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ENVIRONMENT AND RAW MATERIAL COMMITTEE

Fact sheet on:

Gypsum and Water

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I. Background

Gypsum is one of the most common minerals in sedimentary environments. It is an evaporite and can be found in massive beds, formed after precipitation and evaporation of highly saline waters. Gypsum is usually white or grey, but can also have shades of red, brown and yellow.

Chemistry: $CaSO_4,2H_2O$ - Hydrated Calcium Sulphate

II. Sulphate in Ground Water

A. European legislation on water

At European level, the fresh waters are governed by 4 directives:

- The **Water Framework Directive (WFD)** adopted on 23/10/2000 aims to establish a framework for the protection of inland surface waters, transitional waters[1], coastal waters and groundwater[2].

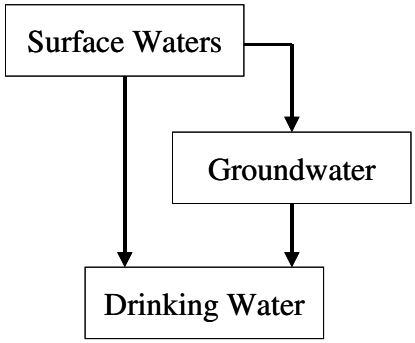
and 3 so-called "daughter directives":

- The **Groundwater Directive (GWD)**, adopted on 12/12/2006.
- The **Environmental Quality Standards (EQS)** Directive for surface waters, whose publication is expected soon (see annex C).
- The **Drinking Water Directive (DWD)**, adopted in 1998 and being revised soon.

The content of the Directives is driven by the diagram below: Surface waters feed the groundwater bodies, and drinking water (as well as water for other uses, including industrial) is abstracted from either surface or groundwater.

[1] bodies of surface water in the vicinity of river mouths which are partly saline

[2] **Note**: In the WFD **pollution** is intended **by human activity**, which means that a water whose poor status is due to a natural effect is considered as not polluted, when a water with a good status, but altered by human activity is considered as polluted.



This is why the three Directives (4 with the framework Directive) are closely linked and why we shall address all parameters listed in them.

B. What about sulphate in Water?

At 25°C, a litre of water saturated with calcium sulphate contains 1.45g of sulphate (SO_4^{2-}) and 0.65g of calcium (Ca^{2+}). When the water is saturated, an addition of calcium sulphate will not change the concentration of sulphate. This concentration can only increase if another sulphate (e.g. Magnesium sulphate) is added into the water. An example is seawater, which contains 2.65g of sulphate.

The concentration of sulphate in groundwater highly depends on the nature of the natural ground: in gypsum areas groundwater may be saturated (1.45g of sulphate per litre) and in this case the addition of gypsum will not change the sulphate concentration.

Groundwater values of up to 2950mg of SO_4^{2-} per litre are reported in Belgium and up to 4300mg SO_4^{2-} per litre in France. In South-East Lower Saxony, a maximum value of 1455mg SO_4^{2-} per litre is found, while 28.5 % of the drinking-water production installations show sulphate concentrations of over 250 mg/l. In Thuringia, maximum values of up to 2496mg SO_4^{2-} per litre (Muschelkalk) are reported, as well as an arithmetical average of 683mg SO_4^{2-} per litre (Keuper).

Within the context of the implementation of the Ground Water Directive, Eurogypsum produced a **case study analyzing the geological impact on background values of ground- and surface waters with sulphates in Gypsum Deposits in Germany on** the basis of a survey carried out by Ingenieur büro Völker in December 2006.

The conclusion of this case study was that unpolluted water normally shows concentrations less than 50 mg/l sulphate. But, this concentration will be often exceeded in gypsum karst regions. The sulphate concentration in those regions normally can be detected in a range between 500 mg/l and 1400 mg/l. Those sulphate concentrations result from the dissolving of natural gypsum. In those areas no acidic water is formed and the ecological damage known for sulphate acidic water is absent. In the gypsum karst areas the pH value of the water is slightly alkaline (pH 7.2). The geological background sulphate does not show any toxic effects on environment. The dissolving of sulphate from gypsum deposits is a hydro-geological effect that cannot be stopped by any measures.

Therefore, Eurogypsum **recommends** that, if it is demonstrated that sulphate is of natural origin only and it is proven that no anthropogenic input occurs, threshold values for sulphate do not need to be established by Member States. Where sulphates result from both origin (natural and anthropogenic), deriving a TV remains mandatory as long as it represents a risk of failing good status. In this case, investigating on cations (ex Cu++) could lead to a better understanding.

As a minimum requirement chloride (to detect seawater intrusion) and pH (to detect sulphide oxidation from pyrite) have to be detected additionally to sulphate.
Eurogypsum could also **further recommends** that in countries with gypsum deposits or any other gypsum-containing rock-sequences groundwater threshold values for sulphate should only be established on a local level and under the knowledge of all human activities.

III. Sulphate and health

Sulphate is proven to have no adverse effect on health[3], and some bottled mineral waters provide evidence of this:

	Concentration in mg/l		
	Sulphate	Calcium	Magnesium
Orée du bois (Delhaize)	641	235	66
Contrex (Pavillon)	1163	464	80
Hépar	1539	572	116

600 million bottles of Contrex mineral water are sold worldwide each year.
In Austria, the term 'Mineralwasser' can only be used for water with a minimum concentration of 200mg SO_4^{2-} /l.

In Germany new federal states, 20 % of the measured sulphate concentration in drinking water is higher than the norm of 240mg/l.

An abundant bibliography exists to prove that, instead of having an adverse effect on health, sulphate is necessary to living organisms.

