The use of Olivine nano-silica in the construction industry

James Baker

Nano-particle products from new mineral resources in Europe
ProMine
CP- ProMine FP7-NMP-2008-LARGE-2, 228559

http://promine.gtk.fi
Nano-silica team for construction materials

Extractive Industry → R&D demo → End user industry

SELOR eeig

Grecian Magnesite
Mineral Industrial Shipping and Commercial Co.

Hellas Gold
Kassandra Mines

TU/e
Technische Universiteit Eindhoven
University of Technology

Calduran Kalkzandsteen

Levi, Finland 23 – 25 April 2013
# From concept to product

- **Background knowledge**  
  SELOR

- **Laboratory scale optimisation nanosilica from Olivine**  
  TU/e SELOR

- **Olivine beneficiation from dunitic rocks**  
  IGME-GR Grecian Magnesite

- **Evaluation of reserves of raw materials in N Greece**  
  IGME-GR, HG (WP1 & 2)

- **Nanosilica pilot design and operation in the Netherlands**  
  SELOR TU/e

- **Production of 400 kg olivine concentrate for pilot**  
  Grecian Magnesite

- **Construction and operation of pilot at Stratoni model site**  
  Hellas Gold

- **Industrial testing in construction materials**  
  Kijlstra, TU/e (Calduran)
Background knowledge

Schematic process flowsheet of the Olivine Process

5 process steps to the sustainable production of precipitated nano silica

Commercial
Olivine nano-silica

Olivine nanosilica of high purity
Lab scale nanosilica optimisation

Reduction of SSA by up to 75%, by hydrothermal treatment of nS

15 litre reaction vessel used for experiments

Kinetics of dissolution

r = 2.08E-10 \cdot a_H^{0.45}

R² = 1.00

Exothermic

Olivine dissolution

[\text{H}^+]
Olivine beneficiation from dunite rocks

Heavy liquid separation has proved to be the only effective manner to produce an olivine concentrate of sufficient purity which can be used for nanosilica production.

Detailed lab work led to a final beneficiated product with >80% olivine.
ProMine

pilot operation in the Netherlands

Capacity
100 kilo nanosilica filter cake per day

Operational
Sept 2011

Levi, Finland 23 – 25 April 2013
The beneficiated material was crushed and sieved to achieve a final grain size of <500μm with <20% of material below 100μm. The material (400kg) was packed in 25kg sacks and dispatched to Hellas Gold at Stratoni.
Nanosilica produced in the Stratoni pilot meets the technical specifications for use in construction materials.
Design and testing of self-compacting concrete (SCC) using nano-silica

- Three concrete mixes were designed using the TU/e mix tool and tested on laboratory scale.
- The designed mixes correspond to one reference concrete without nanoparticles and two concretes with nano-silica.
- Two different commercial nano-silica additives with comparable BET specific surface area (50 m²/g), but different nature (colloidal nano-silica vs. powder nano-silica) were selected to study the differences in their reactivity.

<table>
<thead>
<tr>
<th>Value</th>
<th>Reference</th>
<th>Cembinder® 8</th>
<th>Submicron silica 995</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slump flow (mm)</td>
<td>690 - 720</td>
<td>664 - 701</td>
<td>685 - 720</td>
</tr>
<tr>
<td>Funnel time (s)</td>
<td>35.0</td>
<td>20.5</td>
<td>24.5</td>
</tr>
<tr>
<td>Fresh concrete density (g/cm³)</td>
<td>2.399</td>
<td>2.384</td>
<td>2.392</td>
</tr>
<tr>
<td>Air content (%V)*</td>
<td>1.15</td>
<td>1.79</td>
<td>1.58</td>
</tr>
<tr>
<td>Packing density*</td>
<td>83.55</td>
<td>82.91</td>
<td>83.12</td>
</tr>
</tbody>
</table>

Fresh concrete properties of the tested SCC mixes
Results of testing self-compacting concrete SCC compared to standard

✓ **Mechanical properties:** Better Compressive strength and splitting tensile strength compared to standard concrete.

✓ **Durability properties:** reference mix has slightly lower porosity (12.1%) than the mixes with the two types of nano-silica additions (12.5%). the three SCC mixes studied had a very similar water permeable porosity. the addition of 3.8% nano-silica results in concrete which have high resistance to water penetration. the nano-silica samples have very low effective water permeability.

✓ **The conductivity** of the SCC with nano-silica addition is reduced by more than 50% compared to the SCC reference mix.

