

American Coal Ash Association

May 30, 2014

National Organic Standards Board c/o National List Manager USDA/AMS/NOP, Standards Division 1400 Independence Ave, SW Room 2648-So, Ag Stop 0268 Washington, DC 20250-0268

RE: Petition for the evaluation of synthetic calcium sulfate for inclusion on the National List of Allowed and Prohibited Substances

Dear Members of the National Organic Standards Board,

The American Coal Ash Association respectfully submits this Petition for the inclusion of synthetic calcium sulfate (a.k.a. gypsum) into the National List of Allowed and Prohibited Substances under section 205.601; Synthetic Substances Allowed for Use in Organic Crop Production. This petition is prepared in accordance with the guidelines of the NOSB.

Calcium sulfate is an effective and affordable agricultural soil amendment used to address a variety of soil quality, nutrient management, and environmental health issues. We recognize a significant and growing interest in high-quality synthetic calcium sulfate from organic farmers to better manage their farms and environmental impacts. Synthetic calcium sulfate is demonstrated to be safe and effective, and is being rapidly adopted as a valuable tool in non-organic farming across the country.

We look forward to working with the NOSB to address the value of this amendment to organic agriculture. Please contact me at (720)870-7897 or at <u>thadams@acaa-usa.org</u> if you have any questions or require additional information.

Sincerely,

Thomas H. Adams

Thomas H. Adams Executive Director

Petition for the Addition of a Synthetic Substance to the National List under Section 205.601

Petitioners:

The American Coal Ash Association, 38800 Country Club Drive, Farmington Hills, MI 48331 (720) 870-7897, Tom Adams, info@acaa-usa.org

Beneficial Reuse Management/Gypsoil, 372 W. Ontario St., Suite 501, Chicago, IL 60654 (866) 497-7645, Robert Spoerri, rspoerri@gypsoil.com

Greenleaf Advisors, LLC, 100 North Riverside Plaza, Suite 1670, Chicago, IL 60606 Dan Peerless, dpeerless@greenleafadvisors.net

Item A:

This petition is submitted for this category of substance on the National List: Synthetic substances allowed for use in organic crop production, 205.601

Item B:

1. The substance's common name:

Synthetic calcium sulfate dihydrate, CaSO₄•2H₂0, gypsum, flue gas desulfurization (FGD) gypsum

2. The manufacturer's name, address, and telephone number:

Not applicable; there are multiple manufacturers

3. The intended or current use of the substance:

Intended use: as an agricultural soil amendment to a) remediate compacted, soils containing clay, and/or sodic soils to improve soil structure and water infiltration properties, b) facilitate no-till practices on clay-containing soils, c) address nutrient management and water quality needs by reducing phosphorus transport in controlled drainage and runoff waters, and d) serve as a calcium and sulfur nutrient source in depleted soils.

4. The crop, livestock, or handling activities for which the substance will be used:

The substance will be used as a soil amendment, applied directly to fields. The most common application rate is 1 ton per acre, although application rates and intervals can vary depending on

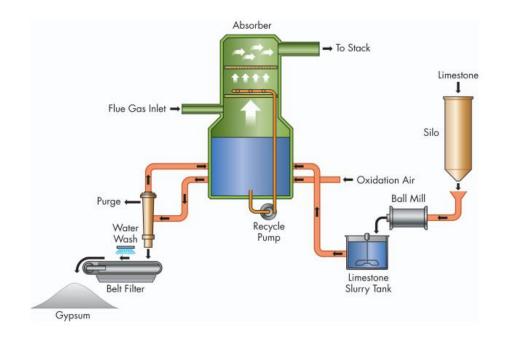
soil conditions, and it is most often spread in the fall after the harvest is complete or in the spring before planting, depending on the crop and weather conditions. Depending on the consistency of the material (powdered or pelletized) different types of common agricultural lime, fertilizer or litter spreaders can be employed.

5. The source of the substance and a detailed description of its manufacturing or processing procedures from the basic component(s) to the final product:

Flue gas desulfurization (FGD) equipment on new and existing coal-fired power plants controls sulfur dioxide (SO_2) emissions, and produces a solid that is removed in either slurry or dry form. These FGD solids are then either used in manufacturing, geotechnical, or agricultural applications, or are disposed of in landfills and ponds.

FDG gypsum (calcium sulfate) is the solid produced by wet FGD systems using a lime or limestone reagent and employing forced oxidation (LSFO). Unlike other systems which may produce calcium sulfite or sodium-sulfur compounds, and may include fly ash in their products, LSFO units produce a relatively pure gypsum product. In wet FGD systems, an aqueous slurry or solution containing the reagent, along with recirculated reaction products, is sprayed into the absorber and contacts the flue gas. The calcium in the reagent reacts with the sulfur in the flue gas to produce calcium sulfite (CaSO₃), which precipitates as a slurry in the reaction tank at the bottom of the absorber. In systems employing forced oxidation on the resulting slurry, the remaining solid product is calcium sulfate dihydrate.

The slurry initially collected in the absorber has low solid content (~5%) and requires dewatering prior to management. Dewatering can be accomplished either by mechanical systems (generally hydrocyclones for primary dewatering, and centrifuges, vacuum drums, or vacuum belt filters for secondary dewatering) or gravity drainage.



6. A summary of any available previous reviews by State or private certification programs or other organizations of the petitioned substance:

Synthetic calcium sulfate was reviewed for inclusion on the National List by the NOSB in September of 1996. The petition was for consideration under section 205.605, non-agricultural (non-organic) substances allowed in or on processed products labeled as "organic" or "made with organic (specified ingredients)." The synthetic substance is currently prohibited, the specific reasons for which are unknown as neither the petition nor the NOSB report are available on the National List website. Calcium sulfate – mined has been added to the list under section 205.605.

