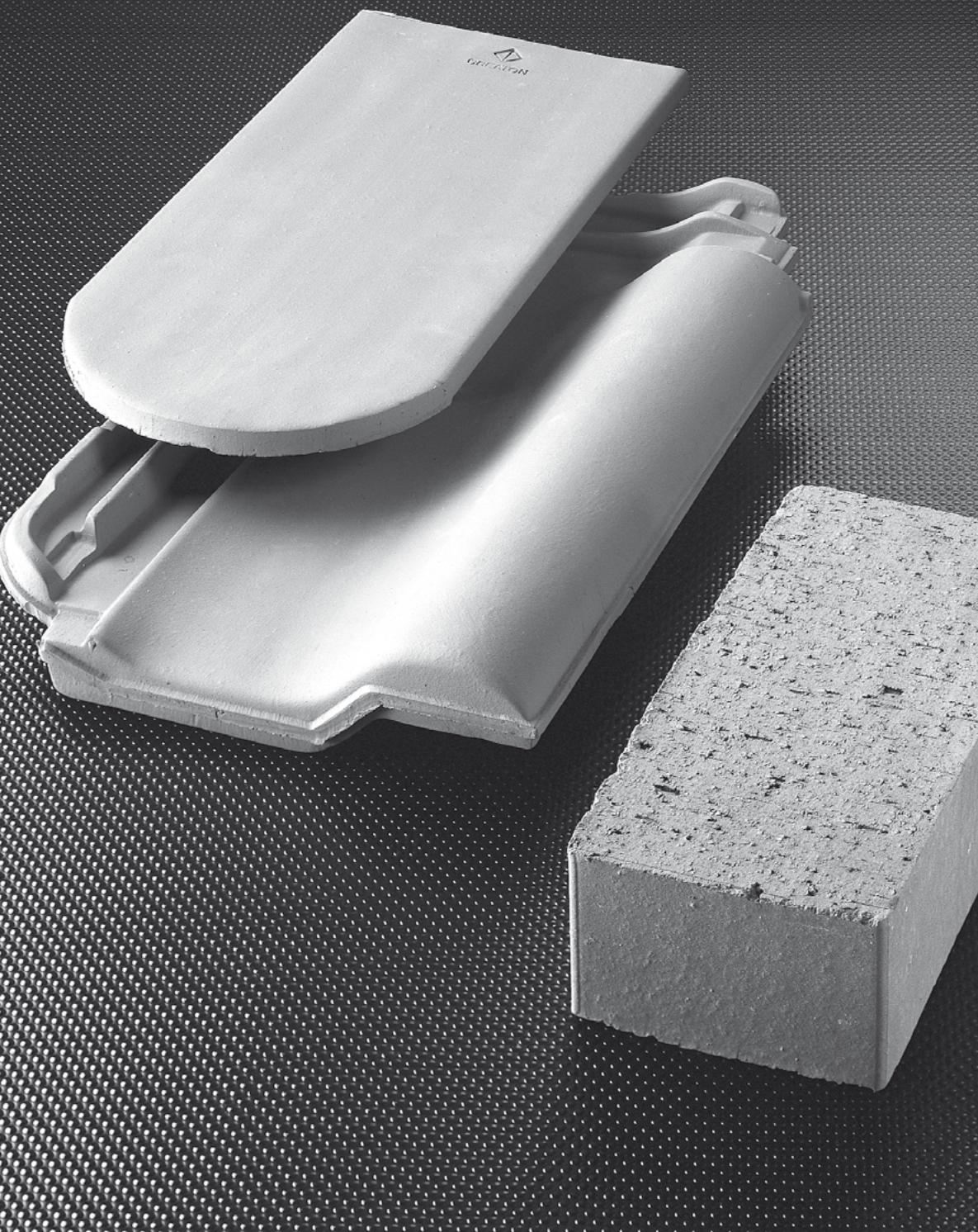




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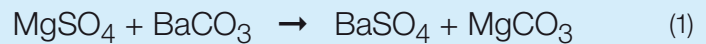


Solvay Barium Carbonate

Avoidance of Dry Efflorescence
in Heavy Clay Products
by Addition of Barium Carbonate

Ceramic raw materials consist of mineral mixtures that can contain harmful components in various concentrations depending on their formation. The presence of soluble, sulphuric acid salts in the clay raw materials causes dry efflorescence which is seen after firing as small spots of discoloration on the surface of the finished product. In clay roofing tiles and facing bricks in particular, this discoloration is unwelcome and must be avoided.

