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Revealing the working principle of sodium trimetaphosphate as state of the art anti-creep agent in gypsum plaster

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ABSTRACT

Sodium trimetaphosphate (STMP) is a state of the art anti-creep agent for gypsum plasterboards. It counteracts the deformation of gypsum in a humid environment under load. Despite the fact that STMP is the industrial standard as anti-creep agent, its working mechanisms is not yet thoroughly understood or published. In this work, the role of sodium trimetaphosphate as anti-creep agent of gypsum is reviewed with fundamentally new approaches and modern analytical methods. The surface interaction of trimetaphosphate with calcium sulfate dihydrate crystals is studied in dependence of different crystallographic facets. Via this approach, it was ultimately possible to reveal the working principle of STMP as a highly effective anti-creep agent and deduce a general understanding for anti-creep agents. These insights could help to find and judge new substances in light of their working principle as anti-creep agents.

1. Introduction

Gypsum is very prominent as an inexpensive and easy to use building material with a wide range of advantageous attributes. Plasterboards possess excellent properties in terms of heat insulation, they comply with the standards for fire safety and help to provide a pleasant room climate [1–3]. However, the use of gypsum materials is limited because of its adverse trait upon contact with water. The mechanical properties of gypsum, i.e., its hardness, compressive strength, flexural strength and elastic modulus deteriorate in humid environment. The reason is that humidity adds additional water to the polycrystalline calcium sulfate dihydrate, which, under static load, eventually is responsible for the creep of gypsum [4–7]. This ultimately leads to a deformation of the building-material, pronounced for instance in the bending of gypsum boards. To overcome this creep behavior in a humid environment, several additives have been proposed during the last hundred years as potential remedy to this issue [8].

In the gypsum industry, surfactants are the state of the art anti–creep agents in order to counteract the creep of gypsum. These chemicals are believed to form a complex with the Ca^{2+}-ions on the surface of gypsum crystals, which is meant to decrease the speed of dissolution of gypsum in water [9,10]. Anti-creep additives in form of surfactants not only influence the surface character, but also the shape of gypsum crystals, resulting in a polycrystalline structure with increased strength [8]. Above all, phosphates and phosphonates such as aminotris(methylenephosphonic acid) (ATMP) and sodium trimetaphosphate (STMP) are applied as industrial state of the art standard [9,11,12].

Despite the fact that STMP is the industrial standard as anti-creep agent, surprisingly, its working mechanisms is not yet thoroughly understood or published. Thus, in this work, we aimed at revealing the role of sodium trimetaphosphate as anti-creep agent of gypsum by employing fundamental approaches and modern analytical methods and from that ultimately deduce general rules for working mechanisms of anti-creep agents.

2. Experimental

2.1. Reagents and materials

Flue gas desulfurization (FGD) calcium sulfate hemihydrate (negligible traces of carbon and rust from the process, X-ray-analysis in previous publication [13]) and calcium sulfate dihydrate single crystals were provided from Knauf Gips KG, Iphofen, Germany. SiO_2 nanoparticles from Chemiewerk Bad Köstritz GmbH. Kojic acid and malic

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acid were purchased from Sigma-Aldrich, Germany. Sodium trimetaphosphate (STMP) was purchased from Alfa Aesar. All chemicals were used without further purification.

2.2. Precipitation of prism-shaped gypsum samples

Prism-shaped gypsum samples were prepared using flue gas desulfurization (FGD) calcium sulfate hemihydrate and deionized water. In the case of modified samples, silica nanoparticles or additives were dispersed or dissolved in deionized water. Water to gypsum ratio of 0.8 was chosen for all samples. The prism-shaped gypsum samples were prepared on a vibrating table and shaken with amplitude of 0.7 mm for 2 min, which ensured that no pores larger than 100 µm could form. The gypsum samples typically hydrated at room temperature. After 2 h of hardening time, the molds were removed and the samples dried until constant weight. The samples were subsequently sawed, sanded and polished to dimensions of 40 × 10 × 1 mm.

2.3. Standard creep tests

A static 3-point bending flexural test was adjusted for fast creep experiments of polycrystalline gypsum samples. The creep experiments were carried out in a conditioning cabinet at a temperature of 50 °C, a relative humidity (RH) of 96% and a mechanical load of 0.8 N, causing a maximal tensile stress of at least 3 N/mm^2 over the period of 5 d. The distance of the supporting pins was 25 mm, the diameter of the loading pin and the supporting pins were 10 mm. The value of interest to compare and evaluate samples was the sag of gypsum samples. The sag was measured after one-day relaxation via a dial gauge. For convenience, the setup, which is in detail discussed in a recent other work [13] is depicted below in Fig. 1.

