Material	kg/m ³ (lb/yd ³)
Cement (CEM II/A-V 42.5 R)	450 (758)
Microsilica, 920 D	20 (33.7)
Aggregates, 0/8 mm	1575 (2655)
Total water	206 (347)
Superplasticizer	4.9 (8.26)
Slump stabilizer	0.4 (0.67)
Total	2256 (3802)

Table 1 -- Concrete mixture proportion

Shotcrete accelerator dosage was 9% of cement weight for all samples.



Fig.5 -- Ongoing shotcrete testing.

Table 2 -- Test matrix temperature setup

<u>Fresh concrete</u> with <u>low temperature</u>	Fresh concrete with high temperature		
<u>Stored</u> in <u>cold</u> surroundings	Stored in cold surroundings		
Fresh concrete with low temperature	Fresh concrete with high temperature		
Stored in warm surroundings	Stored in warm surroundings		

Table 3 -- Temperatures in concrete and storage conditions

	Temperature °C (°F)
Warm fresh concrete	+28 (82.4)
Cold fresh concrete	+13 (55.4)
Warm storage condition	+20 (68)
Cold storage condition	+5 (41)

room, and the other two in a cold area. **Table 3** presents the temperatures in concrete and storage conditions:

The two storage conditions represent the outer limits of practical life. It is normal to have tunnel temperature of +5 °C (41 °F) in the winter time, especially in relatively short tunnels, or near opening. During longer periods of summer weather it can be \sim +20 °C (68 °F) in a tunnel, also more common near opening. The four samples were sprayed with a "first generation" alkali-free shotcrete accelerator, based on Al-sulfate, Al-trifluoride and etanolamines as active chemical components. The shotcrete accelerator dosage was 9% of



Fig. 6 -- Temperature development in the core of the concrete samples: 1. Cold concrete – Warm storing, 2. Warm concrete - Warm storing, 3. Warm concrete - Cold storing, 4. Cold concrete - Cold storing.

cement weight in all samples., and strength development was measured with penetration needle and Hilti-method.²

EXPERIMENTAL RESULTS AND DISCUSSION

The methods for measuring early strength is based on penetration needle 0 - 1 N/mm² (0 - 0.15 ksi) and Hilti-method from ~2 N/mm² (0.29 ksi). None of these two methods are exactly correct and both methods will have a certain error-field.¹ It is therefore harder to distinguish compressive strength levels within the first hours, due to the fact that values are not really significantly different. Temperature development inside concrete samples is believed to be a more accurate measurement, as long as the thermocouple is placed in the same position inside the concrete samples.

In the temperature graph **Fig 6**, it is clear that both samples which are sprayed with warm concrete hold the highest temperature during the first two – three hours. From approximate three hours, the temperature inside the samples seems to be mostly influenced by the temperature in the surroundings. The set of four samples are split into two groups where the two samples which are stored in warm conditions are following more or less the same line. The two concrete samples which are stored cold, seems to have a small difference in temperature from 3 - 24 hours, and it seems like the one sample which was made with warm fresh concrete is continuously 2-3 °C (4-5 °F) higher in temperature compared to the neighbor sample which is made from cold fresh concrete. Generally, the temperature development in all four samples is following the expected and theoretical scenario.

When it comes to strength development, the picture is not so clear and might not follow the expected and theoretical scenario in **Table 4.** The sample believed to have the toughest conditions, cold concrete – cold storage, is showing the lowest value for temperature during

	30 min	60 min	6 hours	12 hours	24 hours
Cold concrete, warm	0.4 (0.058)	0.5 (0.072)	2.7 (0.392)	5.1 (0.740)	6.5 (0.943)
storing					
Cold concrete, cold	0.5 (0.072)	0.7 (0.102)	1.7 (0.247)	2.1 (0.305)	3.9 (0.567)
storing					
Warm concrete, cold	0.6 (0.087)	1 (0.145)	2.1 (0.305)	3.5 (0.508)	7.7 (1.117)
storing					
Warm concrete, warm	0.4 (0.058)	0.7 (0.102)	3.5 (0.508)	6.4 (0.928)	10.8 (1.566)
storing					

