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Mortar and concrete based on calcium sulphate binders

Abstract

In this study both hemi-hydrate and anhydrite are tested as calcium sulphate binders for structural mortar and concrete. The advantage of using calcium sulphates instead of cement as a binder is the fact that the production of calcium sulphate is more environmental friendly than that of cement. For the calcinations of Portland cement, temperatures up to 1480 °C are needed, while the calcination of for instance hemi-hydrate requires a temperature of 170 °C. The global cement industry produces around 1.4 billion tons of CO₂ per year. This is about 6% of the total CO₂ production and thus it has a significant influence on the global warming of the earth /1/. Partially replacing cement by calcium sulphate binder could be one way to decrease the CO₂ production.

Applying new methods on gypsum based concrete could result in a type of concrete with a compressive strength up to 30 N/mm². With the right physical properties like flow ability and segregation resistance this could even be self compacting gypsum concrete (SCGC). Downside of the material is that, unprotected, it can only be used indoors, since it is non water-resistant. The calcium sulphate based concrete that has a compressive strength around 30 N/mm² can have different potentials of appliance. First of all it could replace cement based concretes where low to medium compressive strengths are required. Another application could be gypsum boards. These gypsum boards may be a good alternative for the use of drywall. The gypsum boards are stronger and can be self supporting, while dry wall has to be supported by a steel frame or wall. When the right aggregates and fillers are used these gypsum boards could even be produced at a lower cost than the dry wall, since the hemi-hydrate can be partially replaced by cheaper materials like sand and gravel.

In this study first attempts to develop a competitive concrete based on gypsum are reported. This development follows new mix design methods, based on PSD optimization and oxide balancing, in order to reduce the free water in the hardened gypsum concrete. More detailed information on the study described in this article can be found in the Bachelor thesis of the first author/2/.

Theory

PSD optimization

Optimizing the particle packing can be achieved by considering the right particle size distribution (PSD) for the mix as a whole. The mix design should be build up in such a way that the PSD grading line of the concrete mix as a whole follows a smooth predefined line, the modified Andreasen and Andersen curve. This can be achieved by adding fillers and aggregates with different particle size distributions in the right proportions. Previous experiments prove the positive effect this method has on self-compacting concrete $\frac{2}{4}$. For this study the PSD of the mix will be optimized by adding different filler materials like limestone or trass. An improvement in the particle packing of a concrete mix results in better physical and mechanical properties of the

concrete mix. The flow ability of the fresh concrete mix improves and the fresh mix gets a higher segregation resistance.

When the water content of a concrete mix is reduced, the capillary pores formed by the excess in water will also be reduced. This should give the hardened gypsum concrete a higher compressive strength (Figure 1) and better durability /5/. Optimising the particle packing of the mix as described above has a positive influence on the water content needed in the concrete mix. A good particle packing will increase the workability, this means that the required flow ability can be achieved with less water. Besides that the use of a plasticizer or super plasticizer is known to decrease the need for water in concrete mixes, while attaining the same flowability. The optimised mix designs were calculated following the procedure described by Hüsken and Brouwers /6/.

Oxide engineering

A second method to reduce the free water in hardened gypsum concrete is obtained by chemical binding. By enabling ettringite formation during the hydration process water molecules will be fixed chemically into the crystal structure of ettringite. The chemical reaction for the formation of ettringite is as follows:

$$3C\overline{S}H_2 + 3C + A + 26H \rightarrow C_6A\overline{S}_3H_{32}$$
(1)

This should lead to a situation where the ettringite will fill up the pores caused by water while crystallizing the water. Trass and fly ash can be sources of A and C and are believed to have chemical properties that should enable the formation of ettringite during hydration. As an extra source for calcium oxide quicklime will be used.



Compressive and tensile strength versus water/gypsum ratio

Experiments

Since this study has the aim of evaluating the possibilities of gypsum concrete, the main focus was on the workability of the fresh concrete and the compressive strength of the hardened concrete. The workability will be measured with the standard cement concrete slump flow test. These parameters are considered to be the most important for initial

evaluation and can also be relatively easily measured. The influence of retarding admixtures and plasticizers is also tested. The compressive strength and the tensile splitting strength of the hardened concrete are measured according to the norms, EN 12390-3:2001 and EN 12390-6:2000 which hold for standard cement concrete.

First tests were performed with hemi-hydrate as binder and a binder content of 400 kg/m^3 . For the workability the following could be concluded:

- A retarding admixture is needed to prevent the concrete from setting within the first five minutes. Citric acid proved to be useful for the prolongation of the setting time up to an hour.
- It is possible to increase the slump flow with the same super plasticizer as used for ordinary cement concrete (Figure 2). The effect on the slump flow was comparable with the effect a melment plasticizer had on the concrete mix.



Effect of super plasticizer on a mortar mix with hemi-hydrate as binder and limestone as filler (% SP is based on binder).

As the hardening of hemi-hydrate was difficult to control, a new series of tests on both mortar and concrete was done with activated (premix) anhydrite as binder. Premix anhydrite was chosen instead of hemi-hydrate because it is used in practice for screed floors. The composition of two designed concrete mixes are given in Table 1. The results of tests with these concrete mixes are given in Table 2 and described in more detail below.

