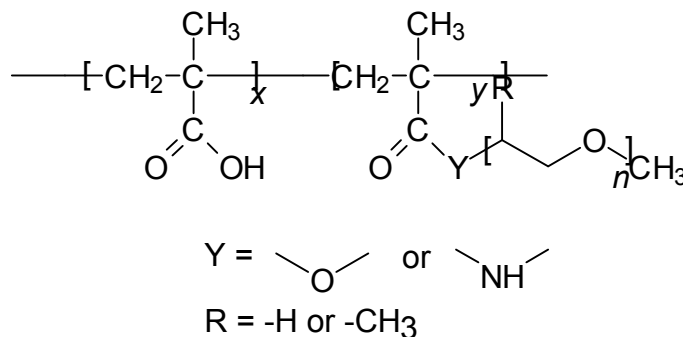


Fig. 3: General structures of PCEs

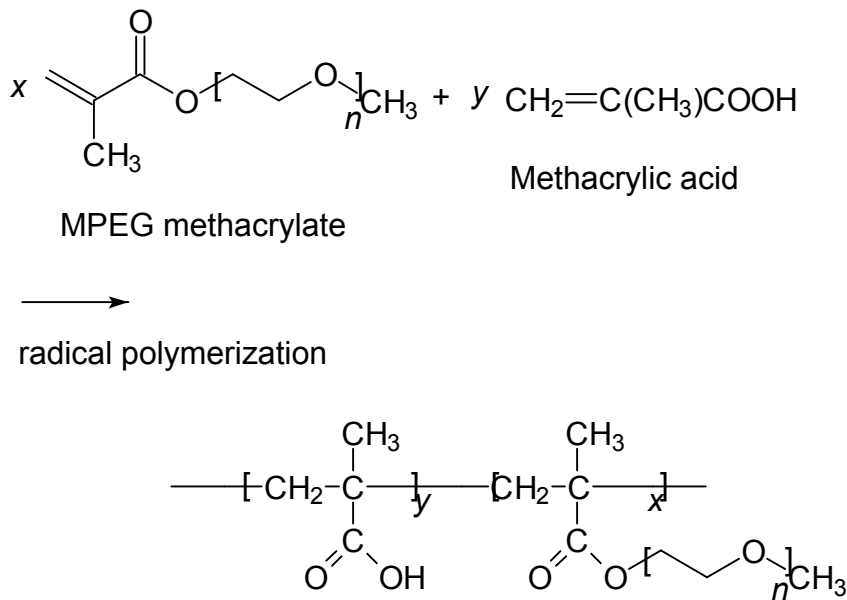


Fig. 4: Synthesis scheme of PCE polymers

## 2.2 Methods

### 2.2.1 Preparation of Cement Paste and MgO Suspension

A total of 100 g of cement or MgO powder was used for all cases. Admixtures were added with the water or electrolyte solutions. For cement pastes, a w/c ratio of 0.45 and PCE dosage of 0.12 s/c% were used. For MgO suspensions, a water to MgO ratio of 0.25 and PCE dosage of 0.05 s/c% were used.

Paste mixing was done using a two-minute mixing cycle, where the powder and water or electrolyte solution were added and mixed in a 250mL plastic cup. The mixture was mixed using a Eurostar Power control viscosity mixer at a speed of 400 rpm. The paste mixture was first mixed for thirty seconds and then stopped for fifteen seconds so that the paste stuck on the side of the cup can be scrapped down with a metal spatula. Finally the paste was allowed to mix for an additional 75 seconds.

### 2.2.2 Flow Measurements

At the end of the mixing regime, the paste was poured into a mini-slump flow cone [11] and was pulled up slowly. The cone measures 57 mm in height, 38 mm for base diameter and 19 mm for top diameter. Two

diameters of the paste patty were measured at 90 degrees from each other and their average was reported. All results reported represent an average of at least two mixes.

### 2.2.3 Adsorption Measurements

Samples used for adsorption studies in this paper were made with water without addition of electrolytes. Flow measurements were not taken. Instead, the MgO suspensions were divided in 25-mL proportions into 45-mL centrifuge vials. At 0.5, 1, 4 and 24 hours, the vials were centrifuged for 5 minutes at 2000 rpm. The supernatant was slowly decanted into individual snap vials and loaded into the Elementar Vario Max instrument for total organic carbon analysis. Standards were made up each day to calibrate the system. All results reported represent an average of two mixes.

## 3. Results and Discussion

### 3.1 Adsorption of PEGs on MgO

The adsorption isotherms of PEG methyl ether and PEG dimethyl ether taken at 0.5, 1, 4 and 24 hours are shown in Figure 4. Results showed that the two PEGs are not adsorbing on the MgO surfaces, even after 24 hours. These results confirm previous findings from literature [3].

