Self-Levelling Flooring Compounds
Based on
Ternary Binder Systems

CIMSA Dry-Mix Mortar Seminar

Istanbul, 21 September 2017

Prof. Dr. Johann Plank
Technische Universität München
Chair for Construction Chemistry
Dry-Mix Mortar Products

Principle Properties of CAC

SLUs - Properties & Composition

Admixtures for SLUs

Raw Materials and Formulations

Ageing of SLUs

Conclusion
Modern Building Technology

Residence of German Chancellor, Berlin

Phaeno Center, Wolfsburg

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The Origin of Dry-Mix Mortar Technology

- rebuilding German cities after World War II
- shortage of workers for construction in the 1960s/1970s
- dry-mix mortar allows to build faster and in better quality

Nuremberg, May 1945
The Origin of Dry-Mix Mortar

- traditional building: manual mixing on construction site
- no quality control
- many workers required

Early mortar mixing machine from Kalkwerk Mathis, Merdingen (early 1970s)

Traditional job-site mortar mixing

In the 1970s, beginning of dry-mix mortar industry

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Thin-Bed Tile Adhesives

- Thin-bed technology invented by Sponagel in Switzerland in 1930s
- First dry-mix CTA introduced in 1959 by ARDEX and Polychemie GmbH (PCI) Augsburg

Laying tiles by conventional „buttering“ method
Laying tiles by modern thin-bed mortar technology

Thin-bed mortar allows to save approx. 35% of material

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Wall Renders and Plasters

Exterior and interior wall plasters / renders

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CTAs and Joint Fillers (Grouts)

Tile grout

Flooring using CTA
External Insulation and Finishing System (EIFS)

Adhesives and mortars for EIFS
EIFs Systems

- difficult to place
- expensive
- problem of waste
- fire hazard
Fire at Grenfell Tower, London

- Fire on 14 June 2017
- At least 80 people were killed
- Polystyrene boards behind Al sheets caught fire
Fire Hazard of Conventional EIFS

Shanghai, 2011

Istanbul, July 2012
Inorganic Insulation Materials

Glass wool

Mineral wool

Aerogel granulate

Application of aerogel render

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Self-Levelling Underlayments (SLUs)

- Perfect self-spreading and self-healing property
- Excellent smooth surface

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Self-Levelling Underlayments (SLUs)

SLU based on a ternary binder system

Demonstration of self-levelling and self-healing property of a SLU

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**SLU Formulation Based on Ternary Binder**

Grey alumina cement (~ 40 % Al$_2$O$_3$) for high early strength

<table>
<thead>
<tr>
<th>Material</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland Cement (CEM I 42,5 R)</td>
<td>18,50 wt.-%</td>
</tr>
<tr>
<td>Calcium Alumina Cement (~ 40% Al$_2$O$_3$)</td>
<td>11,50 wt.-%</td>
</tr>
<tr>
<td>CaSO$_4$ (synthetic anhydrite)</td>
<td>6,50 wt.-%</td>
</tr>
<tr>
<td>Quartz sand (0,1 to 0,315 mm)</td>
<td>41,00 wt.-%</td>
</tr>
<tr>
<td>Limestone powder (10 to 20 µm)</td>
<td>19,40 wt.-%</td>
</tr>
<tr>
<td>Casein or PCE (Superplasticizer)</td>
<td>0,40 wt.-%</td>
</tr>
<tr>
<td>Vinylacetate-Copolymer (Redispersible Powder)</td>
<td>2,00 wt.-%</td>
</tr>
<tr>
<td>NaK-tartrate (Retarder)</td>
<td>0,40 wt.-%</td>
</tr>
<tr>
<td>Li$_2$CO$_3$ (Accelerator)</td>
<td>0,10 wt.-%</td>
</tr>
<tr>
<td>Cellulose ether (Water Retention Agent)</td>
<td>0,05 wt.-%</td>
</tr>
<tr>
<td>Polyglycol (Defoamer)</td>
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</tr>
<tr>
<td>Mixing Water (for 100 wt.-% powder blend)</td>
<td>20,00 wt.-%</td>
</tr>
</tbody>
</table>
Dry-Mix Mortar Products

