PREFACE

This book collects abstracts of the papers submitted to the 14th International Congress on the Chemistry of Cement (ICCC 2015), which was held in Beijing, China between October 13~16, 2015, and organized by China Building Materials Academy and the Chinese Ceramic Society. Since the First International Congress on the Chemistry of Cement started in London in 1918, it has become the most influential event for information exchange and promoting global cooperation on cement and concrete science and technology.

This congress attracted papers and attendee from 43 countries. It covers: (1) clinker chemistry, (2) hydration of portland cement, (3) supplementary cementing materials, (4) chemical admixtures and rheology, (5) durability and service life prediction, (6) alternative binders and (7) standard and codes. A large number papers discuss the considerable progress towards understanding chemistry, microstructure, and durability of cement and concrete. The challenge still remains of finding new ways to reduce CO₂ emission during cement and concrete production, to extend the service life of concrete. Considering cement and concrete as viable construction materials must be retained and sustained, considerable efforts still should focus on the environmental challenges that the industry and society now face. The main objective of this congress was to provide a platform for interactions between researchers, producers and engineers all over the world to produce cross-fertilization ideas aimed at developing rational multiple-disciplinary ideas.

Caijun Shi and Yan Yao
Editors
PAN Wenhao, NIU Wanyang, CHEN Yanwen, XUE Shouli

Robustness of Lignosulfonate- versus Polycarboxylate ether based chemical admixtures in concrete

Mirko Gruber, Philip Chuah, Srikanth Kalahasti

Influence of LiAl-layered double hydroxides with 3D micro-nano structures on the properties of calcium sulphoaluminate cement clinker

Haiyan Li, Xuemao Guan, Shuqiong Luo, Xiaoxing Liu, Jianwu Zhang

C-S-H - PCE Nanocomposites for Enhancement of Early Strength of Portland Cement

Kanchanason, V. and Plank, J.

Role of different superplasticizers on hydrated lime pastes and mortars


Interaction between VAE-copolymer dispersion and cementitious systems

Daniel Jansen*, Friedlinde Goetz-Neuhoeffer¹, Jürgen Neubauer¹, U. Dietrich², W.-D. Hergeth²

Research on Adaptability Between Aliphatic-Polycarboxylic Compound Water Reducer and Cement

Sijia Zhang, Yaqing Jiang

A new method to investigate the impact of PCE on the first minutes of cement hydration

Dalas F., Pourchet S., Nonat A., Mosquet M., Rinaldi D., Sabio S.

Interaction between VAE latex stabilized with PVOH and Portland cement

Yu Jin, Dietmar Stephan

Influence of nanosilica on the microstructure of the cement matrix

Pawel Sikora, Elzbieta Horszczaruk, Krzysztof Cendrowski, Ewa Mijowska

Suppression of hydrogen gas evolution from aluminun cement-solidified MSWI fly ash

Tsuneki Ichikawa , Kazuo Yamada, Kazuko Haga, Masahiro Osako

Effect of Heat Curing History on Silicate Structures and Hydration of Cement and Silicafume in Ultra High Strength Concrete

M. SATO, Y. UMEMURA, K. KOIZUMI

Effect of Molecular Structure of Polycarboxylate Superplasticizer on the Hydration of Portland Cement

Liu JP, Yu C, Dong SQ, Ran QP

New accelerating admixture based on metal silicate hydrates

Giorgio Ferrari, Vincenzo Russo, Davide Salvioni, Gilberto Artioli, Maria Chiara Dalconi, Marco Favero, Luca Valentini, Michele Secco, Marco Geppi

Competition and incompatibilities between superplasticizer and retarder in cement paste

Hela Bessaies Bey, Robert Baumann, Nicolas Roussel

Phase change materials (PCMs): A novel means to mitigate thermal cracking in restrained concrete elements

Gabriel Falzone, Zhenhua Wei, Fabio Fernandes, Mathew Aguayo, Narayanan Neithalath, Laurent Pilon, Gaurav Sant

Synthesis and Performance on Cement of a Retarding Grinding Aid
Role of different superplasticizers on hydrated lime pastes and mortars

MIMED Research Group, Department of Chemistry and Soil Sciences, University of Navarra, 31008 – Pamplona, Spain