Table 4 -- Compressive strength N/mm² (ksi) in concrete samples:

the whole period, and is also having the lowest compressive strength at 6, 12 and 24 hours. At 30 and 60 minutes, however, it is more or less similar to its opposite, warm concrete – warm storage. Again, the values at 30 and 60 minutes are measured with penetration needle which is a rather manual method. The spraying equipment might also influence the strength development in the surface of the sample. It is important that accelerator is homogenously distributed in the concrete in the spraying process and that the concrete is evenly compacted all over, and between the parallel samples. The spraying thickness of these samples was approx. 10-12 cm (4-5 in).

As described in the Background, the recommended fresh concrete temperature in Norway is normally +20 °C (68 °C). It is however, not unusual to see temperatures quite above +20 °C (68 °C), as the concrete producer wants to be on the safe side. It has also been seen examples of too cold fresh concrete being delivered and used in projects. +13 °C (55.4 °F) might be way too low, but in this experiment cold water and cold aggregates gave +13 °C (55.4 °F).

FURTHER RESEARCH

The shotcrete test center will further be used to test conditions regarding cement quantity and type, water cement ratio, aggregates, concrete admixtures (plasticizers, slump stabilizers), concrete temperature and consistence, and the dosage effect of accelerators.

CONCLUSIONS

Based on the results of this experimental investigation the following conclusions are drawn:

1. Warm fresh concrete seems to be important for the strength development within the first hour.

2. At 6, 12 and 24 hours, the temperature in surroundings has a stronger effect on strength development compared to fresh concrete temperature.

3. At 24 hours the one sample with both cold fresh concrete and cold storage has obtained significantly lower strength compared to the three other samples. This single sample does also show the lowest strength value at 6 and 12 hours.

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Designing Alternative Binders Utilizing Synergistic Reactions

by Harald Justnes and Tone Anita Østnor

Alternative binders are defined as binders without portland cement. Two synergy principles have been described for making improved binders based on slaked lime and pozzolanic SCMs. One showing how neutral salts may accelerate by forming strong alkaline solutions in situ and another showing how calcium carbonate can play a role when alumina containing SCMs are used by leading to an even higher conversion of liquid water into solid hydrates, which subsequently leads to lower porosity and higher strength. Examples are given when the SCMs are calcined kaoline clay contaminated with feldspar and calcined smectite rich marl, respectively. Mortar strengths exceeding 25 MPa (3626 psi) when cured at ambient temperature for 28 days were achieved. Predicted phases in the microstructure, such as calcium monocarboaluminate hydrate, were confirmed by X-ray diffraction. Other details of the microstructure were studied by capillary suction of water, thermal analysis and scanning electron microscopy.

Keywords: Alternative binders; Accelerators; Calcined clay; calcium carbonate; SCM; Synergy.

INTRODUCTION

Alternative binders are here defined as binders without portland cement. In this paper, the alternative binders are based on calcined clay as a source of reactive silica and alumina in combination with lime and calcium carbonate to stabilize special calcium aluminate phases such as calcium monocarboaluminate hydrate. Gaining strength is all about maximizing the transformation of liquid water to hydrates with hydraulic properties as fast as possible. Hence, admixtures speeding up the reaction kinetics can be part of the formulations as well.

Lime mortars were used by the Romans who also discovered that these mortars became stronger when blended with supplementary cementing materials (SCMs) such as volcanic ash, diatomaceous earth or even crushed, ground ceramics. In terms of today's demand of sustainability with minimized CO_2 emissions, these binders were even worse than portland cement due to their higher CaO content coming from limestone (unless totally re-carbon-ated), and the present alternative binder concept is therefore trying to minimize the required lime content relative to SCMs. However, with the requirement of fast construction of the

modern world, accelerators are crucial for fast hardening. The alternative is curing at elevated temperatures for prefabricated elements.