Principle Properties of CAC

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**Definition and Origin of CAC**

- Cements with at least 35% of $\text{Al}_2\text{O}_3$
- Main hydraulic phases: $\text{CA}$, $\text{C}_{12}\text{A}_7$ and less reactive $\text{CA}_2$

1840  J.L. Vicat realized the sulfate resistance of CAC

1908  Industrial development of Aluminate Cement is associated with the work of J. Bied (British Pat. 8193)

1918  Ciment Fondu first CAC marketed by Lafarge Company

Alumina cement based concrete used in WW I for heavy guns

After World War II, aluminate cement was developed as binder for refractory castables

In the 1950's, development of complex mortars containing combinations of aluminate cement, Portland cement and Ca-Sulfates for the building industry (dry mortars)
Chemical Composition of Aluminate Cements

- Portland Cement
- Aluminate Cement
Main Phases in CAC

- Monocalcium aluminate CA
- Grossite CA₂
- Mayenite C₁₂A₇
- Gehlenite C₂AS
- Belite C₂S
- Ferrite C₄AF
# Chemical Composition of Aluminate Cements

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Aluminate Cement</th>
<th>Portland Cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>36% to 80%</td>
<td>4% to 8%</td>
</tr>
<tr>
<td>CaO</td>
<td>20% to 42%</td>
<td>60% to 70%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0,2% to 8%</td>
<td>18% to 24%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0,2% to 20%</td>
<td>1% to 5%</td>
</tr>
<tr>
<td>TiO₂</td>
<td>&lt; 2%</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>&lt; 1%</td>
<td>&lt; 3%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt; 0,3%</td>
<td>&lt; 1%</td>
</tr>
<tr>
<td>K₂O</td>
<td>&lt; 0,1%</td>
<td>&lt; 1%</td>
</tr>
</tbody>
</table>
XRD Diagrams of Aluminate Cement

Type

Secar 71
(white)

Secar 51
(grey)

Fondu
(dark)

CA
CA
CA
CA
CA
CA
CA

CA
CA
CA

CA
CA
CA
CA

CA
CA
CA
CA

Mayenite

Gehlenite

Ca3Fe2TiO8

Brownmillerite

Perowskite

Perowskite
Manufacture of Aluminate Cements

Raw Materials: Limestone and Bauxite
   In many cases, red mud from the Bayer process is used as raw material

**Standard grade Aluminate Cement**

- Up to 50% $\text{Al}_2\text{O}_3$
- Up to 20% $\text{Fe}_2\text{O}_3$
- Several per cent $\text{TiO}_2$
- Silica content must be fairly low

   Usually made by melting in furnaces at 1600 °C

**Grades of higher Aluminate Cement**

- 60% to 80% $\text{Al}_2\text{O}_3$
- Very low $\text{Fe}_2\text{O}_3$
- Very low $\text{SiO}_2$

   Usually made by sintering in rotary kilns at 1450 °C
Advantages of CAC vs. OPC

Unique properties of CAC:

- Rapid hardening with setting time similar to Portland Cement
- High Resistance to sulfate attack and acids
- Ability to withstand repeated heating to high temperatures
- Ability to hydrate and perform at low temperatures (e.g. 2 °C)
- Resistance to abrasion
- Adjustable properties in mixtures with Portland Cement and calcium sulfates
Alumina Cements harden more rapidly than Portland Cements; within one or two days they reach their specified strength.

Strength development of CAC and OPC

Heat flow of CAC and OPC

CAC is used to accelerate strength development of OPC
Shrinkage Behavior of Calcium Aluminate Cement

Addition of CAC to OPC compensates the shrinkage of OPC through ettringite formation.

Shrinkage as a function of alumina cement content in binder:
A = OPC;  B = OPC-rich blend;  C = CAC-rich blend
Applications of Aluminate Cements

- Corrosive environments
- Sewage pipes
- Dry-mix mortars
- Refractory
- Rotary Kiln, Cement Plant
- Tile grouts

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Benefits from Aluminate Cements

- Self-levelling underlayment
- Tile adhesive
- Cementitious tile grout

- Rapid Hardening
- Shrinkage Compensation
- Quick Drying
- Chemical Resistance

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Tile grouts: CAC vs. OPC

Cleaning machine

Tile grouts based on CAC are much more durable

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Content …..