Abstract
The behaviour of different superplasticizers admixtures was assessed for hydrated lime pastes and mortars. Sometimes, air lime pastes and mortars were modified with two supplementary cementing materials (SCMs), namely nanosilica (NS) and metakaolin (MK). Two different polycarboxylate ethers, a lignosulfonate and a naphthalene condensed sulfonate superplasticizer were added to lime pastes and mortars and their effects on fresh-state properties as well as on the mechanical strengths were evaluated. A close relationship was found between the molecular architecture of the plasticizers and the flowability of the pastes. Zeta potential assessment allowed us to elucidate the main action mechanisms for these admixtures. In the case of polycarboxylate ethers, the large specific surface area of nanosilica led to a large SPs consumption as compared with metakaolin with lower surface area. However, polycarboxylate ethers in MK-lime samples were attached favourably to the C-S-H and aluminate hydrates, so that the dispersing action was greater with respect to NS-lime suspensions.

Originality
The use of plasticizing admixtures in order to improve the handling of cement-based media has been extensively reported. High-range water reducers or superplasticizers (SPs) act reducing the water demand and enhancing the flowability of the fresh mortars, yielding workable materials. So far little attention has been devoted to the study of the performance of superplasticizers in lime-bearing pastes and mortars. The widespread use of hydrated lime and pozzolan-hydrated lime pastes for paints, consolidant products, soil treatments and the obtaining of repair mortars and grouts, especially for architectural monuments of the Cultural Heritage, supports the interest of these materials. In order to design suitable hydrated lime pastes and mortars, the use of compatible and effective SPs seems to be imperative.

Keywords: admixture; pozzolan; zeta potential; nanosilica; metakaolin.

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ROLE OF DIFFERENT SUPERPLASTICIZERS ON HYDRATED LIME PASTES AND MORTARS


Department of Chemistry and Soil Sciences, Research Group on Inorganic Materials & Environment UNIVERSITY OF NAVARRA
Beijing, October, 2015

Nanosilica (NS) and metakaolin (MK) have been extensively used as Supplementary Cementitious Materials to improve the mechanical strength and to short the setting time of air lime mortars.

AIR LIME MORTARS + POZZOLANIC ADD. + SUPERPLASTICIZERS to gain a better understanding on the behavior of different SPs in lime-bearing pastes and mortars

AIM OF THIS WORK

Introduction

Lime mortars
- used in the Built Heritage over centuries
- lime, usually air lime, as the binding material
- renders, repair mortars and other mixes.

Lime mortars + pozzolanic additives: hydraulic mortars

Air lime mortars + pozzolanic add. + SUPERPLASTICIZERS

AIM OF THIS WORK
to gain a better understanding on the behavior of different SPs in lime-bearing pastes and mortars

Materials

Air lime pastes and mortars were obtained by mixing

- Raw materials: Air lime (CL90) + limestone aggregate (1:3, w/w)
- Pozzolanic additives: Nanosilica or Metakaolin (6, 10 and 20% bwoc)
- Superplasticizers (0.5 and 1% bwoc):
  - two different polycarboxylate ethers (PCE1 and PCE2)
  - a polynaphthalene sulfonate-based (PNS) polymer
  - a lignosulfonate (LS)

TEM micrographs showing the particle size as well as the shape of the pozzolanic additives

Spherical shape, 500 m²/g card-house agglomerations, 20 m²/g

Nanosilica
Metakaolin

Superplasticizers molecules were studied by means of different techniques: SEC, FTIR-ATR, MALDI-TOFF mass spectrometry, anionic charge density, acid-base titration and elemental analysis.

Results: Part 1

Elucidation of the molecular architecture of the SPs

Results of the MALDI-TOFF (Matrix Assisted Laser Desorption Ionization Time-of-Flight) analysis

For PCE1:
- wide range of signal intensities (mass/charge – m/z – ratios)
- position of the most intense signal

Longer side chains and Higher Mw than that of PCE2

Results of the MALDI-TOF (Matrix Assisted Laser Desorption Ionization Time-of-Flight) analysis

For PCE2:
- narrower m/z distribution
- lower m/z ratio
shorter side chains (with identical width between the oligomer peaks) and lower Mw.

