Calcium sulfate

Supplement 2007	
$CaSO_4$, calcium sulfate anhydrite	[7778-18-9]
$CaSO_4 \times ½ H_2O$, calcium sulfate hemihydrate	[10034-76-1]
$CaSO_4 \times 2 H_2O$, calcium sulfate dihydrate	[10101-41-4]
$CaSO_4 \times 2 H_2O$, gypsum	[13397-24-5]
MAK value (2006)	**1.5 mg/m³ R**
	4 mg/m³ I
Peak limitation (2006)	**see Section Vg and Vf of the *List of MAK and BAT Values***
Absorption through the skin	–
Sensitization	–
Prenatal toxicity	–
Germ cell mutagenicity	–
BAT value/EKA	–

Since the last documentation of 1989 (in German) (documentation Calcium Sulfate,1991) further studies on calcium sulfate have been published which make a re-evaluation necessary.

Applications/Use

Calcium sulfate occurs as modifications in the forms of gypsum, hemihydrate and anhydrite (I-III). The main field of application of gypsum is in the construction industry (structures above and below ground, structural and civil engineering and prefabrication) as well as the building materials industry. Calcium sulfate products are best known for binding exterior and interior walls as well as for dry mortarless construction: in the production of gypsum boards and fibred gypsum wallboards. Other applications for calcium sulfate products are in the fields of applied art,

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medicine (bone surgery, plaster casts and braces) and in dental technology (Colditz et al. 2002).

Since 1970, natural anhydrite had been used in underground coal mining and as a construction material to stabilize underground mining galleries (hollow supports and insulating structures) (Bauer 1984). This has, in the meantime, been replaced by special mixtures containing gypsum from flue-gas desulfurization ("FGD gypsums").

Solubility

As raw material, the solubility of calcium sulfate in water is low, fluctuating between 0.21 g/100 g for dihydrate and 0.67–0.88 g/100 g for β-anhydrite-III at around 20°C (Frank and Knofel 1983), compared to about 35 g NaCl in 100 g H_2O (Hollemann and Wiberg 1995). The solubility behaviour was tested experimentally with commercially available gypsum using the convention method. No dissolution in water of the material, not even slight quantities, was found in this case (HVBG 2004; Mattenklott 2005).

The pH of calcium sulfate solutions is around 7 or in the very weakly acid range (Dahmann 2006).

Exposure

Mining and production

According to investigations carried out in the period between 1999 and 2005 by the IGF (2006), dust exposure was 0.37 mg/m^3 (respirable fraction) from the ventilation fumes from (upcast) shafts in mines, measured at the main ventilator, and 0.3 mg/m^3 (respirable fraction) in the underground mining work area. The mean personal exposure is higher at workplaces in underground mining, amounting to between 1.00 mg/m^3 for operators of roof-scaling vehicles or blasting (explosives) vehicles and 4.25 mg/m^3 for operators of crushing machines.

Dust exposures are lower in open pit gypsum mining, i.e. at 0.92 mg/m^3 (personal exposure monitoring) or 0.59 mg/m^3 (static measurements).

Between 1998 and 2004 in the dry construction industry the mean dust exposure (respirable fraction) was 1.06 mg/m^3 (arithmetic mean value) for those working in "sheeting, laying and filling" operations, and 3.10 mg/m^3 for those working in the "grinding" process (HVBG 2006).

Use and processing of intermediate products

Depending on the material used, gypsum fibres may also be released when processing products in drywall construction. Especially in demolition, it should be taken into account that asbestos was added to spackle for drywall work both in the USA and in the Federal Republic of Germany in the 1960’s and 70’s. Asbestos contents were between 2 and 25 mass % chrysotile and tremolite in the USA (Fischbein et al. 1979; Verma et al. 1980) or between 2 and 7 mass % chrysotile in Germany (BK-Report 1997). Remarkably high asbestos fibre concentrations of up to 59 F/ml (Fischbein et al. 1979) or 20 F/ml with time weighted average values (TWA) above of 2 F/ml (Verma et al. 1980) are reported for drywall construction in the USA. As light microscopes were used to obtain these values, it was not possible to clearly distinguish between gypsum fibres and asbestos fibres.