….. Dry-Mix Mortar Products

….. Principle Properties of CAC

….. SLUs - Properties & Composition

….. Admixtures for SLUs

….. Raw Materials and Formulations

….. Ageing of SLUs

….. Conclusion
Self-Levelling Underlayments (SLUs)
Three Principle Types of SLUs

<table>
<thead>
<tr>
<th>Component</th>
<th>CAC -rich</th>
<th>w/CSA cement</th>
<th>OPC - rich</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAC 40</td>
<td>27 %</td>
<td>48 %</td>
<td>56 %</td>
</tr>
<tr>
<td>OPC</td>
<td>54 %</td>
<td>-</td>
<td>30 %</td>
</tr>
<tr>
<td>β - HH</td>
<td>-</td>
<td>17 %</td>
<td>14 %</td>
</tr>
<tr>
<td>α - HH</td>
<td>19 %</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CSA</td>
<td>-</td>
<td>35 %</td>
<td>-</td>
</tr>
</tbody>
</table>

Superplasticizer 0.38 – 0.78 %

<table>
<thead>
<tr>
<th>Set Control agents</th>
<th>1 – 2 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₃-citrate</td>
<td>×</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>×</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>×</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>×</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>×</td>
</tr>
</tbody>
</table>

Water-to-Binder 0.59 0.76 0.92
# CAC – Rich SLU Formulation

<table>
<thead>
<tr>
<th>Component</th>
<th>Function</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAC 40 % Al₂O₃</td>
<td>Aluminate Cement</td>
<td>18.00</td>
</tr>
<tr>
<td>CEM I 52,5 N</td>
<td>Portland Cement</td>
<td>3.60</td>
</tr>
<tr>
<td>CaSO₄ · 0.5 H₂O</td>
<td>HH - Binder</td>
<td>6.30</td>
</tr>
<tr>
<td>CaCO₃ powder</td>
<td>Filler</td>
<td>24.35</td>
</tr>
<tr>
<td>Sand</td>
<td>Filler</td>
<td>45.34</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>Retarder for OPC</td>
<td>0.06</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>Accelerator for CAC</td>
<td>0.03</td>
</tr>
<tr>
<td>RDP Latex Powder</td>
<td>Provides adhesion</td>
<td>2.00</td>
</tr>
<tr>
<td>Polyglycol</td>
<td>Defoamer</td>
<td>0.10</td>
</tr>
<tr>
<td>Methyl cellulose</td>
<td>Water retention</td>
<td>0.10</td>
</tr>
<tr>
<td>PCE powder</td>
<td>Superplasticizer</td>
<td>0.12</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td><strong>100.00</strong></td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>23.00</td>
</tr>
<tr>
<td><strong>Water/Cement Ratio</strong></td>
<td></td>
<td><strong>1.06</strong></td>
</tr>
<tr>
<td><strong>Water/Binder Ratio</strong></td>
<td></td>
<td><strong>0.82</strong></td>
</tr>
</tbody>
</table>
## OPC – Rich SLU Formulation

Grey alumina cement (~ 40 % Al\(_2\)O\(_3\))

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<tr>
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</tr>
<tr>
<td>NaK tartrate (Retarder)</td>
<td>0.40 wt.-%</td>
</tr>
<tr>
<td>Li(_2)CO(_3) (Accelerator)</td>
<td>0.10 wt.-%</td>
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<td>Cellulose ether (Water Retention Agent)</td>
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<td>0.15 wt.-%</td>
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<tr>
<td>Mixing Water (for 100 wt.-% Powder blend)</td>
<td>20.00 wt.-%</td>
</tr>
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</table>
Setting Time of Mixtures CAC/OPC

- blends of CAC and OPC often show extremely fast setting
  - no workability

- only CAC/OPC 20:80 or 85:15 work

- retarders for OPC required to prevent rapid setting

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Mixtures of OPC and CAC are used to accelerate setting/strength development of cement.

