INVESTIGATION OF TERNARY MIXES MADE OF CLINKER, LIMESTONE AND SLAG OR METAKAOLIN
IMPORTANCE OF REACTIVE ALUMINA & SILICA

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Calcined clays are very interesting SCM, especially in combination with limestone (LC3)

Clays are often in competition with other SCMs

How compare high quality metakaolin and good quality slag in models systems?

Do synergistic effects play a role with other SCMs and how far can limestone content be optimized with each SCM?
Systematic investigation of strength synergies
OPC-limestone – SCM

- Tested binder compositions

<table>
<thead>
<tr>
<th>OPC (Normo 4, CH)</th>
<th>MK</th>
<th>Slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amorph. Content</td>
<td>&gt;95%</td>
<td>&gt;97%</td>
</tr>
<tr>
<td>BET [m2/g]</td>
<td>&gt;13</td>
<td>&lt;1</td>
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<tr>
<td>XRF</td>
<td>52% Al₂O₃; 45% SiO₂</td>
<td>10% Al₂O₃; 38% SiO₂; 40% CaO</td>
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</tbody>
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- Modified EN tests (w/c=0.5) strength of mortars

- Paste XRD investigation (w/c=0.5)
  Fixed OPC 65%, with & without limestone

Use of Design of Experiment approach to describe strength synergies in ternary blends (total MIC content 50%)
Systematic investigation of strength synergies
OPC-limestone – SCM

• Tested binder compositions

Synergies in ternary blends (total MIC content 50%)

limestone
Fine ground limestone
>90% pure CaCO₃

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Workability issue: maintaining slump requires high dosages of superplasticizer with the use of metakaolin

- Combined addition of limestone can improve flow by 20%

![Graph showing the relationship between metakaolin content and flow improvement with limestone addition. The graph includes bars and a line graph demonstrating the increase in flow with increasing metakaolin content.]
For comparison, flow properties almost unaffected for replacement of slag by limestone

Both slag & limestone (besides higher Blaine) slightly improves flow when substituting for OPC.
With metakaolin:
Very strong synergies at 7days

- Metakaolin-limestone systems show very good synergy potential, very large at 7d
- At 2 days, strength mostly governed by clinker content
With slags
Compressive strength, 2 & 7d

- At 2d: minor effect of limestone, decrease only for limestone content above 20%
- At 7d, for 50% OPC, strength improved for low limestone substitution and can be maintained up to 26% limestone
With metakaolin
Strength synergies very slowly decrease at later ages

Strength synergy are maintained at later ages with calcined clays
Slags-limestone diagram at later ages: synergetic effect of combined addition faster decrease

- At 28d, strength almost maintained for 20% replacement of slag by limestone at CF 50%
- At 91d, limestone purely acts as a filler and dilutes strength
Phase assemblage by XRD, metakaolin system

OPC constant at 65%

- With only MK, monosulfate and strätlingite formation
- With LS, ettringite & hemicarbonate forming at considerable amounts, especially at 7 days. Amorphous reduced
Phase assemblage by XRD, slag system

- With only slag, monosulfate observed
- With LS, formation of ettringite & monocarbonate. Amorphous reduced
Conclusions

• Metakaolin strongly affects workability and require SP, but limestone combined addition improves the picture.

• Until 2 days, strength mostly relates to fineness, metakaolin > slag. Physical / nucleation contribution dominate

• At 7 days, important strength synergies observed for both slag & mk, stronger for metakaolin (high fineness, high dissolution rate).
  Strength synergies correlate well with appearance of carboaluminates & ettringite.
  At 7d, Aluminates contribution dominates
Conclusions

• At 28 days & later
Strength of slags systems tend to catch up. Consequence of (slower) slag dissolution
  ▶ Slag $\text{Al}_2\text{O}_3$ content lower but $\text{SiO}_2$ & $\text{CaO}$ higher.
    ⇒ Limestone synergy less important, total AFm+AFt content lower than with metakaolin, but amorphous & C-A-S-H higher
  ▶ At 28d, the global SCM composition to be taken into account & silicate contribution increasingly important.

• For those both SCM, combined limestone addition is an option
  ▶ Metakaolin allow higher limestone content than slag while maintaining strength
  ▶ Durability the limitation parameter?