When ginding present-day asbestos-fibre-free gypsum board and gypsum fiberboard, the concentration of WHO-fibre for gypsum up to 2.4 F/ml (phase contrast microscope) or 5.2 F/ml (scanning electron microscope) have been measured (Rödelsperger and Roth 2004). In contrast, only a few fibres are released (0.17 or 0.07 F/ml) from ready-made coating materials containing gypsum. Little of the gypsum released from the boarding had a length to diameter (L/D) ratio greater than 10:1. Considerably more long fibres ($L > 10 \mu m$) are emitted from gypsum/fiberboard compared with gypsum/carton board.

Dust formation and exposure to it, during the demolition and destruction of buildings also needs mentioning. For example, when the World Trade Center towers in New York were destroyed on September 11, 2001 and immense quantities of dust were released, their principal mineral components were in the $PM_{2.5}$ and PM_{10} gypsum and calcium carbonate fractions. The dusts also contained asbestos and quartz as well as traces of heavy metals (about 100–700 ppm), and additional traces of combustion products, which were not defined in any greater detail (McGee et al. 2003).

Analytical procedures

When work processes result in human exposure to calcium sulfate dusts, either static sampling or personal sampling units are used. The equipment must be able to record respirable or inhalable fractions complying with the criteria laid out in Chapter V entitled “Aerosols” of the *List of MAK and BAT Values*. Dust monitoring equipment are tested in accordance with (German Industrial Norm/DIN) EN 13205.

Toxic Effects and Mode of Action

After inhalation of calcium sulfate dust, the inhalable dust particles are, as a rule, removed via the cleansing function of the respiratory tract. A portion is eliminated via the gastrointestinal tract after swallowing. Fine dust may reach the alveoli (respirable fraction). The inhalable as well as the respirable dust fractions can cause a general particle effect. Both calcium and sulfate ions are essential nutrients.

Only at the comparably high concentration of 40 mg/m³ does calcium sulfate dihydrate produce irritation in nose and throat mucosa, but not in the eyes. No sensitization has been observed with calcium sulfate. It is not genotoxic *in vitro*. No data on carcinogenicity are available.

Effects in Humans

Single exposure

Rescue workers at the World Trade Center and persons subjected to massive exposure during its collapse, as well as those with particularly sensitive reactions to dust (no other details), complained of coughing, irritation in throat and nose together with other signs of mucosal irritation (Gavett 2003; Gavett et al. 2003). The major components of World Trade Center (WTC) dusts were calcium (22–33%) and sulfate (37–43%). The authors suspect that the effects were produced by gypsum and calcite. Other WTC dust components were asbestos, silicon dioxide and organic compounds such as polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and polychlorinated dibenzodioxins (PCDD).

Repeated exposure

High concentrations of calcium sulfate in the drinking water (600 mg/l) had laxative effects in children and adults, also producing partial dehydration. These effects were limited in time, and habituation effects may occur (no other details) (BIBRA 1989).

The effects of dusts from underground support structures (called roadway packs) and their building materials on the health of coal miners was investigated in cross-sectional studies. Over a period of about 20 years in Saarland mines, pneumatically transported building materials (transported as powder using compressed air through pipes) were used for the construction of roadway packs; building materials based on anhydrite made up for about 50%. Natural anhydrite is anhydrous calcium sulfate, which is converted into the dihydrate ($CaSO_4 \times 2\ H_2O$) by the absorption of water. To increase rapid and pressure-resistant solidity, so-called activators (iron (II) sulfate and potassium sulfate) are added to the anhydrite. The change in particle size distribution during pneumatic transport of anhydrite through pipelines over long distances is an important factor when examining the exposure of mine workers. After a haul of 3000 meters, an increase in the proportion of respirable dust from a concentration of 3 % to 14 % (mass) was measured in the load. Whereas the proportion of activators in the initial product was 1 % mass before blowing, activator ingredients in the inhalable dust made up to 10 % mass in the surrounding air after blowing. No data on the concentration of calcium sulfate in the ambient air are reported.

Two collectives were included in the cross-sectional study. The first was a group consisting of 52 (out of a total of 150) miners whose total dust exposure values were the highest for anhydrite dust. These miners had not started working underground before 1963 and had been exposed to anhydrite dusts in the mine for at least five years. The other collective was a reference group consisting of 51 miners who had also not started mining prior to 1963 and had spent at least five years underground and who showed respirable total dust values (concentration c_R times the number of shifts) as similar as possible, but had never been exposed to anhydrite dusts. Precise data on calcium sulfate concentrations in the air were not given. Basic and exposure variables,were recorded: age, height, weight, smoking habits (smoker: yes or no), family history in the context of asthma or skin conditions, time underground, cumulative exposure to coal mine dust (respirable fraction) as well as exposure time to anhydrite dusts (respirable fraction). Data on spirometric and plethysmographic lung function parameters as well as on clinical symptoms were obtained for both collectives. In addition, radiographs of all study participants were obtained and evaluated in accordance with ILO Classification 1980.