Synergy principles are described on how inorganic binder alternatives to portland cement can gain strength more rapidly at ambient temperature. One example shows how neutral salts may accelerate binders by forming strong alkaline solutions in situ to avoid hazardous handling of high pH chemicals and another example how calcium carbonate can form calcium monocarboaluminate hydrate when alumina containing SCMs are used. The latter principle will lead to an even higher conversion of liquid water into solid hydrates that subsequently lead to lower porosity and higher strength.

RESEARCH SIGNIFICANCE

The research is focused on making cement-less binder that is more environmentally friendly than portland cement. For instance binders based on less high quality raw materials, for instance ordinary blue clay or marl (clay containing limestone). These materials are also calcined at a much lower temperature (800° C or 1472° F) than portland cement clinker (1450° C or 2642° F) leading to less energy consumption and CO₂ emission. The required lime is kept at a minimum since it inevitable will lead to CO₂ emission coming from limestone, but it is still calcined at lower temperature (900° C or 1652° F) saving energy.

UTILIZING SYNERGISTIC REACTIONS IN DESIGNING ALTERNATIVE BINDERS

The reaction rates for SCM/lime binders are increased by high pH, but since solutions with high pH are hazardous to handle, the first synergy principle is to find accelerators that by themselves are close to neutral but that will generate high pH in situ in reaction with lime. The second synergy principle is to combine the lime/calcined clay blend with calcium carbonate (limestone) so that the calcium aluminate hydrates formed by the pozzolanic reaction between lime and clay will react further with calcium carbonate and form calcium carboaluminate hydrates. This last step will lead to increased transfer of liquid water to solid hydrates and therefore contribute to higher strength. An alternative to calcium carbonate in the second principle is to use calcium sulphate that depending on the ratio to the reacted aluminate from the clay will form ettringite (AFt) or calcium monosulphoaluminate hydrate (AFm). However, using calcium sulphate may lead to unwanted excessive expansion by AFt.

Principle of accelerator synergy

To speed up pozzolanic reactions between lime and SCMs, highly alkaline solutions are usually effective and work merely as catalysts as sketched for the reaction loop of limesilica fume by Justnes¹ (using cement chemist's short hand notation; C = CaO, $S = SiO_2$, $H = H_2O$, $N = Na_2O$ and $K = K_2O$):

$$S(s) + (N,K)H(aq) \rightarrow (N,K)SH(aq) \uparrow +$$
(1)

 $CSH(s) + (N,K)H(aq) \leftarrow CH(aq \text{ or } s)$



Fig. 1 - Comparison of compressive strength (relative to 63.9 MPa at 84 days = 100%) development of mortar with reactivity of silica fume in the cementitious material lime /SF with C/S = 1.11 and water-to-solid ratio 0.70.¹

Reaction (1)) is leads to the well-known overall pozzolanic reaction;

$$S + CH = CSH \tag{2}$$

Alkalis are very important, as blending pure lime (CH) and pure silica fume (S) will take several days to harden, while using simulated pore water of pH 13.5 gives decent 3 day strength¹ at ambient temperature as shown in **Fig. 1**. However, for the sake of the work-environment, strong alkalis present a hazard to handle. It is much safer to handle neutral, soluble salts that will form alkali hydroxides in situ when reacting with calcium hydroxide. This is the first synergy principle, and the only requirement of the neutral alkali salt is that its anion will form insoluble calcium salts:

$$xCa(OH)_2 + 2(Na,K)_xA = Ca_xA_2(s) + 2x(Na,K)OH$$
 (3)