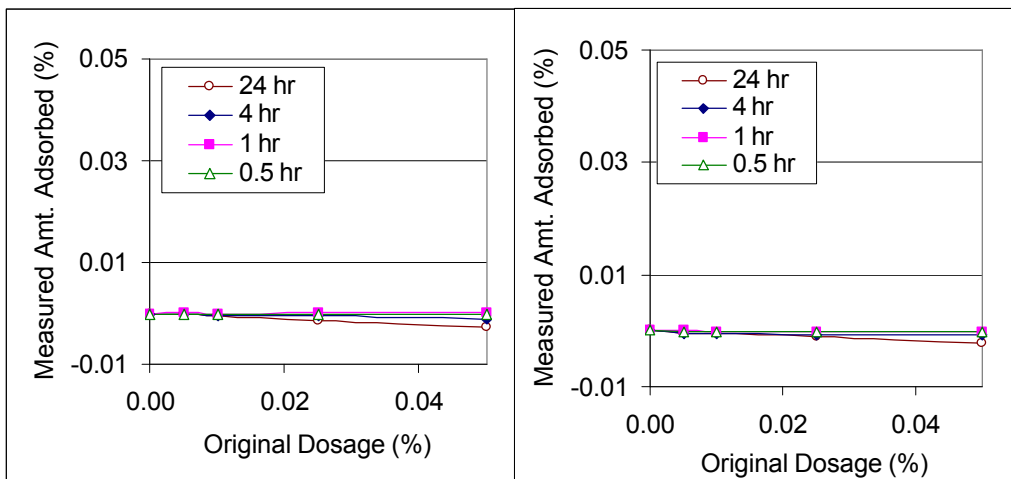


Fig. 4: Adsorption Isotherm on MgO treated with PEG-methyl ether (left) and PEG-dimethyl ether (right)

### 3.2 Adsorption Isotherms of PCEs on MgO

The adsorption isotherms of PCE 3 and PCE 4 taken at 0.5, 1, 4 and 24 hours are shown in Figure 5. The backbone MW of both polymers were similar. PCE 3 has shorter teeth (MW = 1,500) but a higher acid/teeth ratio of 5.5. PCE 4 has longer teeth (MW=3,600) with an acid/teeth ratio of 3.4. Results showed differences in adsorption from the different configurations, with more adsorption from the shorter teeth and higher acid/teeth polymer (PCE 3).

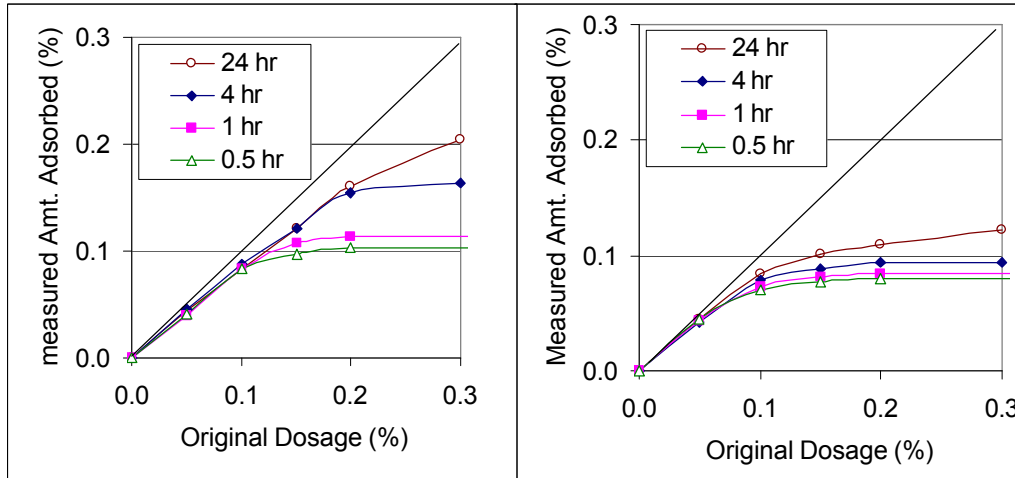


Fig. 5: Adsorption Isotherm on MgO treated with PCE 3 (left) and PCE 4 (right)

### 3.3 Flow behaviors of PCEs under different alkali conditions

The flow behaviors of cement pastes and MgO suspensions made with PCE1 and PCE2 are shown in Figure 6. The required amount of PCE and water needed to give similar flow are different for the two systems. In the case of the cement pastes, a w/c of 0.45 and a PCE dosage of 0.12% was used. In the case of the MgO suspensions, a water to MgO ratio of 0.25 and a PCE dosage of 0.05% was used. The origin of the difference is not clearly understood, but may be attributed to the difference in hydration areas created between the two powders. Pastes and suspensions made without PCEs began at a flow value of around 65-75mm.



Cements with different soluble alkali contents and MgO suspensions made with different electrolyte solutions were used to determine if the flow behavior of PCEs behave similarly. Figure 6 shows the results of flow as a function of alkali levels. All results are averaged from two preparations. Overall, it is noted that the flow behavior of the cement pastes are similar to the MgO electrolyte suspensions. The only exception is the 0.25 M total alkali point for PCE 2. The reason for this difference is not apparent. The results also demonstrates that the flow behavior is greatly influenced by the water soluble alkali content. Thus, care to adjust for the correct alkali levels must be taken when designing experiments using model powder systems.

