Investigating the Electrokinetic Behavior of Cement-Based and Alternative Cementitious Materials

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CNF REU Project and Primary Source(s) of Research Funding: 2022 Cornell NanoScale Science & Technology Facility Research Experiences for Undergraduates (CNF REU) Program via the National Science Foundation under Grant No. NNCI-2025233
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Primary CNF Tools Used: Malvern Zetasizer, Scanning Electron Microscope

Abstract:
Portland cement production is a major contributor of carbon dioxide emissions. The need to incorporate large amounts of Supplementary Cementitious Materials (SCMs) to reduce the carbon footprint arises. Various SCMs were dispersed in diluted pore solutions that mimic native pore solutions of cement pastes characterized by their high pH and ionic nature. Chemical additives such as sodium glucoheptonate retarders and naphthalene sulfonate-based superplasticizers were employed to track their efficacy with the SCMs. Electrokinetic properties such as zeta potential was of primary interest in this study to ensure cement pastes have adequate rheological properties. Factors that influenced zeta potential such as electrical conductivity and pH were also measured in optimized particle solid concentrations. Stable zeta potentials have an absolute value measurement of 30 mV or above. Without the use of admixtures, it was found that majority of the particles were unstable and tended to aggregate in the pore solutions, with zeta potential values ranging from -3.13 mV to 11.5 mV. Silica flour displayed the most stable behavior in the diluted pore solution concentration, with a zeta potential around -22 mV. The use of chemical additives led to increases in the zeta potential values as compared to those of the neat particles, demonstrating that the additives are compatible with some of the particles and effective in improving the stability of the solution. Furthermore, scanning electron microscope imaging was used to view the shape and size of the cementitious particles as these factors also affect the rheology of the cementitious paste.

Summary of Research:
This research aimed at characterizing the electrokinetic behavior of Supplementary Cementitious Materials (SCMs), such as silica flour (SFL), class F fly ash (FAF), class C fly ash (FAC), metakaolin (MK) and ground granulated blast-furnace slag (SLAG) in DI water and pore solutions. Additionally, class H cement (CEM-H) was also analyzed as a baseline. To study the electrokinetic behavior, zeta potential values were tracked using a zetasizer, Malvern Instrument. 800 µL of these neat (in the absence of chemical additives) pore solutions was injected into a reusable cuvette, which was then placed into the zetasizer. The zetasizer measured the sample’s electrophoretic mobility at six measurements per sample and used the Smoluchowski approach to calculate the zeta potential values.

Figure 1: (a) Zeta potential values of various SCM particles with increasing solid concentration in deionized water, (b) Zeta potential vs. conductivity for one concentration.
We found that SFL had most stable behavior in DI water, with zeta potential values above 30 mV for all concentrations. FAC experienced aggregation, which was attributed to the pH and conductivity of the solution. After graphing zeta potential vs. conductivity, it was found that as conductivity increased, the zeta potential decreased, and solutions became less stable. These trends are summarized in Figure 1.

Then we used a synthesized pore solution made up of 0.6 g/L calcium sulfate dehydrate, 5.2 g/L sodium hydroxide, 17.9 g/L potassium hydroxide, and 2.4 g/L calcium hydroxide with a pH of 13.5 to test our SCMs and class H cement particles. Pore solution concentration used was 25 mL pore solution / 375 mL DI water. We mixed 100 mL of this diluted solvent with 100 mg particles through a 15-minute sonication.

Opposite was true when using pore solution as a solvent, except for SFL. CEM-H interactions with the retarding additive SGH in the pore solution indicated that this additive improves the stability of the solution to a certain point, after which increasing the SGH content results in aggregation. CEM-H in the presence of the superplasticizer additive showed that stability of the solution increased up to a saturation point, after which there is no significant effect.

To observe aggregation of particles, along with measuring zeta potential we will also measure the particle size of each of the SCMs. This will be achieved by adding an additional sieving and filtering process to limit particle sizes to 5 µm. We will also aim at conducting adsorption tests of polymer-based additives onto the SCM particles using an ultraviolet-visible (UV-vis) light device. In future experiments, there will be further optimization of pH and conductivity versus zeta potential.

Conclusions and Future Steps:
Zeta potential values of SCMs such as MK and FAF were similar to those found in literature [1-3], validating the procedure of this study. Majority of SCMs exhibited stable behavior when using deionized water as a solvent, apart from FAC.

<table>
<thead>
<tr>
<th>Particle</th>
<th>Zeta Potential (mV)</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class H Cement (CEMH)</td>
<td>4.5</td>
<td>12.4</td>
<td>7.5</td>
</tr>
<tr>
<td>Silica Flour (SFL)</td>
<td>-22.0</td>
<td>12.2</td>
<td>7.2</td>
</tr>
<tr>
<td>Class F Fly Ash (FAF)</td>
<td>-3.1</td>
<td>12.1</td>
<td>6.9</td>
</tr>
<tr>
<td>Metakaolin (MK)</td>
<td>1.4</td>
<td>12.1</td>
<td>7.6</td>
</tr>
<tr>
<td>Class C Fly Ash (FAC)</td>
<td>2.2</td>
<td>12.1</td>
<td>6.8</td>
</tr>
<tr>
<td>Slag</td>
<td>12.0</td>
<td>12.2</td>
<td>8.0</td>
</tr>
</tbody>
</table>

Table 1: Electrokinetic behavior of various SCMs and class H cement in pore solution.

As shown in Table 1, it was found that majority of the particles became unstable and tended to aggregate in the pore solutions, with zeta potential values ranging from –3.13 mV to 11.5 mV. SFL displayed the most stable behavior in the diluted pore solution concentration, with a zeta potential around –22 mV. The use of chemical additives such as sodium glucoheptonate (SGH) and naphthalene-based superplasticizers led to increases in the zeta potential values of the CEM-H as compared to those without any additives, demonstrating that the additives are compatible and effective in improving the stability of the solution. However, these increases were bounded by certain concentrations of additives. This is illustrated in Figures 2 and 3.

References:

Figure 2, left: Zeta potential values of class H cement in pore solution with an increasing content of the retarder sodium glucoheptonate. Figure 3, right: Zeta potential values of class H cement in pore solution with an increasing content of the naphthalene-based superplasticizer.