STUDY ON INFLUENCE OF LIMESTONE POWDER ON THE FRESH AND HARDENED PROPERTIES OF METAKAOLIN BASED GEOPOLYMER

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PRESENTATION OUTLINE

- Introduction
- Materials & formulations
- Results & discussion
- Conclusions
INTRODUCTION
Construction in China

- Complex environmental condition

Northwest
- Dry, Cold, Strong winds
- Shrinkage, Cracking

North
- Low temperature
- Freeze and thaw

Offshore
- Corrosion
- Freeze and thaw

West
- Salt, Temperature difference
- Sulfate attack, wet-cry cycle

South
- High temperature
- Typhoon
- Strong Corrosion

Durability Problems
Durability problems & Environment pressure

Degradation of concrete

Environment pollution

- How to prolong service life and reduce energy consumption at the same time?
**Geopolymer Materials**

Advantages:
- Easy to produce
- Cheap & eco-friendly
- High strength & low permeability

Disadvantages:
- High water demand
- Workability concerns

Geopolymer seems to be a promising material to partially replace cement-based material.
Limestone has been proven to be capable of improving flowability and has insignificant negative effect on mechanical properties of concrete in OPC system.

Few papers were found on the performance of metakaolin-limestone-alkali system.

The aim of this study is to find out if limestone could be used to improve the performance of metakaolin-based geopolymer.

A deep understanding of the role of limestone as a secondary source material is also expected.
Materials & Formulations
Raw materials

Chemical compositions of metakaolin and limestone

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>SO$_3$</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metakaolin/%</td>
<td>60.85</td>
<td>34.51</td>
<td>0.95</td>
<td>0.5</td>
<td>0.39</td>
<td>0.19</td>
<td>0.34</td>
<td>1.82</td>
<td>0.88</td>
</tr>
<tr>
<td>Limestone/%</td>
<td>0.52</td>
<td>0.83</td>
<td>1.07</td>
<td>53.44</td>
<td>1.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>42.9</td>
</tr>
</tbody>
</table>

- The **metakaolin and limestone** used were all commercially available.
- The **alkali-activated solution** was made from **potassium silicate** (modulus: 2.0; wt%: 32.5%) and **potassium hydroxide** (c: 12.5 mol/L).
Test specimens

Mix compositions of pastes

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Metakaolin/g</th>
<th>Potassium silicate solution/g</th>
<th>Potassium hydroxide solution/g</th>
<th>Limestone (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS0</td>
<td>1000</td>
<td>765</td>
<td>612</td>
<td>0</td>
</tr>
<tr>
<td>LS10</td>
<td>1000</td>
<td>765</td>
<td>612</td>
<td>10</td>
</tr>
<tr>
<td>LS15</td>
<td>1000</td>
<td>765</td>
<td>612</td>
<td>15</td>
</tr>
<tr>
<td>LS20</td>
<td>1000</td>
<td>765</td>
<td>612</td>
<td>20</td>
</tr>
<tr>
<td>LS30</td>
<td>1000</td>
<td>765</td>
<td>612</td>
<td>30</td>
</tr>
</tbody>
</table>

- Metakaolin and limestone were first dry-mixed, and then mixed with the alkaline solution in a paste mixer for 3-5 min.
- After demolding, specimens (40 × 40 × 160 mm) were stored in water at 20±1°C.
Testing procedure

- **Rheological properties**
  - Mini-slump & viscosity test

- **Mechanical properties**
  - Compressive & flexural strength

- **Microstructural characterization**
  - SEM
  - XRD
  - FT-IR
Results & Discussion
Rheological properties

![Diagram showing rheological properties](image)

- Packing density
- Repulsion between the granules

Krieger and Dougherty\[1\]

\[
\frac{\eta}{\eta_{\text{medium}}} = (1 - \frac{\varphi}{\phi_m})^{-[\eta]\phi_m}
\]

Arrhenius equation

\[
\frac{\eta(T)}{\eta(T_0)} = \exp\left[\frac{E_\alpha}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]
\]

Mechanical properties

- Limestone: Adsorb the alkaline solution & Dilute the paste.
- No significant negative influence of limestone on 28d strength.
Microtest - SEM & XRD

<table>
<thead>
<tr>
<th>Element</th>
<th>Surface of limestone</th>
<th>Matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>76.37</td>
<td>58.73</td>
</tr>
<tr>
<td>Na</td>
<td>3.46</td>
<td>3.58</td>
</tr>
<tr>
<td>Al</td>
<td>2.17</td>
<td>12.9</td>
</tr>
<tr>
<td>Si</td>
<td>2.56</td>
<td>15.17</td>
</tr>
<tr>
<td>Au</td>
<td>0.26</td>
<td>0.26</td>
</tr>
<tr>
<td>K</td>
<td>0.86</td>
<td>6.65</td>
</tr>
<tr>
<td>Ca</td>
<td>14.31</td>
<td>2.72</td>
</tr>
</tbody>
</table>

Major phases:

- Q: Quartz
- K: Kaolinite
- C: Calcite
FT-IR results

The dissolution of Al and Si ions from metakaolin was enhanced in the presence of limestone.

<table>
<thead>
<tr>
<th>Absorption bands</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1650 cm(^{-1})</td>
<td>hydration water</td>
</tr>
<tr>
<td>900-1200 cm(^{-1})</td>
<td>Si-O stretching vibrations</td>
</tr>
<tr>
<td>400-500 cm(^{-1})</td>
<td>Si-O bending vibrations</td>
</tr>
<tr>
<td>650-750 cm(^{-1})</td>
<td>Al-O-Si vibrations</td>
</tr>
<tr>
<td>1350-1500 cm(^{-1})</td>
<td>C-O asymmetric stretching vibrations</td>
</tr>
<tr>
<td>850-900 cm(^{-1})</td>
<td>C-H out-of-plane bending vibrations</td>
</tr>
</tbody>
</table>
Conclusions & Acknowledgement
Conclusions

- Limestone is capable of improving the flowability of metakaolin-based geopolymer with a certain amount, and no significant negative influence on mechanical properties was found after 28d.

- Limestone is a reactive material in alkali-activated metakaolin-based geopolymer system, but with only a limited extent of reaction. The presence of limestone enhanced the release of Si and Al from metakaolin.
Thank you for your attention!

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