The soluble sulphuric acid salts are transported with the pit moisture and the mixing water through the capillaries to the surface during the drying process. It is usually the sulphuric acid salts of calcium, magnesium, sodium and potassium. The evaporation of water leads to a supersaturating of the salt solution and thus to crystallization of the sulphates on the surface of the blank. During the subsequent firing, these sulphates are converted into insoluble silicates resulting in white spots which can no longer be removed from the surface. By adding barium carbonate to the raw material mixture, the soluble sulphates can be bonded thus preventing dry efflorescence. In a chemical reaction these salts are converted into insoluble barium sulphate, as in the example of magnesium sulphate shown in the following equation:



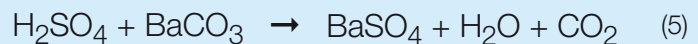
The water desulphurized by the addition of barium carbonate evaporates out of the blank without forming crystals on the surface. For a brick to be free of discoloration and dry efflorescence, all soluble sulphate components in the raw material mixture must be chemically bonded. During storage, the content of soluble sulphuric acid salts in pyritiferous clays can increase through the influence of oxygen. The oxydation of pyrite results in the formation of iron sulphate and sulphuric acid:



The sulphuric acid formed during oxidation undergoes another reaction with other components in the clay raw material (e.g. lime) converting into further sulphates which could effloresce:



The sulphates formed during the oxidation of pyrite are also transformed into insoluble barium sulphate by adding barium carbonate:



In addition to the content of soluble sulphates in the clay raw material and the sulphuric acid salts formed by decomposition of pyrite, the mixing water can also be the source of sulphates with efflorescence potential. High sulphate contents are often observed in pit water in particular, and must be chemically fixed with BaCO_3 to prevent dry efflorescence.

In order to determine the amount of BaCO_3 to be added, it is necessary that the content of soluble sulphates be analyzed. At Solvay & CPC Barium Strontium GmbH & Co. KG, application department Hanover, clay raw materials of various origins are chemically analyzed as a customer service. Commercial mixtures used for facing bricks and roofing tiles normally contain 0.01 to 0.5 % SO_3 . Brick raw materials in which chemical analyses determine considerably higher sulphate contents should not be used if at all possible. However, should the use of clays with SO_3 contents > 0.5 % be necessary due to certain qualitative properties, the sulphates in these clays can still be chemically bonded by adding the corresponding amount of BaCO_3 .

Analysis shows that within one section of a pit or in different depths of a clay pit there can be considerable variations in the sulphate and pyrite concentration. In such cases, constant monitoring of the content of soluble sulphates via chemical analysis or a calcining test is necessary. Should variations in the SO_3 content in the raw material mixture result in over-proportioning of barium carbonate, this will not have a negative effect on the finished product.

As a world leader in the production of barium carbonate, Solvay & CPC Barium Strontium GmbH & Co. KG has over 100 years of experience in its manufacture. Barium carbonate is produced by chemical precipitation at the Bad Hönningen plant from barium-containing, aqueous solutions with the help of naturally occurring carbonic acid.

Not only must the content of soluble sulphates be determined, but the quality of the BaCO_3 used is also decisive for the chemical bond of the soluble sulphates.

From a myriad of standard- and special-grade barium carbonates, a finegrained barium carbonate powder has been developed specially for use in ceramics. The distinguishing feature of this grade of powder is its typical bulk density tapped within specified limits and the consistent grain size distribution that goes with it. Due to the high grain fineness of the powder, it has a correspondingly high (specific) surface area and guarantees a constant, high sulphate-bonding capacity.

Laboratory tests have shown that the use of the same amount of coarser-grained BaCO_3 results in dry efflorescence in bricks and tiles. Because of the lower specific surface area of these powder grades, only part of the barium carbonate added becomes insoluble barium sulphate.

In addition to the qualitative properties and amount of the barium carbonate additive, the timing is also very important. In order to achieve sufficient homogenization of the barium carbonate with the moist raw material, the additive is normally proportioned between the box feeder and the edge mill. Usually the barium carbonate is added in the dry state, however the finegrained powder can also be used as a suspension. Depending on the individual plant's needs, the barium carbonate is proportioned from paper sacks, big bags or a silo. In order to avoid costly disposal of packaging, the delivery of BaCO_3 in reusable big bags or silo trucks has become wide-spread in Germany.

Since barium carbonate's reaction with soluble sulphates is an ion reaction, water must be present during the reaction time. Thus for an optimal reaction it is advantageous when a relatively long holding time between addition of BaCO_3 and drying of the finished product is guaranteed.

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