GYPSUM
NEW BENCHMARK IN GYPSUM RETARDATION

REPRINT OF PAPER PUBLISHED IN CEMENT 12 2012
ABSTRACT

The manufacturing of consistent, high quality, yet economical construction materials is essential for the continued success of a building material producer. In today’s dry-mortar and gypsum industry, challenges such as varying raw-material qualities, rising energy prices and stricter health and environmental regulations need to be addressed and solutions found in an efficient manner.

To ensure the desired application and end-product properties, dry-mortar and gypsum formulations need to be balanced multi-component systems in which each ingredient has to perform reliably.

In our investigation, various commercially available gypsum retarders were tested for their efficiency and compatibility with numerous mix-design components. A new high-performance gypsum retarder – Retardan-200 – was found to set a new standard in retarding efficiency without demonstrating the known negative characteristics of existing technologies.
BACKGROUND

Application fields

Gypsum binders are used in different application fields where the properties of the building material gypsum can vary significantly. Once the suitable gypsum raw materials and calcining methods have been selected, binders tailored to the needs of the specific application can be produced. Nevertheless, the efficient production of high-quality products such as gypsum boards, self-leveling screeds and underlayments would not be possible without the use of chemical additives today.

Gypsum boards, on one hand, are produced in a highly automated continuous process. Quick setting and hardening is of crucial importance to run the production at high speed for maximum capacity utilization. The use of calcined gypsum (mainly consisting of beta calcium sulfate hemihydrate, CaSO4 \(\cdot\) \(\frac{1}{2}\)H2O) in combination with highly effective accelerator, especially, fine ground gypsum (calcium sulfate dihydrate, CaSO4 \(\cdot\) 2H2O) is currently state of the art. Consequently, in this process, hydration and therewith the setting process would start immediately after binder contact with water. This increases the water demand of the binder and potentially causes process interruptions. To avoid these problems, the beginning of setting needs to be delayed. By utilizing a very low dosage of retarder, one can ensure complete homogenization in the mixer and a uniform distribution of plaster slurry at the forming table.

Calcium sulfate dry-mixes, on the other hand, must be designed to give the individual user enough time for their application. Typical gypsum binders are calcium sulfate hemihydrate in alpha or beta form, anhydrite, or a combination of these phases. While hemihydrate typically hydrates within a few minutes after water addition, anhydrite needs to be activated to react in the required time frame. So-called ‘alkaline activation’ by addition of a few percent of CaO, Ca(OH)2 or Portland cement as well as so-called ‘sulfatic activation’ (i.e. by K2SO4 addition) or a combination of both are currently state of the art. The activator dosage is mainly driven by the needed strength development requirements. In addition, it is not uncommon to require a retarder in order to ensure that a certain workability time is available.

Retardation of gypsum binders

Crystallization process generally includes two steps: dissolution and precipitation. In case of plaster hydration, beta-hemihydrate releases Ca2+ and SO42− ions to the liquid phase. Gypsum has a lower solubility than beta-hemihydrate at room temperature, causing it to precipitate from the supersaturated solution. The crystallization of gypsum follows the law of nucleation and crystal growth.

The rate of gypsum binder setting can be precisely controlled by the use of additives. Those additives that interfere with the nucleation are known to have a significantly stronger effect than substances that operate by affecting the solubility. Examples are fine ground gypsum – a highly effective set-accelerator which is used during wallboard production – and retarders.

Various alternative gypsum retarder technologies exist. Retardan is well known as an efficient retarder and has been used in the gypsum and dry-mortar industry for decades. In contrast to significant quality variations of fruit acids, this amino acid based retarder has consistent manufacturing repeatability which results in a uniform and high additive quality. Retardan L (liquid form) and Retardan P (powder form) are still the benchmark for high quality gypsum products, especially when high tolerance with regards to changes in pH value is needed /1/. Other common alternative gypsum retarder technologies are phosphates and phosphonates in acid or salt form, and protein hydrolysates.

Retardan-200 L, a retarder for controlling setting time of gypsum binders, is based on modified amino acid, and was developed to satisfy the market need for a retarder that would minimize and/or eliminate the negative side effects of the traditional retarder technologies. In the present study, the applicability of this new additive versus existing technologies was investigated.