2.4. Complexation on different sites of a single crystal for SEM/EDX analyses

The single crystals were cut, sawed and polished perpendicular to the directions [100], [010] and [001]. The orientation was controlled via X-ray diffraction. The different crystallographic sites were dipped in 0.1 M STMP solution for 1 min, washed three times in deionized water for 10 s and dried until constant weight at 40 °C.

2.5. Analytical instrumentation

The standard creep tests were conducted in a conditioning cabinet SB22 from Weisstechnik. Scanning electron microscopy (SEM) was carried out with a Zeiss Supra 25 SEM at 3 keV, the Energy-dispersive X-ray spectroscopy (EDX) were conducted at working distance 8.5 mm, measuring time 200 s, acceleration voltage 8 kV, counting rate 2300 s^{-1}, and dead time 20%. Transmission electron microscopy (TEM) characterization was carried out using a TEM FEI Titan operating at 300 keV. X-ray diffraction (XRD) was performed on a PANalytical 943006003002 Empyrean Series 2 X-ray diffractometer (Cu Kα radiation λ = 0.15406 nm, step size 0.00165 2θ, typical count time 60 s).

3. Results and discussion

In this work, the most important factors of influencing the creep behavior of gypsum are investigated. Previous work reports that sodium trimetaphosphate (STMP) has an influence on the mechanical stabilization and the solubility of gypsum [14]. Furthermore, STMP is attributed to form complexes with calcium ions of the gypsum crystal surface [12]. A bonding of individual plaster crystals is also often mentioned. In the following sections, attempts were made to examine the overall influence of STMP on a gypsum polycrystal. The effects of STMP on the mechanics (Section 3.1) are investigated as well as STMP complexation (Section 3.2) on the surface of gypsum crystals and its surface affinity (Section 3.3) and finally its effect on different gypsum crystal needles (Section 3.4).

3.1. Increasing the strength of polycrystalline gypsum as a reason for a reduced creep rate

To understand the mechanical stability contribution of anti-creep agents such as STMP, a model system was established: silica (SiO_2) nanoparticles can mimic the increase of strength of gypsum through STMP since they are known for increasing the mechanical properties in composites. Small particles tend to add to the macroscopic steps at contact points of gypsum needles rather than on plain surfaces. Therefore a reinforcement of the contact points of gypsum crystals was expected, which should result in a hindrance for the gypsum crystals to slip past each other. Indeed, it turned out that silica nanoparticles were observed to preferentially attach at contact points between individual gypsum crystal needles (Fig. 2).

Gypsum samples containing silica nanoparticles indeed showed reduced sag behavior in comparison to pure gypsum samples (Table 1). Thus, the attachment of silica nanoparticles to the contact surfaces of gypsum crystals could increase the strength of the polycrystal. Consequently, a slipping of these crystals is hindered, which is a precondition for the creep of gypsum.

The following Table 1 shows the lowest degree of sag achievable in gypsum samples for different “stabilizers” and the amount (concentration in the sample) needed to achieve it.

When comparing SiO_2 with STMP, it becomes obvious that a very high amount of particles is needed in order to at least get roughly in the region of low sag as it is observed for comparably very low amounts of anti-creep agent STMP. From this insight it can be concluded that there must be further/other mechanisms that cause the creep resistance of gypsum when agents such as STMP are used.

Thus, a potential further contribution is the formation of a complex of SMTP with calcium ions on the surface of gypsum crystals, which could influence the dissolution velocity and thus the creep rate of gypsum. In the following section, substances which do complex calcium ions in a way equal to STMP are compared to learn about this influence on the creep behavior of gypsum.

3.2. Complexation of Ca-ions on the crystal surface as a reason for a reduced creep in bulk gypsum

The most frequently given explanation for a reduced creep behavior in gypsum is that STMP is accounted for complexing calcium on the surface of the gypsum needles [12], thus causing a reduced dissolution rate at the interface of the needles which is ultimately said to hinder creep [4,11,15]. In order to test the dependence of complexation of additives on the creep velocity, Kojic acid and malic acid were studied

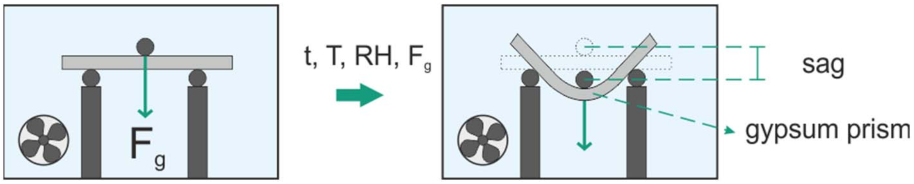

Fig. 1. Standard creep test for sag measurements of gypsum samples with different additives.