	Mix 1		Mix 2		— 11
Material	mass (g)	volume (cm ³)	mass (g)	volume (cm ³)	Table
anhydrite (premix)	575.0	197.2	552.3	189.4	1.
Sand 0-1	104.6	39.7	87.4	33.1	Concr
Sand 0-2	0.0	0.0	0.0	0.0	ete
Sand 0-4	611.0	231.3	638.1	241.5	mixes
gravel 2-8	280.8	107.2	297.5	113.5	with
gravel 4-16	473.8	181.8	518.5	199.1	premiz
Water	212.8	212.8	193.3	193.4	ed
air	0.0	30.0	0.0	30.0	anhyd
total	2258.0	1000.0	2287.1	1000.0	Ite as

	Mix 1	Mix 2	T 11 0
compressive strength, 7 days (N/mm ²)	21.65	37.2	Experimental results.
tensile strength, 7 days (N/mm ²)	no data	3.02	
compressive strength, 28 days (N/mm ²)	29.41	no data	
slump flow (mm)	638	280	Compressive strength

The mechanical properties of the gypsum concrete depend, as might be expected, strongly on the binder content. The first tests with a binder content of 400 kg/m³ were unsuccessful since they resulted in a 28 days compressive strength lower than 10 N/mm². Concrete mixes with a higher content, about 550-575 kg/m³ were more successful. A decrease of 30% in the binder content resulted in a 70% drop in the compressive strength of both mortar and concrete. The 7-days compressive strength of 37.2 N/mm² found for Mix 2 gives reason to believe that for the 28-days compressive strength a value of more than 40 N/mm² can be achieved easily.

From the results of the compressive strength tests on the gypsum concrete it becomes once more clear that the water content in the mix also has a large influence on the final compressive strength. In Figure 3 therefore the compressive strengths are set out against the water/powder ratios.



Fig. 3: Compressive strength (Mixes 1 and 2) versus w/b ratio, for anhydrite based concrete.

From the tests on the anhydrite mortars it can be concluded that an optimised PSD curve with addition of for instance fly ash is beneficial for the strength development in mortars. A mortar without filler was found to have a 28 days compressive strength of 5.0 N/mm^2 . A mortar with the same water/binder ratio and the same binder content, but with fly ash as filler, was found to have a 28 days compressive strength of 7.8 N/mm^2 . In Figure 4 it can be seen that the mortar mix containing fly ash has a PSD curve much closer to the target curve than the mix with sand 0-1 mm. It is expected that this is also true for concrete.



Tensile strength

With anhydrite based concrete a value for the tensile strength of 3.02 N/mm^2 was found. This value is in line with the formula used for calculating the tensile strength from the compressive strength for cement based concrete /7/:

$$f_{t} = 0.27 f_{c}^{2/3}$$
(2)

For a compressive strength of 37.2 N/mm^2 , this equation yields a tensile strength of 3.01 N/mm^2 , which is very close to the measured one. This implies that eq. (2), derived for cement based concrete, also seems to hold for gypsum concrete.

Workability

Initial tests showed that concrete based on hemi-hydrate or anhydrite as the only binder, with a binder content of 400 kg/m^3 does not have a good workability. This is due to the fact that the designed mixes should contain more powder materials if one wishes to follow the Andreasen & Andersen curve. Since the only powder material in these mixes is the gypsum, which is restricted by the binder content, the amount of fine powders is too low in these mixes. Therefore it is necessary to add filler materials.

From the anhydrite concrete tests it was found that the water/binder ratio should be in the range of 0.35 to 0.40 for a 'good' workability. This is based on a binder content of $550 - 575 \text{ kg/m}^3$. Since the water/binder ratio is dependent on the binder content it is hard to establish one suitable range for every mix. For this reason one should give more attention to the water/powder ratio of a mix, which enables the replacement of binder by a filler. The water/powder ratio of the anhydrite mixes, with fines being defined all particles <125 μ m, were in the range of 0.34 to 0.37 (Figure 5). Figure 5 shows that a slight decrease in the water/powder ratio has a major effect on the slump flow of the fresh concrete.



Hardness

Some hardness tests were performed on the surface of 7-days old cubes. These tests showed that the surface of the calcium sulphate based concrete cubes is quite soft. With an iron rod one could easily scratch the cube surface. Also the impact of the Schmidt hammer caused some noticeable damage on the surface.

Conclusions

Based on the results of this study it seems possible to compose a calcium sulphate based structural concrete. With a 28 days compressive strength of 35 to 40 N/mm² this material is suitable to have a structural function indoors (and outdoors with a protection against water). However, there are still some points of attention. One of these is the negative impact the water content has on the compressive strength. In order to have a concrete mix with reasonable working properties like slump flow, the water content has to be at such a high level that the compressive strength will be decreased significant. Basically a good balance between workability and strength has to be found, which is not so easy to achieve.

Another challenge is the high binder content needed to give the calcium sulphate based concrete the strengths mentioned above. The required content of 550 kg/m³ is about twice as high as is needed for cement based concrete with the same compressive strength /6/. Despite this, calcium sulphate based concrete could still have an economic and environmental advantage since gypsum is a by-product of the flue gas desulphurization process. It is also a by-product with the phosphate fertilizer refining process, but because of the low radioactive levels this gypsum is not allowed on the commercial market at this moment yet.

Concerning the ettringite formation a more extensive research and analysis is needed. The results indicate that reaction (1) did not (or hardly) take place. From the

information found on ettringite formation it seems to be a delicate and complex process /8/. Temperature, pH-value and concentration of the different substances are all aspects that influence the formation reaction. Therefore an extensive analysis of the reaction products that are in the concrete at different points in time will give a better insight in the hydration process. X-ray analysis could be used for this purpose. Besides this, it is believed that actually the reaction of trass and fly ash is too slow to act as source for aluminium oxide. A better option would be to use pure aluminium oxide, which is available on the market.

In future research the present experience will used as a starting point for further improvement of the mix, e.g. the reduction of binder by the introduction of fillers and the addition of more reactive aluminium oxide (to promote water binding by ettringite formation). The main issue is to find a good balance between workability, reactivity and strength. Another issue that will be addressed is the practical adoption of this new building material. A research on the market possibilities for this product and the requirements in order to be adopted is important for the practical implementation in the market.

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