Such mixtures show lower compressive strength than pure OPC or CAC.

Compressive strength of OPC and CAC combinations.
Combinations of CAC and Portland cement are very sensitive to variations in OPC composition.

Influence of OPC type on setting time

Influence of OPC type on 1 day compressive strength

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Rapid Hardening Owed to Ettringite Formation

Ettringite crystals formed in the matrix of a ternary binder

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Rapid Drying of SLU

„Chemical“ drying owed to huge water consumption for ettringite formation

\[
3 \text{CaAl}_2\text{O}_4 + 3 \text{CaSO}_4 \cdot 0.5 \text{H}_2\text{O} \rightarrow [\text{Ca}_3\text{Al(OH)}_6 \cdot 12\text{H}_2\text{O}]_2 \cdot (\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}
\]

ettringite

Structure of ettringite, showing plenty of water molecules

Ettringite crystals

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Shrinkage Behavior of SLUs

- Shrinkage compensation through addition of alumina cement
- Reason for reduced shrinkage: expansion because of ettringite formation
Shrinkage of OPC

- OPC develops high shrinkage
- After addition of superplasticizers shrinkage becomes even much higher
- Ettringite formation in ternary binder compensates shrinkage from OPC

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Shrinkage of Hardened Cement

Chemical shrinkage

Drying shrinkage

Only pores between 10 and 100 nm cause shrinkage
Shrinkage Problem of Floor Screeds

Dry Shrinkage
- Severe at high w/c ratio (e.g. 0.70)

Chemical Shrinkage
- Severe at low w/c ratio (e.g. 0.40)
Experimental Determination of Chemical and Drying Shrinkage

- Chemical shrinkage
  - Mortar specimen stored at 23 °C covered with foil (chemical shrinkage only)
- Chemical and dry shrinkage
  - Total shrinkage — storage of mortar specimen at 23 °C and 65 % rel. humidity — surface uncovered (chemical and dry shrinkage)
Contents:

- Dry-Mix Mortar Products
- Principle Properties of CAC
- SLUs - Properties & Composition
- Admixtures for SLUs
- Raw Materials and Formulations
- Ageing of SLUs
- Conclusion
<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Percentage</th>
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<tr>
<td>Portland cement (CEM I 42,5 R)</td>
<td>18.50 mass-%</td>
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<td>Grey alumina cement (ca. 40 % Al₂O₃)</td>
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</tr>
<tr>
<td>Calcium sulfate (anhydrous, synthetic anhydrite)</td>
<td>6.50 mass-%</td>
</tr>
<tr>
<td>Silica sand (0.1 - 0.315 mm)</td>
<td>41.00 mass-%</td>
</tr>
<tr>
<td>Limestone powder (calciumcarbonate, 10 - 20 μm)</td>
<td>19.40 mass-%</td>
</tr>
<tr>
<td>Superplasticizer casein or PCE</td>
<td>0.40 mass-%</td>
</tr>
<tr>
<td>Latex polymer (redispersible powder based on vinylacetate)</td>
<td>2.00 mass-%</td>
</tr>
<tr>
<td>Retarder (K/Na tartrate / trisodium citrate)</td>
<td>0.40 mass-%</td>
</tr>
<tr>
<td>Accelerator (lithium carbonate)</td>
<td>0.10 mass-%</td>
</tr>
<tr>
<td>Stabilizer (cellulose ether, low-viscosity type)</td>
<td>0.05 mass-%</td>
</tr>
<tr>
<td>Defoamer (powder)</td>
<td>0.15 mass-%</td>
</tr>
<tr>
<td><strong>Sum of powder components</strong></td>
<td><strong>Total 100.00 mass-%</strong></td>
</tr>
<tr>
<td>Water (for 100.00 mass-% powder):</td>
<td>20.00 mass-%</td>
</tr>
</tbody>
</table>
Casein Superplasticizer

- casein content in bovine milk 2,5 - 3%
- heterogeneous mixture of partly glycosylated phosphoproteins
- manufactured by acid precipitation from milk at pH 4,6 / 20 °C

