Influence of the Gypsum Raw Material on the Performance of PCE-based HRWRA during Gypsum Board Production

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ABSTRACT

An extensive experimental series was carried out to test PCE-based superplasticizers in plasters from different gypsum board plants. Although ViscoCrete® G-2 performed very well in the majority of the gypsum binders, the results indicate that no universal additive solution performs best in all binder types. Based on a general understanding of interactions between different gypsum binder components and polycarboxylate polymer design, new target-oriented PCE formulations were developed. These tailor-made solutions are characterized by even further improved plastification at significantly reduced set-retarding effect of the additive.

BACKGROUND

Gypsum Board Production

Gypsum boards are made of a thin core of gypsum between 2 cardboard sheets. It is manufactured in a highly automated continuous process (as described i.e. in /1/). To produce gypsum boards, natural or synthetic gypsum – present as calcium sulfate dihydrate – is transferred by thermal dehydration (so-called ‘calcination’) into purest possible beta-calcium sulfate hemihydrate. The most appropriate calcination procedures and the required burning temperature depend on the raw material type. Particle shape, size and distribution affect strongly the dehydration behavior. Of importance for the binder properties is the fact that the original particle dimensions retain during the calcination process.

The plaster is mixed with water and various additives to form a slurry which is then poured onto a cardboard sheet, homogenously distributed and covered with a second cardboard layer. On a long setting-line beta-hemihydrate reacts with water to form calcium sulfate dihydrate again. The forming crystalline structure causes the setting and hardening process and gives the gypsum board a certain strength. After the setting process, boards are cut from the continuous line to the appropriate length and transferred into the dryer, where excess water is dried out of the boards to give the finished product.

Gypsum Raw Materials

Approximately 60 % of all calcined gypsum originates from natural gypsum and 40 % from synthetic gypsum and the recycling of gypsum products /2/. Most of the synthetic gypsum used in the gypsum industry is FGD-gypsum.

For more than three thousand years sulfate containing rocks are processed manually and in modern times also industrially. With regard to processing and final product quality, the qualitative requirements of the sulfate rocks significantly increased. Gypsum raw material processed from the gypsum industry can be contaminated with (partially large amounts of) other minerals like limestone, dolomite, quartz or clay.

In general, for the manufacture of gypsum products at least 80% of the rock must be gypsum. By sieving and, occasionally, even washing the usual impurities in the natural gypsum deposits can be reduced.

At the end of the 1980s great efforts were made to show the applicability of synthetic gypsum from flue gas desulphurization systems (FGD) in coal-fired power stations for the manufacture of gypsum products. In comparison with natural gypsum there were positive aspects with respect to chemical, mineralogical, physical and biological criteria. Despite initial reservations, it has been established in the ‘Beckert Study’ /3/ that FGD-gypsum can be used for producing building materials without any restrictions.

Besides the mentioned influence of the gypsum raw material on the calcination process, impurities in gypsum raw material can have a negative impact on further processing and final product quality. For example, inert ingredients with high specific surface area increase the water demand of gypsum binder, thus making a negative contribution to the strength development of gypsum products. During gypsum board production impurities can cause discolorations of the gypsum core, but this is less critical if they are not visible through the cardboard. Contaminants such as dissolved salts can be problematic, if they accumulate between the cardboard and the gypsum core (for example during the drying process) and affect negatively the cardboard adhesion. Furthermore, adverse effects of impurities on the effect of additives are known.

Water Demand

Pure β-hemihydrate stoichiometrically requires 18.62% of its own weight of water to rehydrate to gypsum (CaSO₄ · 2H₂O). With other words, the theoretical water demand – expressed as water/binder-ratio (w/b) – is 0.1862. To produce a flowable slurry, excess water is required. Typical water demand of plaster of Paris is above w/b = 0.50. That results in the fact, that today large amounts of excess water (65-75 % of total water) must be evaporated from the board after rehydration of the plaster.

Up to ½ of total energy utilization in gypsum board production is consumed in the drying stage. Especially in today’s times of rising energy costs and shortage of resources (fossil fuels and water), there is rising interest in reducing the water content of the plaster slurry. Additionally, by reducing the evaporative load to a minimum, line speed and therefore yield of the board plant can be maximized. Furthermore, a substantial water reduction contributes to the improvement and stabilization in gypsum board quality.

As described in /1, 4/, the gypsum raw material source, gypsum processing as well as numerous other factors influence the gypsum board production process and the end product properties. Today great efforts are made by the gypsum industry to reduce the water consumption and with it the negative impact on manufacturing process and end product quality (i.e. /5/).
It is common practice to add dispersing agents to binder slurries to achieve reduced water content at a given flowability (or to increase slurry flowability at given water content). This allows shortening the drying step, which is beneficial with respect to energy savings and reduction of total production costs.