Results: elucidation of the molecular architecture of the SPs

Results: elucidation of the molecular architecture of the SPs

For PCE1:
- lower anionic charge density
- larger Mw
- longer side length

For PCE2:
- higher anionic charge density
- lower Mw
- shorter side length

Short main backbone (low amount of COO- groups)
Long main backbone (high amount of COO- groups)

Results: elucidation of the molecular architecture of the SPs

Acid-base titration:
- PNS 2.44 meq of anionic charge/g of polymer
- LS 1.04 meq of anionic charge/g of polymer

Results: Part 2
Fresh state properties of the air lime samples with superplasticizers

Results: fresh state properties

Particle size measurements (laser diffraction)
Formation of large agglomerations in the presence of NS

Results: fresh state properties

**Results: fresh state properties**

**Particle size measurements (laser diffraction)**

Disappearance of the large agglomerations

Addition of PCE1

Disappearance of the large agglomerations

**Slump values of air lime samples**

PCE1 and LS showed the best slump retention abilities

**Results: fresh state properties**

Particle surface adsorption parameters for both PNS and LS

<table>
<thead>
<tr>
<th>Model</th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>(a_m) (mg g(^{-1}))</td>
<td>(b_m) (mg dm(^{-3}) mg(^{-1}))</td>
</tr>
<tr>
<td>PNS</td>
<td>0.67</td>
<td>1.17 (0.83)</td>
</tr>
<tr>
<td>PNS + MK</td>
<td>2.59</td>
<td>1.17 (0.83)</td>
</tr>
<tr>
<td>PNS + PCE1</td>
<td>2.58</td>
<td>1.17 (0.83)</td>
</tr>
<tr>
<td>PNS + PCE2</td>
<td>2.59</td>
<td>1.17 (0.83)</td>
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**Results: fresh state properties**

**Langmuir and Freundlich adsorption parameters for both PNS and LS**

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<td>PNS + PCE2</td>
<td>2.59</td>
<td>1.17 (0.83)</td>
</tr>
</tbody>
</table>

**Results: fresh state properties**

**Setting time (min)**

- The decrease in the zeta potential was caused in PCE2 by:
  - the displacement of the polyanion chains that disturbs the Ca(OH)\(_2\) gelation
  - PCE2 was adsorbed in a 3- to 4-fold when compared to PCE1,
  - high consumption of polycarboxylates in the presence of pozzolanic additives → high specific surface area (500 m\(^2\) g\(^{-1}\) nanosilica).

- **PCE was adsorbed in a 3- to 4-fold when compared with PCE1, in plain air lime samples.**
- **high consumption of polycarboxylates and lime-MK pastes (20 wt. % of pozzolanic additive) fitted according to Freundlich model.**
- **The polymer adsorbed onto NS was not able to be adsorbed onto C–S–H**
- **the overall zeta potential was modified to a limited extent for NS-bearing samples**
- **the compensation of the PCEs attachment onto NS retarded the pozzolanic reaction**
- **the displacement of the PCEs caused stronger delays in the setting time as compared with lime-MK samples.**
- **between NS and Ca(OH)\(_2\)**
- **in plain air lime samples.**
- **the overall zeta potential was modified to a limited extent for NS-bearing samples**
- **PCE2 was adsorbed in a 3- to 4-fold when compared with PCE1, in plain air lime samples.**
- **high consumption of polycarboxylates in the presence of pozzolanic additives → high specific surface area (500 m\(^2\) g\(^{-1}\) nanosilica).**

**Results: fresh state properties**

- **The PCEs attachment onto NS retarded the pozzolanic reaction between NS and Ca(OH)\(_2\),**
- **the increasing amounts of superplasticizers caused stronger delays in the setting time as compared with lime-MK samples.**
- **Air lime pastes with 10 wt. % of NS**
- **Air lime pastes with 10 wt. % of MK**
Zeta potential of lime-NS and lime-MK pastes titrated with PNS and LS

Results: fresh state properties

- PNS caused a sharper decrease in zeta potential
- LS produced Ca\(^{2+}\) complex salts, with low adsorption onto portlandite or CSH
- LS yielded higher slump values and presented a lower slump loss over the time
- Free LS molecules in the interstitial solution may act as a steric hindrance to prevent particles from agglomeration

Polynaphthalene sulfonate
- Higher anionic charge density
- Flat adsorption
- Linear shape
- Attached molecules surrounded by the growing carbonation/hydration products, yielding organo-mineral phases.
- Lower dispersion effectiveness, poor dispersion maintaining ability

Lignosulfonate
- Adsorption would be more perpendicular to the surface of the particles.