Four major casein fractions:

- α-casein ~ 50%
- β-casein 35- 40%
- κ-casein ~ 10%
- γ-casein < 5%

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Casein Superplasticizer in SLU

Superplasticizers:  
Casein  
Melamine Formaldehyde Sulfite (MFS) Polycondensate  
Polycarboxylate (PCE)
Casein micelle according to WALSTRA (1999)

Sub-micelles: hydrophobic core, consisting of 20-25 $\alpha$-/$\beta$- caseins and calcium phosphate

Micelle: Electrostatic and steric stabilization through formation of an outer "hairy layer", containing hydrophilic saccharide residues from the $\kappa$-caseins
$\alpha$-Casein

Tertiary structure of $\alpha_{s1}$-casein

~ 50.8% in bovine casein

- 199 amino acids with 8 phosphate groups
- phosphate groups esterified with serine
- net anionic charge: $-24$ (at pH 6.7)
- above 2 mmol/L Ca$^{2+}$ charge neutralization $\rightarrow$ precipitation

[Diagram of $\alpha_{s1}$-casein structure]
β– Casein

Tertiary structure of β₁-casein

~ 36.3 % in bovine casein

209 amino acids and 5 phosphate groups

net anionic charge –13 (at pH 6.7)

Formation of Ca precipitate depends on temperature

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κ-Casein

Tertiary structure of κ₁-casein

- 169 amino acids, up to 5 trisaccharide groups
- only one phosphate group
- net anionic charge –11 (at pH 6.7)
- charge derives from glutamine and asparagine and saccharides
- soluble in presence of calcium

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Dispersing Effect of Casein Protein Fractions

Spread of SLU in mini slump test:

- α-casein
- β-casein
- κ-casein

Flowability [cm] vs [min]
Problems Associated with Casein

- Unstable quality
- Decomposes in alkaline cement ➔ strong smell of ammonia!
- Enhances proliferation of mould ➔ “sick house syndrome“

Replacement by PCEs
PCEs in SLUs

- Excellent dispersing performance…….
  
  but…….

- poor compatibility with retarders (tartrate, citrate)

- no self-healing property

This PCE is not compatible with citrate
Adsorption of Casein with/without Retarder

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Adsorption of PCE with / without Retarder

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Optimized PCE For Ternary SLU

Optimized PCE has high anionic charge density

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Rapidly Dissolving PCE Powder

Modified PCEs which hydrate and adsorb immediately (e.g. Melflux® 5581)

Cementitious flowing floor screed

PCE Molecule

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Self-Healing Property of PCE-Based SLU

- requires a **second admixture**: „viscosity-modifying agent“ (VMA)
- e.g. copolymer of AMPS/NNDMA („Starvis“, BASF)
- combination of PCE and VMA provides comparable properties than from casein

![AMPS/NNDMA copolymer](image)
Tartrate and Citrate Retarders

- generally, tartrate works better as retarder than citrate and is more compatible with superplasticizers.
- however, tartrate is more expensive.
- tartrate has to be the NaK salt of natural tartaric acid („Seignette salt“, L(+) type), not of the D(-) type or the racemic mixture!

![L(+)](image1.png) tartaric acid
![citric acid](image2.png)

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Dry-Mix Mortar Products

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# CAC - Rich PCE-Based SLU

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<td>CAC 40 % Al₂O₃</td>
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</tr>
<tr>
<td>CEM I 52.5 R</td>
<td>4.0</td>
</tr>
<tr>
<td>α - hemihydrate</td>
<td>7.0</td>
</tr>
<tr>
<td>Durcal 15 (limestone)</td>
<td>19.0</td>
</tr>
<tr>
<td>Durcal 130 (limestone)</td>
<td>9.0</td>
</tr>
<tr>
<td>Sand (0 - 0.315 mm)</td>
<td>37.8</td>
</tr>
<tr>
<td>Li₂CO₃</td>
<td>0.1</td>
</tr>
<tr>
<td>Citric acid, Na salt</td>
<td>0.02</td>
</tr>
<tr>
<td><strong>PCE (Melflux, BASF)</strong></td>
<td>0.25</td>
</tr>
<tr>
<td>VMA (Starvis, BASF)</td>
<td>0.05</td>
</tr>
<tr>
<td>MHEC Dow</td>
<td>0.05</td>
</tr>
<tr>
<td>RDP (Vinnapas, Wacker)</td>
<td>2.00</td>
</tr>
<tr>
<td>Defoamer (Agitan, Münzing)</td>
<td>0.10</td>
</tr>
<tr>
<td>Water</td>
<td>24.00</td>
</tr>
</tbody>
</table>