**High-Range Water Reducing Additives (HRWRA)**

Plasticizing agents are surface-active substances. There are currently four families of fluidizing agents used: lignosulfonates, sulphonated naphthalene formaldehyde condensates (NFS), sulphonated melamine formaldehyde condensates (MFS) and polycarboxylates (PC).

Most efficient plasticizers are polycarboxylate based, such as Sika® ViscoCrete® product family. The high dispersing effect is based on electrostatic repulsion – which show all plasticizers – and on a steric repulsion of the particles /6/. Today, those high-range water reducing additives (HRWRA) are widely spread in the field of concrete technology. Based on the variability in polymer design, in the past 25 years several PCEs were customized for specific applications (such as ready-mix and precast concrete).

In contrast to cementitious systems, in gypsum based systems conventional plasticizers based on melamine or naphthalene sulfonate condensates are still widely used today. When most currently available PCEs are applied in plaster systems, they cause an insufficient plastification and must therefore be used at high dosages. In addition, they often lead to a strong retardation of the setting of plasters. Especially in the manufacture of plasterboard this is a great disadvantage, because the setting time determines the speed of the production process.

As it was studied by HAMPEL ET AL. /7/, the structure of the polymers affects the liquefaction of calcium sulphate phases differently than it is known from cementitious systems. Deep understanding of the gypsum-PCE interaction was needed to develop superplasticizer tailored to the requirements of the gypsum industry. In /1/ the large-scale applicability of the new superplasticizer generation was exemplary proven.

**RESULTS AND DISCUSSION**

In the following, selected results from the development of customized solutions for gypsum board producers are presented. In a large test series, 20 different industrially produced plasters provided by gypsum board producers were investigated. Table 1 contains some essential characteristics of the selected binders A-G.

**Table 1: Characterization of selected plasters**

<table>
<thead>
<tr>
<th>Binder</th>
<th>Gypsum source</th>
<th>Impurities</th>
<th>Calcium sulfate phases</th>
<th>BET surface</th>
<th>Water demand (as w/b)</th>
<th>Initial setting</th>
<th>End of setting</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>FGD</td>
<td>—</td>
<td>4.05 77.00 4.40</td>
<td>7.95 0.64</td>
<td>2:15 7:25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>natural</td>
<td>quartz, dolomite, clay</td>
<td>3.90 74.45 0.60</td>
<td>7.23 0.67</td>
<td>2:30 6:50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>natural</td>
<td>quartz, limestone, dolomite, clay</td>
<td>0.00 85.20 2.95</td>
<td>5.35 0.58</td>
<td>3:15 9:45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>natural</td>
<td>quartz, dolomite</td>
<td>22.95 42.00 9.50</td>
<td>6.45 0.77</td>
<td>2:20 7:20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>natural</td>
<td>quartz, limestone, dolomite, clay</td>
<td>0.00 85.40 2.80</td>
<td>n.d. 0.58</td>
<td>5:45 12:15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>FGD</td>
<td>—</td>
<td>0.00 81.50 4.10</td>
<td>n.d. 0.60</td>
<td>2:30 8:05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>natural</td>
<td>quartz, dolomite</td>
<td>0.00 65.20 9.30</td>
<td>n.d. 0.55</td>
<td>3:30 10:55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The selected binders represent a large variety in gypsum raw material sources and processing (milling and calcining) technologies. Especially natural gypsum based plasters partially contained large amounts of impurities like quartz, limestone, dolomite and clay. Next to the purity of the raw material, the graphimetric phase analysis pointed out large differences in calcium sulfate phase composition of the binders as a result of differing calcining procedures.

To further describe the materials, images of selected plaster samples were taken by scanning electron microscopy (SEM). Figure 1 and 2 show exemplary the differences in particle size, shape and distribution between FGD- and natural gypsum based plasters. Binders based on FGD gypsum show a relatively uniform particle size distribution, where compact particles with the typical gypsum crystal morphology are visible. In contrast, binders based on natural gypsum show the typical wide particle size distribution of a milling product.

Additional information about the mineral composition of the specimen was generated by energy-dispersive X-ray spectroscopy (EDX) analysis conducted by means of SEM (Figure 3 and 4). Binders based on FGD gypsum were identified to be mainly consisting of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ with low contents of limestone and carbon black. In contrast to that, selected natural gypsum based binders contained large amounts of impurities like limestone, dolomite, quartz and clay.