Differences between the groups were tested using t tests and Fisher tests or LR-chi^2 tests on a univariate basis. Lung function parameters were investigated both with and without external reference values (ECSC values; ECSC = European Coal and Steel Community). Multiple linear regression models that included age, smoking habits, family history regarding asthma or skin conditions and the cumulative coal mine dust exposure (respirable fraction) as potential confounders were used to investigate the association between anhydrite dust exposure duration and lung function parameters with and without external reference values (ECSC values).

Both collectives were considerably consistent in nearly all basic and exposure data, only the time underground was significantly longer ($p < 0.05$) in the control group. In the exposed collective, exposure to anhydrite dust (respirable fraction) was on average 9 years (5 to 18 years), with a mean time underground of 12 years. Clinically, auscultatory bruits of the lung and a positive cough test were found in seven of those exposed. In the non-exposed, auscultation revealed only three bruits (cough test: $p < 0.02$). Radiography revealed three subjects with a non-specific profusion category 0/1 ILO 1980 in the anhydrite collective. Only one such case was found in the control group, though two subjects in this collective had profusion categories 1/0 and ½, ILO 1980. At 94.2% (exposed) and 94.9% (controls), vital capacities were significantly reduced compared with the ECSC reference values ($p < 0.005$ in both groups). Bronchial resistance tended to be higher in the anhydrite-exposed group, though this difference was not significant. Multiple linear regression models found no dependency of lung function parameters on duration of exposure to anhydrite dust (respirable fraction) (for example vital capacity relative to the ECSC reference value: $p = 0.95$).

In the authors' opinion, from an anamnestic and clinical perspective there were certain indications of an increased strain on the broncho-pulmonary system among persons exposed to anhydrite dust (respirable fraction), accompanied by an increase in data on family-related diseases. No significant difference between either group could be determined in all clinically relevant lung function parameters. The authors concluded that no conspicuous health problems had developed in coal miners exposed to anhydrite dust. But they indicate that effects on the broncho-pulmonary system cannot be excluded with certainty, especially because exposure to anhydrite dust and its effect on the respiratory organs was not investigated over a working lifetime (30 up to 40 years) in the study (Lampert et al. 1989, 1992, 1993).

Three cases of idiopathic interstitial pneumonia in teachers exposed to dust from blackboard chalk have been described. Data from four persons with idiopathic pneumonia who had not been exposed to chalk were used as controls. In an analysis of the mineral content in the lungs, two of the exposed teachers showed an increased amount of total dust, but also of silicon dioxide and calcium compared with controls (Ohtsuka et al. 1995).

Local effects on skin and mucous membranes

In the Belgian coal mines, anhydrite paste was used for gap filling. Miners who had skin contact with this paste complained of itching and burning sensations on the skin (face, neck, forearms and thighs). After replacement with hemihydrate paste ($CaSO_4 \times ½H_2O$), the complaints significantly decreased. The originally used anhydrite contained traces of calcium fluoride and hydrofluoric acid. Aqueous suspensions of this anhydrite showed an alkaline pH of 11.2. The hemihydrate used later contained traces of phosphoric acid, calcium phosphate and fluoride residues which showed a pH of 5.8 in aqueous solution (Lachapelle et al. 1984). Due to mixed exposures, the effects can not be attributable to calcium sulfate alone.

According to available information, calcium sulfate particles are not irritant to the eyes (no other details) (BIBRA 1989).

