Environmental Toxicity of airborne Gypsum Particles

R. Arno Wess
IES Ltd, Benkenstrasse 260, 4108 Witterswil, Switzerland

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Introduction

While the calcium sulphate in Natural and Flue Gas Desulphurization (FGD)-gypsum is basically non-toxic, metal, metalloid and fluorine impurity profiles were investigated in order to assess risk control for occupationally exposed people as well as for the general public. Beckert et al. 1990 have precociously performed a comprehensive health assessment on gypsum inter alia based on FGD gypsum samples from coal and lignite power plants. In-depth analysis included concentrations of 15 trace elements in gypsum compared with a human-toxicological review, based almost on MAK values. As a summary result the scientists concluded that the production and the following application in gypsum products are unlikely to cause harm to exposed people.
During the last 25 years some framework conditions had changed, those have been included in this recent study:
- The scope of trace elements has been extended from 15 to 20, covering now all detectable impurity elements (metals, metalloids and fluorine).
- The sample data base has been extended - it now includes all relevant FGD gypsum sources from power plants all over Europe.
- Recent internationally established threshold and limit values have been taken into account.
- The exposure scenario has been modelled and additionally based on measured scientific results.
- A generally accepted toxicological assessment approach has been used.

Therefore a revised human health assessment on FGD gypsum taking the precautionary principle into account was supported, contracted from a consortium of power plant and gypsum industry for assessment by the author.

Material and Methods

Toxicity threshold levels have been collected from the literature. Due to the limited exposure on the oral route in combination with related high toxicity thresholds, and due to the expectation of absence of relevant dermal exposure, the study focused on long-term inhalation toxicity. Any acute and subacute inhalation exposure was way below any toxicity threshold, and accordingly subchronic and chronic exposure was considered. For Mercury an Minimal Risk Level (MRL, inhalation, chronic) of 0.2 µg inorganic Hg/m³ as derived from ATSDR (2013), was used. Comparable established safe levels were used when available for the remainder of impurities. In cases where no general population value was established, existing worker safety levels (IOELV, TLV and PEL-TWA were used after division by 3 to account for continuous exposure over the day (i.e. 24 h) and an additional UF of 10 was applied to these worker safety levels to account for the possible higher susceptibility of more sensitive sub-populations of the general public, however such sub-populations will not normally work full days in gypsum dust.
Exposure: In the context of the REACH registration requirements, an exposure scenario (ES) for gypsum according to generally accepted standards has been calculated. In addition to that, workplace measurements were performed. Considering the regulatory requirement to distribute the ES with the eSDS, it was kept short and represents therefore a generic level avoiding also sub-scenarios for consumers and workers. Significant refinement should therefore be applicable to the concluded worst case exposure assumptions.
The higher-tier Advanced REACH Tool (ART version 1.5) was applied and the exposure calculation was based on PROC 26 and corresponding activities, as they represent the highest dust release potential. The result was then corrected assuming dust exposure during only 80 % of the assumed working time. To make the derived impurity air levels, which are still related to workplace exposure, comparable to chronic safe inhalation threshold and limit levels, they were divided by 3 to account for a 24-h daytime and then multiplied with a factor of ca. 0.715 (5 working days / 7 weekdays) to correct for work-free weekends.
Natural and FGD-gypsum share a comparable metal, metalloid and fluorine impurity profile. The only marked difference is the content of Mercury, being slightly higher in FGD-gypsum, whose levels were thus considered for assessment, thus covering also natural gypsum. 664 analysis results per impurity element (see Table 1, below), determined by accredited and independent laboratories, were used as basis for this study. From this data the 95th percentile level of each individual impurity concentration was considered for exposure modelling. 90th percentile values may be more common, preferably for use in acute scenarios, while in chronical exposure mean levels are justifiable. Therefore the 95th percentile choice illustrates a conservative approach. In result the assessment bases on levels significantly above a chronical average being appropriate for long-term low-level inhalation exposure situations as assessed.
It has to be additionally emphasized that these 95th percentile values indicate element-related worst cases which cannot be expected to be all present at these levels in any individual sample. Thus summarizing any concentrations from the Table presented below would be inappropriate. For such purpose mean levels, e.g. 50th percentiles, must be used - preferably evaluated in a way that for each sample the sum of the elements of interest (e.g. on the basis of a shared hazard classification when applying the summation method from the Globally Harmonized System of Classification and Labelling of Chemicals) is calculated and then the average is to be taken into account.
The mass fraction of the impurities in airborne gypsum dust particles was assumed to be their exposure. The impurity exposure concentrations in dust were directly derived from this concentration in that the mass fractions of the individual impurities were multiplied with the derived gypsum concentration.