Such possible salts are listed in **Table 1** together with the solubility product (K_{sp}) of their corresponding calcium compounds and the equilibrium concentration of calcium. The lower the [Ca²⁺] for salts relative to Ca(OH)₂, the more reaction (3) is expected to be shifted to the right, and the more effective the accelerator is expected to be. **Fig. 2** shows strength development for lime -silica fume mortars with different accelerators capable of giving pH 14.2 in pore water if Eq. 3 was shifted all the way to the right. In terms of 1 and 3 days compressive strength, the order of efficiency is Na₃PO₄ > NaF > Na₂CO₃ > K₂CO₃ > 2K₂CO₃ + Na₂CO₃ > KF > Na₂SO₄. It is not known why potassium salts do not perform as well as the corresponding sodium salts, but potassium is thought to have higher affinity to be bound by the CSH gel than sodium, which may be the reason. It is important to note that the common sodium sulphate does not perform very well, while sodium carbonate does due to much less soluble calcium carbonate than gypsum.

Table 1 - The solubility product (K _{sp}) and equilibrium concentration of
calcium for salts of general composition Ca_xA_2 (A = anion). x is the factor in
Eq. 3

X	Α	\mathbf{K}_{sp}	[Ca ²⁺] (mM)
1	OH-	5.5.10-6	11.1
1	F-	5.3.10-9	1.1
2	CO3 ²⁻	2.8.10-9	0.053
2	SO4 ²⁻	9.1.10-6	3.0
3	PO4 ³⁻	2.0.10-29	0.019



*Fig. 2 - The compressive strength evolution of silica fume/ lime mortars*² *with equimolar dosage of different accelerators (i.e. capable of forming same amount of OH).*

Principle of maximizing volume of hydrates

Silica fume is the simplest SCM chemically, while aluminosilicates like fly ash and calcined clays are much more complex. In addition to producing amorphous CSH in their reaction with lime, they can also form a wide range of crystalline calcium aluminate hydrates (CAH), including mixed products (CASH) like strätlingite, C₂ASH₈.

The CAH formation opens up for another principle of synergy to convert even more liquid water into solid hydrates, and hence reduce porosity and increase strength. Let us for simplicity assume the CAH to be calcium aluminate hexahydrate (C_3AH_6) that will react with limestone to form calcium carboaluminate hydrate (\underline{C} is short hand for CO₂). According to Eq. 4, 100 g calcium carbonate (1 mol) would then bind 90 g (5 mol) extra water. The total increase in volume of solids according to Eq. 4 is then (2.618-(0.375+1.500))·100vol%/(0.375+1.500) = 40 vol%. So with a lot of C_3AH_6 produced, this will matter.

$$C\underline{C} + C_3AH_6 + 5 H = C_4A\underline{C}H_{11}$$
(4)

m = 1.00 g 3.78 0.90 5.68 M = 100.09 g/mol 378.29 18.02 568.50 n = 9.99 mmol 9.99 49.95 9.99 p = 2.67 g/ml 2.52 0.998 2.17 V = 0.375 ml 1.500 0.902 2.618

Oxide	NORCEM FA	STEAG FA	Marl	Clay
SiO ₂ , %	52.9	38.7	49.6	61.7
Al ₂ O ₃ , %	26.4	19.6	18.1	30.5
Fe ₂ O ₃ , %	6.3	6.0	10.6	3.5
CaO, %	3.3	17.9	14.1	0.1
MgO, %	2.8	2.0	2.9	0.4
K ₂ O, %	3.0	2.5	2.4	3.3
Na ₂ O, %	1.0	0.7	0.7	-
SO3, %	0.2	6.6	0.5	-
Sum above, %	95.9	94.0	98.9	99.5
Blaine, m ² /kg (ft ² /lb)	250 (4.88)	734 (14.34)	-	-
Density, g/cm ³ (lb/ft ³)	2.2 (137)	2.6 (162)	-	-

 Table 2 - Chemical composition and physical properties of fly ashes, marl

 and clay

The above synergy principle has been studied for fly ash blended cement with limestone, and it has been shown that the fly ash blended cement containing limestone resulted in higher compressive strength than without.³⁻⁶

MATERIALS AND EXPERIMENTS

Materials

Since the source of aluminosilicate for the alternative binder can be both fly ash (FA) from coal fired energy plants or from calcined clay (after all, fly ash comes from clay contaminations in the coal) and marl (mixture of clay and calcium carbonate), both sources were tried initially with compositions as given in **Table 2**.