- Large fluctuations of sulphates in soils and groundwater are natural environmental characteristics[i,ii,iii,iv,v,vi,vii,viii] and there is no evidence of toxicity caused by calcium sulphate in living organisms[ix,x,xi].
- Since sulphate constitutes a basic need for man and all living organisms[xii,xiii], its different levels of concentration are also a prerequisite for biodiversity.
- Man needs 2 to 3.5 g of sulphate a day[15] and most foods contain substantial amounts of sulphate[xiv] (typical values between 100 and 2000 mg/kg), likewise all biological fluids[xv,xvi].
- Sulphate conjugation is essential for biotransformation. It also allows elimination of xenobiotics and transformation residues through the kidneys[11,15,xvii].
- Calcium sulphate is registered under code E 516 as a food additive.
- Sulphate is one of the four basic plant nutrients and is essential for crop growth[xviii].

Several studies failed to find any association between exposure to high levels of sulphates (i.e. sodium and/or magnesium sulphates in concentrations mostly up to 1200 mg/l, sometimes up to 2000 and more mg/l) and diarrhoea or other adverse health issue[xix].

Neither the WHO nor the EC-directive on drinking water creates a limiting parameter for sulphate[xx,]. However, the sulphate indicator parameter in these documents has been frequently misinterpreted as a parameter that should be regulated.

Due to misconceptions on taste and aggressiveness of drinking water, sulphate content has been limited for water instead of the accompanying cations (H^+, Na^+, K^+, Mg^{2+}, Al^{3+} …) that really

[3] Sulphate in drinking water – interaction with human health –by Dr. Maurice Arnaud- Eurogypsum workshop 25 October 2007

matter. In the most abundant sulphate deposits on earth, i.e. gypsum and anhydrite, sulphate combined with calcium is showing neither taste deviations[xxi,xxii], nor aggressiveness.

IV. Sulphate and taste

Sodium, potassium, ammonium, magnesium, iron and aluminium sulphates are much more soluble than calcium sulphate (gypsum) and are known to have some adverse effect on the taste of water. They have also been suspected of causing diarrhoea by ingestion of water containing high concentrations of these sulphates.

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[i] *BRGM, Sulphate concentrations in groundwater in France, data from. „Ministère de l' Environnement, Observatoire National de la Qualité des Eaux Souterraines". Cfr. Attachment 1.*

[ii] *G.Holzhey, Geogener Sulfat-Gehalt im Bereich der Hautgrundwasserführung, Figures for Thuringia.*

[iii] *Grundwasser in Bayern, Wasserbeschaffenheit 1993/97, Informationsberichte Heft 1/98.*

[iv] *Untersuchung der Veränderung von Wasserinhalstoffen in rinkwassergewinnungsanlagen im Raum Süd-Ost-Niedersachsen, Siedlungswasserwirtschaft, TU Braunschweig, 1984. Cfr. Attachment 2.*

[v] *UBA-Jahresbericht 95, p.191, Häufigkeit von Überschreitungen des Grenzwerts der Trinkwasserverordnung im Grundwasser (in %) bezogen auf die Zahl der durchgeführten untersuchungen in den neuen Ländern. Cfr. Attachment 3.*

[vi] *A. Forster et al., Regional distribution of sulphate in rocks and soils of Britain, Geological Society Engineering, Special Publication No.10, pp 95-104.*

[vii] *BGR, Geotechnologien, VIII. Stoffkreisläufe: Bindeglied zwischen Geosphäre und Biosphäre, Projektskizze, Quantifizierung und Modellierung des geogenen, biogenen und anthropogenen Schwefelkreislaufs, Stand 12.10.00.*

[viii] *AMINAL, Gegevens van het grondwatermeetnet voor de provincies Antwerpen en Limburg. Values between 0.05 and 2920 mg sulphate per litre.*

[ix] *Internal test Bayer AG: LC_0 >2000 mg/l, Poecilia reticulate, 96h.*
Patrick et al., Progressive Fish-Culurit, 30, 137-140 (1968): LC_{50} 2980 mg/l, Lepomis macrochius, 96h.

[x] *Wallen et al., Sewage and Industrial Wastes, 29, 695-701 (1957): TLm >56000 mg/l Gambusia affinis, 96h.*

[xi] *BIBRA toxicity profile calcium sulphate: NOEC > 2000 mg/l rainbow trout, 28d.*

[xii] *Ullmann's Encyclopedia of Industrial Chemistry, 1995, Vol. B28, Water, p.23.*

[xiii] *The Biological Chemistry of the Elements, 1991.*

[xiv] *Florin et al., Journal of Food Composition and Analysis, 6, 140-151 (1993): The Sulphate Content of Foods and Beverages*

[xv] *Robert F. Pitts, The physiological basis of diuretic therapy, Charles C. Thomas, Publisher, 1959.*

[xvi] *M. Arnaud, Water Institute, Perrier Vittel, Vol.1, No.2, September 1999. Cfr. Attachment 4.*

[xvii] *Ullmann's Encyclopedia of Industrial Chemistry, 1995, Vol. B7, pp 195-6.*

[xviii] *Ullmann's Encyclopedia of Industrial Chemistry, 1995, Vol. A25, Sulfur, p.563.*

[xix] *Health Effects from Exposure to High Levels of Sulfate in Drinking Water Study, U.S. Environmental Protection Agency, Office of Drinking Water and Ground Water, 21 January 1999.*

[xx] *WHO, Guidelines for Drinking-Water Quality, April 1993.*

[xxi] *WHO, Guidelines for Drinking-Water Quality, 2nd edition, Vol.2, Health criteria and other supporting information, 13.30 Sulfate, p.351.*

[xxii] *Martindale, The Extra Pharmacopoeia, 26th Ed.*