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# CAC - Rich PCE-Based SLU

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<tr>
<td>CAC 40 % ( \text{Al}_2\text{O}_3 )</td>
<td>60.00</td>
</tr>
<tr>
<td>CEM I 32.5 R (Heidelberg)</td>
<td>39.00</td>
</tr>
<tr>
<td>Anhydrite (Solvay, Hannover)</td>
<td>36.00</td>
</tr>
<tr>
<td>Quartz sand (H33, 0.1 - 0.315 mm)</td>
<td>83.70</td>
</tr>
<tr>
<td>( \text{CaCO}_3 ) powder (Omyacarb 20 - BG)</td>
<td>72.70</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>4.50</td>
</tr>
<tr>
<td>PCE (Melflux PP 100 F, BASF)</td>
<td>2.70</td>
</tr>
<tr>
<td>RDP (Vinnapas RE 523 Z, Wacker)</td>
<td>4.50</td>
</tr>
<tr>
<td>Tartaric acid (L(+), Merck)</td>
<td>0.90</td>
</tr>
<tr>
<td>( \text{Li}_2\text{CO}_3 ) (&lt; 40 ( \mu ), Chemetall)</td>
<td>0.90</td>
</tr>
<tr>
<td>MHEC (Walocel MT 400, Dow)</td>
<td>0.09</td>
</tr>
<tr>
<td>Defoamer (Agitan P 800, Münzing)</td>
<td>0.60</td>
</tr>
</tbody>
</table>

**Water demand:** ~ 20 mL for 100 g dry blend
## CAC - Rich Melamine-Based SLU

<table>
<thead>
<tr>
<th>Component</th>
<th>Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAC $\text{40% Al}_2\text{O}_3$</td>
<td>200.00</td>
</tr>
<tr>
<td>CEM I 32.5 R (Heidelberg)</td>
<td>100.00</td>
</tr>
<tr>
<td>Anhydrite (Solvay)</td>
<td>125.00</td>
</tr>
<tr>
<td>Sand (H33, Quartzwerke Köln)</td>
<td>300.00</td>
</tr>
<tr>
<td>$\text{CaCO}_3$ powder (Omyacarb 20 - BG)</td>
<td>240.00</td>
</tr>
<tr>
<td>MFS (Melment F 10, BASF)</td>
<td>6.00</td>
</tr>
<tr>
<td>RDP (Vinnapas RE 523 Z, Wacker)</td>
<td>25.00</td>
</tr>
<tr>
<td>Tartaric acid (L(+), Merck)</td>
<td>1.00</td>
</tr>
<tr>
<td>MHEC (Tylose H 300P, SE Tylose)</td>
<td>1.00</td>
</tr>
<tr>
<td>$\text{Li}_2\text{CO}_3$ (&lt; 40 µ, Chemetall)</td>
<td>0.80</td>
</tr>
<tr>
<td>SRA (1,6 - Hexanediol, BASF)</td>
<td>5.00</td>
</tr>
<tr>
<td>Defoamer (Agitan P 800, Münzing)</td>
<td>2.00</td>
</tr>
</tbody>
</table>

**Water demand:** 22 mL for 100 g dry blend  
**Open time:** ~ 20 min  
**Walk-on time:** ~ 2.5 hours (shore D ≥ 50)
OPC - Rich Melamine-Based SLU