Fig. 1: SEM-image of plaster based on FGD-gypsum (A)

Fig. 2: SEM-image of plaster based on natural gypsum (C)

Fig. 3: SEM-EDX-image of plaster based on FGD-gypsum (A)

Fig. 4: SEM-EDX-image of plaster based on natural gypsum (B)
Following the large variety in mineral composition, physical binder properties like water demand and setting times differ strongly, too. For example, the water demand to produce a plaster slurry with similar flow behaviour (slump flow 120…130 mm) varied from w/b = 0.55 to 0.77.

The influence of a conventional naphthalene based plasticizer and a PCE-based product developed for gypsum applications (Sika® ViscoCrete® G-2) was tested. The shown results of four different plasters A-D are representative for all 20 samples tested:

- Sample A stands representative for 7 different FGD-gypsum based plasters
- Sample B stands representative for 2 different natural gypsum based plasters
- Sample C stands representative for 5 different natural gypsum based plasters
- Sample D stands representative for 6 different natural gypsum based plasters

Based on a general understanding of interactions between gypsum binder components – different calcium sulphate phases as well as impurities – and PC-molecule design, new target-oriented PCE formulations were developed. Main focus of this development step was on improved liquefaction at reduced retarding effect of the additives. The influence of different PCE formulations (A1, A2, B1, B2, B3) on the slump flow and setting time of different plasters versus a reference ‘gypsum-PCE’ formulation (0) was tested. As diagrams 2 -4 show, an adaption of the PCE formulation can have a significant impact on the additive effect. Both, improved flow properties, as well as significantly decreased setting times can be achieved by adjusting the additive formulations. This concerns plasters based on FGD-gypsum (F), as well as plasters based on natural gypsum (E, G). As expected, it turned out that the additive formulation which performs best in one particular binder is not necessarily the best performing in another binder. This result indicates that no universal additive solution exists for all binder types.

As visible in diagram 1, the conventional product showed a constantly low liquefying performance in all plaster types. In contrast, the gypsum-PCE performed at the same dosage much better in plasters based on FGD-gypsum as well as in most natural gypsum based binders. Especially in different natural gypsum sources, ViscoCrete® G-2 showed big fluctuations in liquefying performance. In 18 out of 20 different plasters (i.e. plasters A, C and D), the product performed well to very well. In average, for the same plastification the dosage ratio compared to naphthalene was 1 : 3…4. Especially in some natural gypsum based binders the dosage ratio went up to 1 : 5 (i.e. plaster D).

Two natural gypsum plaster samples were incompatible with the PCE-based plasticizer (i.e. sample B). In both cases the origin of the incompatibility was identified as impurities within the gypsum raw material.
Diagram 2: Influence of different PCE formulations (dosage constantly 0.2 %) on flow and setting-time characteristics of plaster E (natural)

Diagram 3: Influence of different PCE formulations (dosage constantly 0.2 %) on flow and setting-time characteristics of plaster F (FGD)

Diagram 4: Influence of different PCE formulations (dosage constantly 0.2 %) on flow and setting-time characteristics of plaster G (natural)
In a positive example, at the same superplasticizer dosage, the slump flow of the plaster slurry increased from 190 mm to 202 mm, while the end of setting was reduced from 14:30 min to 10:45 (plaster G, PCE formulation B3). To compare the result with the performance of a conventional plasticizer: At the given low water/binder-ratio a naphthalene based product does not meet the flowability requirements but still causes setting times in the range of the adapted PCE formulation.

SUMMARY AND CONCLUSIONS

First, a systematic study of polycarboxylates with different polymer architecture was carried out to understand fundamental relationships between polymer structure and mode of action as HRWRAs in calcium sulphate systems. Based on these results, a superplasticizer tailored to the requirements of the gypsum board production was designed /7/. In large-scale trials it was proven, that the product is a cost-efficient solution to substantially reduce the water content of the plaster slurry (to reach a defined level of fluidity) /1/.

Further tests with different gypsum raw materials and at varying plant-specific parameters showed performance fluctuations of the existing additive. Based on a general understanding of interactions between gypsum binder components – different calcium sulphate phases as well as impurities – and polycarboxylate polymer design, new target-oriented PCE formulations were developed. These tailor-made solutions are characterized by even further improved liquefaction at significantly reduced set-retarding effect of the additive.

Although ViscoCrete® G-2 performed very well in the majority of the gypsum binders, the results indicate that no universal additive solution performs best in all binder types. To fully use the high performance potential of the PCE-technology, tailor-made solutions must be developed for gypsum systems in analogy to the already advanced application of PCE-based superplasticizers in cement systems. On basis of the generated knowledge, gypsum board manufactures can be supported individually by finding customized solutions for each plant.

REFERENCES

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