Results

Exposure: The corrected, calculated (by ART and corrected as described above) dust concentration was 1.3 mg gypsum/m³ (chronic workplace TWA), and found still higher than workplace measurements indicating a level of 0.94 mg/m³
Risk Characterisation Ratio (RCR): Compared with the established toxicity threshold levels (see Table 1, below), risk control was demonstrated for all impurities considering the relation of the exposure to the non-toxic concentration (RQ). The Risk Quotient (RQ) for Mercury was found to be 0.002. FGD gypsum showed RQ-values below 1 for all trace elements and thus risk control is demonstrated. It has been shown that - by meeting an RQ below 1 for all impurities investigated - the use of FGD gypsum is confirmed to be safe, underlining the result of the former study of Beckert et al. (1990).

Discussion and conclusion

Indeed a number of worst case assumptions were made so that an RCR close to 1 would nonetheless indicate the absence of risk with a large safety margin.
In conclusion no negative human health effects are expected by the supported uses of gypsum and products made thereof.

Table 1. Impurity levels in Flue Gas Desulphurization (FGD)-gypsum and safe threshold concentrations

Impurity	Level in FGD gypsum used for assessment; 95 Percentiles [ppm = mg/kg]	Safe Level for chronic exposure [µg Element/m³]
Antimony (Sb)	5	0.67 (Acceptable ambient air concentration, ATSDR 1992, p. 110)
Arsenic (As)	5.1	0.066 (AQG ELRL 1:10’000, WHO 2000, p. 127)
Barium (Ba)	58	16.7 (8 h TWA IOELV/(3·10), EC 2006, Directive 2006/15/EC)
Beryllium (Be)	2	0.00167 (TLV-TWA/(3·10), ACGIH 2013, p. 14)
Cadmium (Cd)	1.6	0.005 (AQG (annual average), WHO 2000, p. 32, 138)
Chromium (Cr)	15	0.1 (MRL, inhalation, subchronic, ATSDR 2013)
Cobalt (Co)	4	0.1 (MRL, inhalation, chronic, ATSDR 2013)
Copper (Cu)	16	33.33 (PEL-TWA/(3·10), ACGIH 2013, p. 21)
Fluorine (F)	70	0.99 (i.e. >1, AQG, WHO 2000, p. 33, 144)
Lead (Pb)	56	0.15 (AQG (annual average) WHO 2000, p. 33, 151)
Manganese (Mn)	76	0.05 (RfC, IRIS 1996)
Mercury (Hg)	1.4	0.2 (MRL, inhalation, chronic, ATSDR 2013)
Molybdenum (Mo)	5	16.67 (PEL-TWA/(3·10) ACGIH 2013, p. 42)
Nickel (Ni)	20	0.09 (MRL, inhalation, chronic, ATSDR 2013)
Selenium (Se)	46	0.667 (MAK/(3·10), DFG 2012, sections IIa, p. 125 & III.3B, p. 158)
Tellurium (Te)	2	3.33 (PEL-TWA/(3·10) ACGIH 2013, p. 54))
Thallium (Tl)	3	0.667 (TLV-TWA/(3·10) ACGIH 2013, p. 56)
Tin (Sn)	3	66.67 (PEL-TWA/(3·10) ACGIH 2013, p. 57)
Vanadium (V)	15	0.1 (MRL, chronic inhalation (1 year or longer) ATSDR 2013)
Zinc (Zn)	47	133.33 (PEL-TWA(3·10) recalculated from Zinc oxide fume (5’000 µg ZnO/m³ corresponds to 4’000 µg Zn/m³), OSHA 1989)

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a.wess@ies-Ltd.ch | www.ies-ltd.ch