Designing binders

Both calcined clays and fly ashes are largely aluminosilicates and the binder mix design was based on the proceeding reasoning. As a first approximation we can say that the maximum consumption of lime (CH) for all silica (S) is molar 1:1 according to the following reaction (using cement chemist short hand notation where C = CaO, $S = SiO_2$, $A = Al_2O_3$, $\underline{C} = CO_2$, $\underline{S} = SO_3$ and $H = H_2O$):

$$CH + S = CSH$$
(5)

The maximum consumption of lime (CH) for all alumina (A) is molar 3:1 according to the following reaction:

$$3 CH + A + 3 H = C_3 AH_6$$
(6)

If gypsum is added to the system in excess, ettringite may form;

$$C_3AH_6 + 3 C\underline{S}H_2 + 26 H = C_3AH_6 \cdot 3\underline{C}S \cdot 32H$$
(7)

If too little gypsum is added, ettringite may convert to calcium monosulphate hydrate when sufficiently aluminate has reacted to C_3AH_6 or equivalent:

$$C_3AH_6 \cdot 3C\underline{S} \cdot 32H + 2 C_3AH_6 = 3 C_3AH_6 \cdot C\underline{S} \cdot 12H + 8 H$$
 (8)

But if excess limestone (C<u>C</u>) is added with it, the initially formed ettringite being good for early strength will be stabilized since calcium monocarboaluminate hydrate will form instead:

$$C_3AH_6 + C\underline{C} + 6 H = C_3AH_6 \cdot C\underline{C} \cdot 12H$$
(9)

So there should be a content of gypsum (3:x) to improve early strength and the rest of the A balanced with limestone (1:1-x) for later strength in order to avoid detrimental delayed ettringite formation (DEF) in a dense system. The gypsum should be kept so low that the initial ettringite formation does not lead to unacceptable expansion in the early age.

The mortars were made according to **Table 3**, while paste mixture compositions are given in **Table 4**. The w/b ratio was 0.63 in all the mortars while maintaining the flow by varying the amount of superplasticizer in the range 0.4 - 2.0% (of binder weight). The mortar mixes were cast in 40x40x160 mm (1.575x1.575x6.300 inch) moulds and ϕ 100x200 mm (ϕ 3.937x7.874 inch) cylinders. After 24 hours the prisms and cylinders were removed from the moulds and stored in a cabinet at 90% RH and 23 ± 2 °C (73±2 °F).

Strength measurements

The compressive and flexural strength were measured on the 40x40x160 mm (1.575x1.575x6.300 inch) prisms at 1, 3, 7, 28 and 90 days of curing at 90% RH and 23 °C (73°F) according to EN 196-1.⁷ There were 3 parallel prisms for the flexural strength and six parallels for the compressive strength since it was measured on the end-pieces of the three prisms.

Capillary suction measurements

The capillary suction technique was performed on four parallel 20 mm (0.787 inch) slices sawn from cast cylinders from each mortar mixture. The specimens were dried at 105° C (221°F) drying before capillary suction measurements.

The procedure consists of 6 important steps for the specimen:

1. Drying the specimen to constant weight at 105°C (221°F)

2. Water saturation by submersion 3 days in water at 1 atm (14.7 psi)

3. Pressure saturation by submersion 3 days in water at 80 atm (1176 psi)

4. The external volume (V) is recorded by differential weighing the specimen under water and saturated surface dry in air according to the principle of Archimedes.

5. Drying the specimen to constant weight at 105°C (221°F)

After these 5 steps, the initial moisture content, total porosity (ε_{tot}), capillary porosity (ε_{cap}), entrained air volume (ε_{air}), average density of mortar solids (ρ_s) and dry density of mortar (ρ_d) were calculated as described more fully by Justnes et al.⁸