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 32.5 R (Heidelberg)</td>
<td>300.00</td>
</tr>
<tr>
<td>CAC 40 % Al₂O₃</td>
<td>70.00</td>
</tr>
<tr>
<td>Anhydrite (Solvay, Hannover)</td>
<td>50.00</td>
</tr>
<tr>
<td>Quartz sand (H33, Quarzwerke Köln)</td>
<td>379.20</td>
</tr>
<tr>
<td>CaCO₃ powder (Omyacarb 20 - BG)</td>
<td>165.00</td>
</tr>
<tr>
<td>MFS (Melment F 10, BASF)</td>
<td>6.00</td>
</tr>
<tr>
<td>RDP (Vinnapas RE 523Z, Wacker)</td>
<td>20.00</td>
</tr>
<tr>
<td>Tartaric acid (L(+), Merck)</td>
<td>1.70</td>
</tr>
<tr>
<td>Li₂CO₃ (&lt; 40 µ, Chemetall)</td>
<td>0.60</td>
</tr>
<tr>
<td>MHEC (Walocel MT 400, Dow)</td>
<td>1.00</td>
</tr>
<tr>
<td>SRA (1,6 - hexanediol, BASF)</td>
<td>5.00</td>
</tr>
<tr>
<td>Defoamer (Agitan P 800, Münzing)</td>
<td>1.50</td>
</tr>
</tbody>
</table>

Water demand: 22 mL for 100 g dry blend
Open time: ~ 35 min
Walk-on time: ~ 7 hours (shore D ≥ 50)
## OPC - Rich Casein-Based SLU

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Mass %</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 32.5 R (Heidelberg)</td>
<td>54.00</td>
<td>Mass %</td>
</tr>
<tr>
<td>CAC 40 % Al₂O₃</td>
<td>36.00</td>
<td>Mass %</td>
</tr>
<tr>
<td>Anhydrite (Solvay, Hannover)</td>
<td>21.00</td>
<td>Mass %</td>
</tr>
<tr>
<td>Quartz sand (H33, 0.1 - 0.315mm)</td>
<td>120.00</td>
<td>Mass %</td>
</tr>
<tr>
<td>CaCO₃ powder (Omyacarb 20 BG)</td>
<td>61.95</td>
<td>Mass %</td>
</tr>
<tr>
<td>Casein (Ardex)</td>
<td>1.20</td>
<td>Mass %</td>
</tr>
<tr>
<td>RDP (Vinnapas RE 523Z, Wacker)</td>
<td>4.50</td>
<td>Mass %</td>
</tr>
<tr>
<td>Na₃ - citrate (Merck)</td>
<td>0.60</td>
<td>Mass %</td>
</tr>
<tr>
<td>Li₂CO₃ (&lt; 40 µ, Chemetall)</td>
<td>0.30</td>
<td>Mass %</td>
</tr>
<tr>
<td>MHEC (Tylose H 300P, SETylose)</td>
<td>0.15</td>
<td>Mass %</td>
</tr>
<tr>
<td>Defoamer (Agitan P 800, Münzing)</td>
<td>0.30</td>
<td>Mass %</td>
</tr>
</tbody>
</table>

**Water demand:** ~ 20 mL for 100 g dry blend
Content ......

...... Dry-Mix Mortar Products

...... Principle Properties of CAC

...... SLUs - Properties & Composition

...... Admixtures for SLUs

...... Raw Materials and Formulations

...... Ageing of SLUs

...... Conclusion
<table>
<thead>
<tr>
<th>Basic SLU formulation</th>
<th>Function</th>
<th>(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM I 52.5 N (Milke, HeidelbergCement, Geseke)</td>
<td>Binder</td>
<td>52.00</td>
</tr>
<tr>
<td>Calcium aluminate cement (grey, 40 % Al$_2$O$_3$ Cement Fondu, Kerneos)</td>
<td>Binder</td>
<td>36.00</td>
</tr>
<tr>
<td>Anhydrite (Fluoroanhydrite Solvay Fluor und Derivate, Bad Wimpfen)</td>
<td>Binder</td>
<td>21.00</td>
</tr>
<tr>
<td><strong>Melflux 2651 F or casein</strong></td>
<td>Superplasticizer</td>
<td>0.44 for casein 0.12</td>
</tr>
<tr>
<td><strong>tartrate or citrate</strong></td>
<td>Retarder</td>
<td>0.44</td>
</tr>
<tr>
<td>Li$_2$CO$_3$</td>
<td>CAC accelerator</td>
<td>0.3</td>
</tr>
<tr>
<td>Water</td>
<td></td>
<td>27.5</td>
</tr>
</tbody>
</table>