INVESTIGATIVE METHODS AND MATERIALS

Retarder tests were performed on various industrially produced plasters based on FGD gypsum and natural gypsum. Common commercially available retarders were compared, including technologies based on amino acid and protein hydrolysate and citric acid.

The setting behavior of the plaster was characterized by common penetration procedures (knife cut for initial setting and thumb pressure for final setting) as well as continuously by ultrasonic testing. The plaster hydration process was analyzed by following the heat development of this exothermal reaction. For rheological measurements, a cylinder of 50 mm inner diameter and height of 50 mm was used. The spread diameter of the dispersion, as the average of two perpendicular diameters, was defined as slump flow.
RESULTS AND DISCUSSION

Retarding efficiency
As described above, a time frame is required for the application of calcium sulfate based dry-mortars. In most cases, it is given only by the use of retarders. One example is the evaluated alpha-hemihydrate binder for the manufacture of self-leveling underlayments. The effect of different powder retarders on binder setting and hardening was evaluated continuously by ultrasonic testing. The result is shown in Diagram 1.

Without retarder, significant binder setting is evident within 30 minutes. At constant additive dosage, tested retarders performed very differently: citric acid had the weakest effect, followed by amino acid A and protein hydrolysate. The strongest set-retarding effect was shown by the Retardan-200 P. This study also shows that a much lower dosage of Retardan-200 P can be used to achieve the same retardation as compared to the other tested additives. Selected retarders have also been tested in plaster based on beta-hemihydrate. This binder is typically applied in wallboard production but also in dry-mortars i.e. for manufacture of self-leveling screeds. The additive effect on setting, hardening and hydration is shown in Diagram 2 and Diagram 3.

The parallel increase of all temperature and ultrasonic velocity curves indicate that hydration, and associated gypsum crystal growth (which causes setting), simply start at later times. Once started, the setting process runs apparently unaffected. There is no further selective inhibition of crystal growth, as seen in the case of citric acids /2/. Therefore, all tested retarders are suitable for wallboard production and lead to fast strength development without final strength loss. The results confirm that Retardan-200 L is a significantly stronger gypsum retarder than tested amino acid A and protein hydrolysate. The potential for dosage reduction is illustrated in Diagram 4.
Diagram 4 also shows that for all tested substances, plaster setting time correlates with retarder dosage. In addition, it confirms that the retarding efficiency rises from amino acid A to protein hydrolysate and even more to Retardan-200 L. As one example, when comparing additive dosage at 40 minutes setting time, only about 30% of Retardan-200 L is required versus the protein hydrolysate, and less than 20% versus dosage of amino acid A.

Rheological influence
As described above, the use of accelerator is required for efficient wallboard production. When common fine-ground gypsum is used, the formation of gypsum crystals starts immediately after contact with supersaturated solution (in the plaster slurry). That leads to deterioration of the flow behavior. The addition of retarder should prevent this negative effect.

Table 1: Influence of retarders on slump flow of accelerated beta-hemihydrate plaster slurry (0.1% accelerator)

<table>
<thead>
<tr>
<th>Retarder Type</th>
<th>Dosage (% of pure active subst.)</th>
<th>Slump flow (mm) - Natural plaster (w/g=0.70)</th>
<th>Slump flow (mm) - FGD plaster (w/g=0.65)</th>
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<td>- blank</td>
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<tr>
<td>Amino acid A</td>
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As shown in Table 1, all retarders tested significantly improve the flow behavior of accelerated plaster with both natural and FGD-gypsum. Interestingly, dosage variations of Retardan-200 L do not have an influence on the slump flow. As generally known, during hydration, water gets chemically bound and new crystals are formed thus increasing the requirement for water. It is obvious, that the retarder prevents the hydration and the formation of new surfaces due to crystallization. Thus the retarders tested had a positive side effect: They act as water reducers. An optimized gypsum board formulation can be designed in a way that the crystal growth starts immediately after the mixing and forming process. Thus, water and therewith energy for board drying can be saved.

Interactions with other mix-design components
The applicability of the retarders in different plasters as well as the compatibility with accelerator has been successfully proven above. Further investigations were carried out to determine potential interactions between retarders and other potential system components.

PCE-based superplasticizer (like Sika ViscoCrete) are extensively used as High Range Water Reducing Additives (HRWRA) during wallboard production (see i.e. /4/) and in dry-mixes.

Retardan-200 was found to be compatible with the liquefier at any dosage. The flow behavior of plaster slurry is actually improved slightly further.