In a single blind study, healthy men aged between 18 and 35 who had not smoked for at least the last year were exposed to randomized concentrations of calcium sulfate, calcium oxide and sodium borate (Cain et al. 2004). To simulate light physical exercise, the volunteers were tested ergometrically with 60 W. The calcium sulfate dust was produced by grinding drierite (CAS No. 7778-18-9) and hydrated over standing water for 24 hours. Each application lasted 20 minutes using a hood over the volunteer's head. Calcium sulfate was applied in concentrations of 10, 20 and 40 mg/m^3. A mass median aerodynamic diameter (MMAD) of 8.24 ± 1.08 µm and a geometric standard deviation (GSD) of 2.43 ± 0.12 µm was given for the calcium sulfate. Irritant effects to eyes, nose and throat as well as nasal resistance, nasal secretion and nasal mucociliary clearance were recorded using visual analogue scales. Significant irritation of the nose and throat occurred at 40 mg/m^3 only. No significant effects were observed in the eyes. Nasal secretion showed minimal effects as the calcium sulfate concentration was increased. There were no changes in nasal clearance after any of the exposures. Immediately after the ergometric test, nasal resistance decreased slightly but increased again at the second measurement 15 minutes following exercise. All changes were slight. Calculated across all three substances used, the correlation between subjective irritating effect and increase in nasal secretion was high ($r = 0.88$). The authors concluded that the subjects perceived time-dependent irritations, most noticably in the nose, secondarily in the throat, and least noticably in the eyes The relatively short study duration constitutes a limitation as it is not possible to identify further diluting effects arising, for example, from an increased secretion or other adaptation mechanisms.

The varying data on the irritant effects of calcium sulfate in secondary and tertiary literature reflect a lack of systematic investigations on the subject. With exposure durations of up to 20 minutes, the publication of Cain et al. (2004) indicates at best a slight irritant effect to nose and throat at concentrations of 40 mg/m^3, and no effects (compared with a sham exposure) at 10 and 20 mg/m^3 calcium sulfate dust with particle sizes of 8.24 ± 1.08 µm (MMAD).

Allergenic effects

There are no reports on sensitizing effects of calcium sulfate. Eczema from working with gypsum has only rarely been reported (Weiler and Rüssel 1980). The eczema was attributed to contamination from chromium, cobalt and nickel compounds.

Animal experiments and *in vitro* studies

Subacute, subchronic and chronic toxicity

Inhalation

Short-term studies with mice (oropharyngeal and nasopharyngeal inhalation) were carried out using a number of dust samples collected after the collapse of the World Trade Center towers ($PM_{2,5}$). Groups of 10 CD-1 mice were exposed to 10, 31.6 and 100 µg dust (no other data).

No change in respiration rate was found in the mice investigated, though slight inflammations in the lung as well as coughing occurred. BAL analysis showed no unusual findings for the WTC dusts. A clear hyperresponsiveness was found in the methacholine test. These short-term effects occurred at high doses of 100 µg (Gavett 2003, Gavett et al. 2003). No statement can be made on the effects of $CaSO_4$ as dust mixtures were tested.

Intratracheal instillation

After intratracheal instillation of 35 mg calcium sulfate anhydrite, the total lipid and total hydroxyproline contents in the lungs of treated rats were within the range found in controls three months after treatment (Breining et al. 1988). From the results of the mixtures of anhydrite and quartz DQ 12, an inhibiting effect of anhydrite on the effects of quartz was found for the first time in this study. Six months after intratracheal instillation of 5 mg FGD gypsum in rats, no effects on lung wet weight were found. Total hydroxyproline and total lipid contents in the lung were, however, increased by about 30% to 40% versus dust-free controls. Fibrogenic effects were only found after instillation of a mixture of FGD gypsum and quartz DQ 12 (Bramertz and Holuša 2001).

Intraperitoneal administration

The effects of dust from "new" insulating materials was investigated by intraperitoneal administration to rats. Doses of 50 mg/kg body weight were injected, and the animals killed after three or six months. Body weight, lung wet weight, total hydroxyproline/lung and total lipid/lung were determined. Results were in the range of controls for the animals treated with natural anhydrite, α-hemihydrate and FGD gypsum (dihydrate), as well as mixtures of these. Histological investigations revealed no signs of significant tissue reactions. In contrast, clear cytotoxic and fibrotic effects were found in animals treated with mixtures containing quartz, cement or accelerators (Rosmanith and Weller 1991).

Female Sprague Dawley rats were given intraperitoneal injections of 50 mg anhydrite dust per animal; controls were given 1 ml 0.9% NaCl solution. The animals were killed after 14 weeks to investigate the abdominal organs (greater omentum, cranial mesenterial lymph nodes and pulmonary lymph nodes) that had reacted to the injection. The weight changes for the greater omentum and the lymph nodes were slight. At necropsy, small brown granulomas in the greater omentum were found in the animals treated with anhydrite. A few lymph nodes were dark, but hardly changed otherwise. The authors evaluate this as a marked fibrotic reaction. However, the anhydrite dusts contained amounts of fine quartz dust, which were not quantified (Weller et al. 1987).

Genotoxicity

In vitro

Calcium sulfate (no other details) was found to be non-mutagenic in tests with *Salmonella typhimurium* and yeast cells (*Saccharomyces cerevisiae*) (BIBRA 1989).