✓ **The freeze-thaw resistance:** Better resistance to the freeze-thaw cycles of the SCC with nano-silica additions can be attributed to its denser and more compacted microstructure. Excellent freeze-thaw resistance to exposure.
Industrial testing

- Nano-silica powder (Hellas Gold)
- Nano-silica cake (SELR)
- High energy mixing
- Dosing
- Concrete mixer (adjusting)
- Casting
- Spread-flow and J-ring
- V-funnel and stability
- Fresh properties determination

Levi, Finland 23 – 25 April 2013
Two products have been tested at the Kijlstra Beton facility in the Netherlands:

- Vibrated concrete
- Self compacting concrete
Industrial testing
Vibrated concrete with Olivine nS

- Optimum strength with 5% vol. replacement level (20% higher).
- Increased content of SP (more than 2X for the same Slump class).
- Further research is needed.
Conclusions of testing:

- The optimum replacement level of olivine nano-silica in VC would be around 5.0% by volume.

- The addition of nano-silica causes an increase in the required superplasticizer amount (1.5 vs 3.3 kg/m³) to obtain the same slump class (S2).

- Higher (20% more than reference) and comparable compressive strength to reference vibrated concrete (VC) was obtained, but with increased amount of SP (more than 2X).
Industrial testing

Self-compacting concrete with Olivine nS

Mix design parameters:
Exposure class XA3-C51/55
q=0.28
w/b=0.43
Spread Flow F7 (650 and 850 mm)
V-funnel time: 12/13 s

CO$_2$ indicators taken from:
1) De Vereniging van Ondernemers van Betonmortelfabrikanten in Nederland (VOBN).
2) ProMine project.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reference</th>
<th>Optimized SCC (Lab)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kg/m$^3$</td>
<td>KgCO$_2$/m$^3$</td>
</tr>
<tr>
<td></td>
<td>Kg/m$^3$</td>
<td>KgCO$_2$/m$^3$</td>
</tr>
<tr>
<td>Olivine nano-silica*</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>CEM I</td>
<td>95</td>
<td>77.90</td>
</tr>
<tr>
<td>CEM III</td>
<td>255</td>
<td>71.40</td>
</tr>
<tr>
<td>Fly ash</td>
<td>160</td>
<td>0.40</td>
</tr>
<tr>
<td>Sand 0-8</td>
<td>825</td>
<td>3.14</td>
</tr>
<tr>
<td>Gravel 4-16</td>
<td>845</td>
<td>0.93</td>
</tr>
<tr>
<td>Water</td>
<td>163</td>
<td>0.06</td>
</tr>
<tr>
<td>SP</td>
<td>3.5</td>
<td>2.52</td>
</tr>
</tbody>
</table>

1 ton of CEM I52.5R = 779 kg CO$_2$
1 ton of OnS = 277 kg CO$_2$
Estimated CO₂ reduction

Binder content 382 kg/m³

Reference

Proposed recipe

Binder content 369 kg/m³
The optimum replacement level of olivine nano-silica in SCC would be around 3.8% bwoc.

• The addition of nano-silica causes an increase in the required superplasticizer amount (3.5 vs 5.2 kg/m³) to obtain the same workability class.

• With the right balance between added water and SP, 1 kg of nano-silica could replace 5 kg of CEMI 52.5 R (60% less) and 13 kg/m³ of the total binder should be decreased (CEM I + CEM IIIB), while maintaining the required properties (in fresh and hardened state). As a result a more ecological SCC could be manufactured (CO₂ foot print 18% less).
Use of ProMine nanosilica in construction materials

- Industrial trials show that ProMine nanosilica produces concretes meeting all technical specifications.
- CO2 footprint reduced by almost 20%.
- Addition of ProMine nanosilica results in major savings in raw materials; 1 kg nanosilica replaces 5 kg cement.
- Economy of scale, the price per ton of ProMine nanosilica is currently too high for standard concrete applications.
- The production cost of ProMine nanosilica is OK for specialised applications, such as oil well cement and high performance concretes.
Nanosilica production plans

- Protection of Foreground IP: Within ProMine, and the production process of nanosilica, involves only SELOR and TU/e
- Everything in place to start and achieve a small production of 100 tons of nanosilica in 2013
- Realistic to scale up to 1000 tons per year in 2014
- The big IF…!
- Currently discussing inside and outside ProMine with different potential or launching customers in order to find the investment capital.
- Looking at a range of applications, not only concretes but also paper industry, which will be presented in the next talk.
END