Furthermore, the effectiveness of the new retarder was determined in varying pH conditions, as they may occur typically during application. Therefore, the pH-value of the plaster slurry was increased by adding different amounts of Ca(OH)2. Retardan-200 was proven to be most effective in neutral to slightly alkaline conditions. The product is also compatible with other retarders like fruit acids and their salts.

Retarder performance requirements for dry-mixes for plastering are known to differ from other dry-mix applications and wallboard production. To ensure the smooth run of all required plaster processing steps, not only retardation of initial setting, but also extension of the setting period is required. For this purpose tartaric acid is commonly used. Because of variations in quality, availability and therewith price of tartaric acid, dry-mortar producer are desperately looking for alternatives. A cost-efficient solution was found: strongly reduced dosage of tartaric acid combined with a low concentration of Retardan-200 P results in similar setting-behavior.
Additive dosing
As it is common practice during wallboard production, pure retarder concentrate is pre-diluted with water prior to usage in the plant (typically 1:20...1:50) to ensure accurate additive dosing under plant-specific conditions. To ensure compatibility with existing dosing practices, diluted versions of Retardan-200 L are also available on demand. In addition, diluted versions of the powder, Retardan-200 P, are also available for dry-mix formulations.

SUMMARY AND CONCLUSIONS
Today's dry-mortar and gypsum formulations are out-balanced multi-component systems in which each ingredient has to perform reliably. That includes retarders, which are of crucial importance for gypsum binders to ensure the desired application process and end-product properties.

In our investigation, various commercially available gypsum retarders were tested for their efficiency and compatibility with numerous mix-design components. Initial results of this extensive study have been presented in /5/. A new high-performance gypsum retarder – Retardan-200 – was found to set a new standard in retarding efficiency without demonstrating the known negative characteristics of existing technologies. The new retarder is available in powder and liquid form. It gives excellent performance at both high and low dosage rates to control the setting in the range of seconds (as required during wallboard production) to several hours (for dry-mix applications). Retardan-200 is displacing the initial setting of gypsum binders without loss of setting, hardening and hydration intensity. The retarder was proven to be applicable in different gypsum binder types as well as at varying pH conditions. It is compatible with other commonly-used system components such as accelerators and superplasticizers.

REFERENCES
Новый подход в замедлении схватывания гипса

FINNBE Чтобы обеспечить требуемые свойства производимой продукции, необходимо своевременно менять состав компонентов, чтобы поддерживать необходимую скорость твердения. Как показывают исследования, замедлители схватывания являются важной составляющей в технологии производства гипсовых вяжущих. В данной работе исследовались свойства различных замедлителей и определены их эффективность по предсказанию на основе оценки их свойств в гипсовом растворе. Данные результаты показывают, что Retardan-200 может быть эффективным замедлителем схватывания, что подтверждается его эффективностью в замедлении процесса.

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Замедление схватывания гипса

Результаты показывают, что Retardan-200 обладает улучшенными характеристиками по сравнению с другими замедлителями. Величина замедления схватывания гипса также зависит от дозировки замедлителя. Увеличение дозировки замедлителя приводит к увеличению времени начала схватывания гипса. Эти результаты подтверждают, что Retardan-200 может быть эффективным замедлителем схватывания гипса, что позволяет контролировать процесс твердения в зависимости от требований производства.

Влияние кислот на скорость схватывания гипса

Влияние кислот на скорость схватывания гипса также было исследовано в данной работе. Результаты показывают, что аммонийная кислота A, сульфат кальция, а также хлорид кальция могут вызывать замедление схватывания гипса. Эти результаты подтверждают, что кислоты могут влиять на процесс схватывания гипса, что позволяет контролировать процесс твердения в зависимости от требований производства.

ЛИТЕРАТУРУ
WHO WE ARE
Sika AG, Switzerland, is a globally active specialty chemicals company. Sika supplies the building and construction industry as well as manufacturing industries (automotive, bus, truck, rail, solar and wind power plants, façades). Sika is a leader in processing materials used in sealing, bonding, damping, reinforcing and protecting loadbearing structures. Sika’s product lines feature high-quality concrete admixtures, specialty mortars, sealants and adhesives, damping and reinforcing materials, structural strengthening systems, industrial flooring as well as roofing and waterproofing systems.

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