SLU prehydrated for 1 or 3 days at 35 °C @ 90 % RH

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Rapid Moisture Uptake by SLU

SEM images

fresh SLU

SLU aged 1 day

SLU aged 3 days

Ettringite crystals

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Impact of Moisture on Flow Behaviour of SLU

System PCE - Tartrate

- fresh SLU – good flowability at w/b = 0.25
- aged SLU – no flowability at w/b = 0.25

Ageing affects SLU stronger than variation of w/b ratio in fresh SLU

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Impact of Moisture Uptake on Flow Behavior of SLU System PCE - Tartrate

Workability of aged SLU with tartrate significantly lower

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After only 1 day of exposure to moist air, SLU containing tartrate or citrate was no longer fluid; but tartrate system behaved better than citrate system.
In the aged SLU, the **retarding effect of citrate becomes stronger**, leading to longer open times but poor fluidity.
Lower compressive strength because of higher water demand and air voids

Compressive Strengths: Fresh vs. Aged SLU

SLU: citrate + PCE

SEM
Compressive Strengths: Fresh vs. Aged SLU

Comparison of different admixture combinations

- **citrate + PCE**
  - Fresh: 80 N/mm²
  - Aged 1 d: 40 N/mm² (-40 %)

- **citrate + casein**
  - Fresh: 80 N/mm²
  - Aged 1 d: 40 N/mm² (-40 %)

- **tartrate + casein**
  - Fresh: 40 N/mm²
  - Aged 1 d: 20 N/mm² (-50 %)

1 day compressive strengths

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Water Demand and Appearance of SLU

SLU with citrate and PCE, aged 1 day

Prism prepared from fresh SLU (w/b = 0.25)

w/b ratio adjusted to 18 cm flow

Aged SLU contains air voids

Prism prepared from aged SLU (w/b = 0.27)

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Compressive Strengths: Fresh vs. Aged SLU

SLU aged 1 day contains *unreacted binders* (CAC, anhydrite)
Appearance of Aged SLU

Gypsum
Packaging Requirements For SLUs

- bags must have a plastic inlet which functions as a water vapor barrier
- some SLU producers use bags with Al foil inside, similar as in some food products
Dry-Mix Mortar Products

Principle Properties of CAC

SLUs - Properties & Composition

Admixtures for SLUs

Raw Materials and Formulations

Ageing of SLUs

Conclusion
Summary - Part I

- SLUs are high-performance dry mixes
- SLUs provide a perfect smooth substrate for tiles, carpets, parquet, vinyl floors etc.
- SLUs are easy to place and spread
- SLUs develop strength rapidly, owed to CAC
- Especially CAC-rich formulations can be walked on within 2 - 3 hours
- Rapid and massive ettringite formation provides "chemical" drying and shrinkage compensation

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Summary - Part II

- SLUs require high quality packaging (bags) and fresh cements
- SLUs require proper on-site mixing device

Western Europe: batch mixing in bin
Scandinavia: mixing by machine
Why CAC - Based SLU?

- SLUs can be formulated as well based on α-hemi hydrate ….
  
  **but ………**

- CaSO₄-based SLUs show longer walk-on times and slower strength development
- CaSO₄-based SLUs develop a *glass-like skin of CaCO₃/superplasticizer on the surface which prevents proper adhesion of the next layer (tiles, carpet…)*
- Glassy layer has to be removed by using a milling machine
  → **costly additional step!**
- Gypsum is not water-resistant!

---

Milling machine

Removing glassy skin of gypsum-based SLU
SLUs – Perfect Products For Modern Building

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2nd International Conference on Polycarboxylate Superplasticizers (PCE 2017)

September 27 - 28, 2017
Munich, Germany

www.pce-conference.org

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