In micronucleus tests with SHE cells and human mesothelioma cells, calcium sulfate did not significantly increase the micronucleus frequency compared with untreated cell cultures. In these tests, gypsum (1 µg/cm^2) was used as control substance (Dopp et al. 1995 a; Poser et al. 2004).

In a chromosome aberration test with human amniotic fluid cells, gypsum particles (1 µg/cm^2) do not induce significantly increased rates in chromosome breaks compared with untreated cells (Dopp et al. 1997).

In vivo

There are no data available.

Other effects

Calcium sulfate (1–10 µg/cm^2) was used as a negative control in investigating asbestos and ceramic fibres in the context of apoptosis induction in hamster cells. No apoptosis inducing effects were observed (Dopp et al. 1995 b).

Gypsum dust (150 µg/ml or 200 µg/ml) induced a minimal increase in LDH release of murine peritoneal cells *in vitro*, but did not affect cloning efficiency of A549 cells (Chamberlain et al. 1982).

Tests with a number of isolated pathogenic bacterial strains (*Escherichia coli*, *Staphylococcus aureus*) showed that calcium sulfate without antibiotics (tobramycin sulfate, vancomycin hydrochloride) did not affect bacterial growth. Calcium sulfate had no influence on the effect of the two antibiotics either (Armstrong et al. 2003).

Growth of the bacteria *Prevotella nigrescens* and *Enterococcus faecalis* was also not affected by calcium sulfate in an agar diffusion test (Chogle and Mickel 2003).

Using cell cultivation techniques, it was demonstrated that osteoblasts attach on calcium sulfate hemihydrite, while osteoclasts absorb it stepwise (Sidqui et al. 1995).

Calcium sulfate pellets have been used to fill bone defects for over a 100 years. Insofar as medically pure calcium sulfate is applied, a good tolerance has been described in the great majority of cases. Contamination of natural gypsum with iron, magnesium, strontium, lead and other heavy metals often occurs. Calcium sulfate is absorbed at about the same rate as new bone develops (reviews in Peltier 1961, Damien and Parsons 1991 as well as case reports by Mirzayan et al. 2001). Absorption of calcium sulfate is complete at the latest after 24 weeks. Histologically, no inflammation reactions and no rejection reactions beyond the usual extent are observed. In contrast, severe inflammation was reported after calcium pellet implantation following resection of bone tumours in 3 of 15 cases (Robinson et al. 1999). In one case, an allergic reaction obligated graft removal. The authors concluded that, due to rapid graft resorption, the resulting fluid incites inflammation.

Investigations in rabbits involving bone cement containing calcium sulfate are described in which small cylinders of the material were implanted into holes drilled into the bone. After four weeks, the material was surrounded by new bone. The authors concluded that the material used stimulates bone formation. No complications were reported (Ohura et al. 1996).

Calcium sulfate bone cement and calcium sulfate pellets were implanted into holes drilled into the rabbit tibia (*methaphysis tibialis*). After four weeks, resorption of the calcium sulfate was nearly complete, and the bone defects almost compensated. No inflammatory cells were found in any of the specimens (Orsini et al. 2004).

Calcium sulfate pellets were tested in rabbits for the use as a biodegradable delivery system for the local administration of antibiotics in musculoskeletal infections (with delayed release during biological degradation of the pellets). Experimental infection with *Staphylococcus aureus* healed more effectively by this means than after intramuscular injection of the same antibiotic (Nelson et al. 2002).

Manifesto (MAK value, classification)

From studies in humans and animals, no suitable data are available to derive a MAK value. In humans, exposure to high calcium sulfate concentrations of 40 mg/m^3 produced irritation of the mucosa in nose and throat. After chronic inhalation of gypsum dust, no increase in inflammatory reactions in the airways was found. Due to its relatively low solubility, the particle effect is considered to be a decisive factor when dealing with calcium sulfate as dust. No other indications of a substance-specific toxicity of calcium sulfate dust are available which would exclude application of the general threshold limit value for dust. Therefore, the general threshold limit value for dust of 4 mg/m^3 for the inhalable fraction and of 1.5 mg/m^3 for the respirable fraction applies for calcium sulfate dust in all its modifications. A limitation of exposure peaks applies as given in Sections Vf) and Vg) of the *List of MAK and BAT Values*. As no sensitization has been demonstrated, the substance is not designated with “Sh” or “Sa”.

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