Results: Part 3

Influence of the SPs on the mechanical strength and durability of the tested mortars

Results: impact on the mechanical strength

Compressive strength values of mortars with PCEs

SEM examination of mortars with PCE1

The textural characteristics (SEM) showed reduced porosity, and, on the other hand, the growing of calcite crystals resulted in a more homogeneous and continuous matrix, allowing the aggregate particles to be embedded.
Results: impact on the mechanical strength

Compressive strength values of mortars with PNS and LS

<table>
<thead>
<tr>
<th>Compressive strength (MPa)</th>
<th>7 curing days</th>
<th>28 curing days</th>
<th>45 curing days</th>
<th>63 curing days</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% NS</td>
<td>2.5</td>
<td>3.2</td>
<td>3.8</td>
<td>4.2</td>
</tr>
<tr>
<td>0.5% SPP1</td>
<td>2.7</td>
<td>3.4</td>
<td>4.0</td>
<td>4.4</td>
</tr>
<tr>
<td>1% SPP1</td>
<td>2.9</td>
<td>3.6</td>
<td>4.2</td>
<td>4.6</td>
</tr>
<tr>
<td>2% SPP1</td>
<td>3.1</td>
<td>3.8</td>
<td>4.4</td>
<td>4.8</td>
</tr>
<tr>
<td>3% SPP1</td>
<td>3.3</td>
<td>4.0</td>
<td>4.6</td>
<td>5.0</td>
</tr>
<tr>
<td>4% SPP1</td>
<td>3.5</td>
<td>4.2</td>
<td>4.8</td>
<td>5.2</td>
</tr>
<tr>
<td>5% SPP1</td>
<td>3.7</td>
<td>4.4</td>
<td>5.0</td>
<td>5.4</td>
</tr>
<tr>
<td>6% SPP1</td>
<td>3.9</td>
<td>5.0</td>
<td>5.6</td>
<td>6.0</td>
</tr>
<tr>
<td>8% SPP1</td>
<td>4.1</td>
<td>5.2</td>
<td>5.8</td>
<td>6.2</td>
</tr>
<tr>
<td>10% SPP1</td>
<td>4.3</td>
<td>5.4</td>
<td>6.0</td>
<td>6.4</td>
</tr>
<tr>
<td>12% SPP1</td>
<td>4.5</td>
<td>5.6</td>
<td>6.2</td>
<td>6.6</td>
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<tr>
<td>15% SPP1</td>
<td>4.7</td>
<td>5.8</td>
<td>6.4</td>
<td>6.8</td>
</tr>
<tr>
<td>20% SPP1</td>
<td>4.9</td>
<td>6.0</td>
<td>6.6</td>
<td>7.0</td>
</tr>
</tbody>
</table>

The micrograph of the LS-bearing sample depicts a wide area covered by C-S-H crystals.

Conclusions

1) Star-shaped polymer PCE1 as compared to PCE2 (worm like polymer)
   - The lowest anionic charge density
   - The largest plasticizing effect in the assayed lime pastes
   - Perpendicular adsorption
   - Steric hindrance
   - With metakaolin provided the best flowability in order to its use as grout
   - Better mechanical resistance and durability (freezing thawing cycles)

2) LS as compared to PNS
   - More effective in increasing the fluidity of the samples
   - Able to form Ca\(^{2+}\) complexes
   - Large number of free LS molecules in the suspension
   - Strong steric effect
   - Favour the formation of C-S-H

3) PNS
   - Formation of organo-mineral phases that increased its consumption
   - Poor plasticizing performance
   - Low slump retention capacity
   - Electrostatic repulsion as the main dispersion mechanism