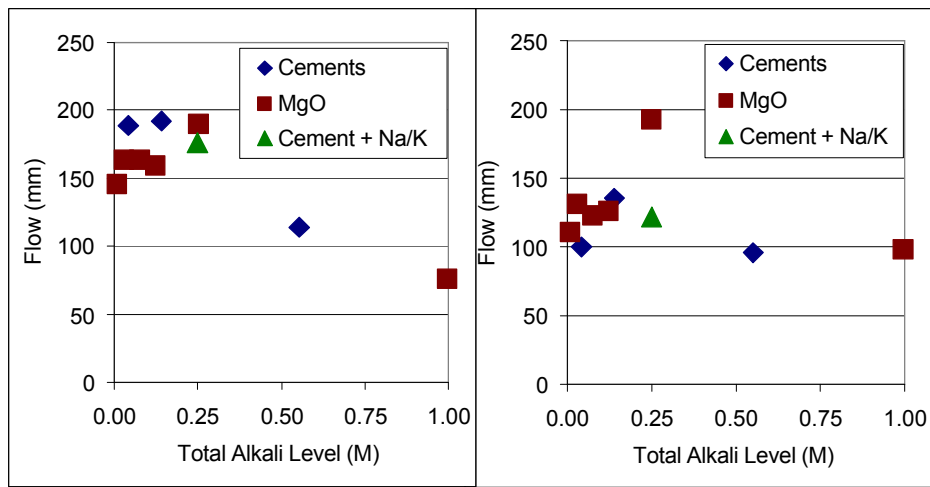


Fig. 6: Impact of Soluble Alkali Levels on Flow of Cement and MgO treated with PCE 1 (left) and PCE 2 (right)

### 3.4 Impact of Na and K levels on Flow of MgO treated with PCE

The impact of Na and K levels on the flow of MgO suspensions is shown in Figure 7. An optimal flow is observed at a total alkali concentration of around 0.125 M or a pH of ~13.0, which is close to the IEP of MgO [12]. The initial increase in flow could be attributed to the favorable adsorption of PCE around the IEP. The subsequent decrease may be a result of the collapse of polymer under a high ionic strength environment. Confirmation experiments are underway and will be reported in later publications.

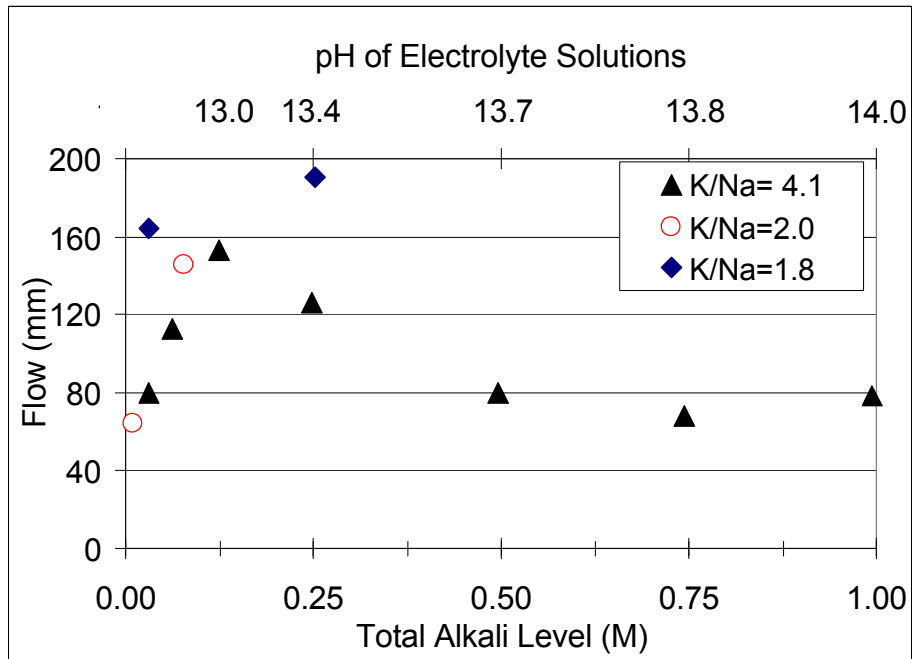


Fig. 7: Impact of total Na and K levels on flow of MgO treated with PCE 1

#### 4. Conclusions

- Based on cement paste and MgO electrolyte suspensions, dead-burnt MgO was confirmed to be a reasonable model surface for cement.
- The flow behavior of a PCE on MgO was noted to begin low, gradually increase and then decrease again as a function of total alkali levels.
- Adsorption results showed no adsorption from the two PEGs, but significant amount with the PCEs, confirming previous studies in literature [3].
- Above adsorption result of PEGs in combination with PCEs results confirmed that PCE is adsorbed on the MgO surface *via* the backbone, which is consistent with a well-accepted PCE adsorption mode on cement surface.
- A PCE with shorter teeth and lower teeth densities was shown to adsorb more readily than that with longer teeth and higher teeth densities.

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