Branded synthetic calcium sulfate product Gypsoil has previously been submitted to OMRI for certification, which was denied because synthetic calcium sulfate does not currently appear on the National List.

7. Information regarding EPA, FDA, and State regulatory authority registrations, including registration numbers:

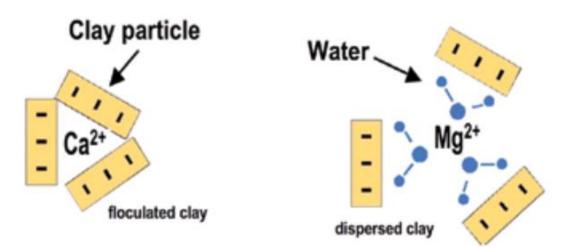
EPA: Not regarded as hazardous. Registration #: 146522-67-0 FDA: Calcium sulfate (CaSO₄, CAS Reg. No. 7778-18-9 or CaSO₄•2H₂O, CAS Reg. No. 10101-41-4), also known as plaster of Paris, anhydrite, and gypsum. It is included in the Code of Federal Regulations Title 21, Part 184, Subpart B: The Listing of Specific Substances Added to Human Food Affirmed as Generally Regarded as Safe (GRAS) (section 184.1230 – Calcium sulfate).

8. The Chemical Abstract Service (CAS) number or other product numbers of the substance and labels of products that contain the petitioned substance:

CaSO₄ (Calcium Sulfate), CAS Reg. No. 7778-18-9 CaSO₄●2H₂O (Calcium Sulfate Dihydrate), CAS Reg. No. 10101-41-4

9. The substance's physical properties and chemical mode of action including (a) chemical interactions with other substances used in organic production; (b) toxicity and environmental persistence; (c) environmental impacts from its use and manufacture; (d) effects on human health; and, (e) effects on soil organisms, crops, or livestock:

Synthetic FGD calcium sulfate is a moderately soluble fine, tan power (it can be pelletized) of relatively high purity and even consistency. Its moisture content is 8-10%. Its chemical mode of action is related to the effects of the dissociated calcium and sulfate ions once they enter the soil column. Calcium ions flocculate clay particles, breaking up the impermeable structures formed in heavy clay soils and allowing for improved water infiltration, soil aeration, and root penetration.



The calcium ions also bind phosphorus, greatly reducing its transport off of the field in water runoff. Phosphorus pollution of freshwater lakes and rivers from agricultural runoff is a major contributor to dramatic water quality deterioration across the country. Previous plot-scale research and ongoing field-scale research performed by researchers at Ohio State University, Purdue University, Auburn University and others have demonstrated reductions in soluble reactive phosphorus (SRP, the most problematic form in freshwater systems) of 40-70% from a single, cost-effective application of calcium sulfate. Furthermore, this bound phosphorus is still available for plant growth, reducing the need for external phosphorus sources. Please see the attached literature review of calcium sulfate for more information.

a) Chemical interactions with other substances, especially substances used in organic production:

There are no known problematic interactions between calcium sulfate and other substances used in organic production when applied in the manner described in this petition.

b) Toxicity and environmental persistence:

Calcium sulfate is considered non-toxic and is classified as a Generally Regarded As Safe (GRAS) food additive by the FDA. Standard handling procedures recommend avoiding ingestion and contact with the eyes and mucous membranes. Calcium sulfate is not particularly persistent under agricultural conditions because of its solubility. Its presence and effects are likely to be gone or significantly reduced within several years of application on a typical farm field.

c) Environmental impacts from its use and/or manufacture:

FGD calcium sulfate is a byproduct of the desulfurization of coal combustion exhaust. The process that leads to its manufacture is mandated by the Clean Air Act amendments of 1990 and is responsible for reductions in atmospheric sulfur dioxide and the acid rain it causes. Finding a beneficial use for this coal combustion byproduct has no impact on methods or rates of coal consumption in the United States, which is a product of the demand for energy. However, as only about half of the FGD gypsum produced annually is currently used, increased agricultural use of this product would divert the excess material from landfills or other disposal methods currently employed. Combined with the water quality benefits of phosphorus runoff reduction, FGD gypsum use has a strong positive net environmental impact.

d) Effects on human health:

As noted above, calcium sulfate is considered non-toxic and is classified as a GRAS food additive by the FDA. It can be an irritant as noted above. Natural calcium sulfate has already been approved by the NOSB for use as a tofu coagulant.

e) Effects on soil organisms, crops, or livestock:

Calcium sulfate has not been demonstrated to have any deleterious effect on soil organisms. In fact, by improving soil structure and allowing for better air and water penetration, overall soil biology can be dramatically improved under the right conditions. The same is true for crops; improved root penetration and water holding capacity can result in more drought tolerant crops. Certain types of crops have demonstrated improved quality and/or yields as a result of gypsum application, including (but not limited to) peanuts, potatoes, tomatoes, alfalfa, corn, melons, and others. No research is known to have demonstrated any reduction in crop quality or yield from gypsum application. Gypsum is non-toxic, but care should be taken to prevent livestock from ingesting significant quantities of un-applied gypsum; the same precaution that would be taken with most other substances.

10. Safety information about the substance including a Material Safety Data Sheet (MSDS) and a substance report from the National Institute of Environmental Health Studies:

Please refer to the attached Material Safety Data Sheet and Chemical Information Review Document for Synthetically and Naturally Mined Gypsum from the National Institute of Environmental Health Studies.

11. Research information about the substance which includes comprehensive substance research reviews and research bibliographies which present contrasting positions to those presented by the petitioner in supporting the substance's inclusion on or removal from the National List:

Please refer to the attached comprehensive literature review and bibliography on agricultural uses of calcium sulfate.

- 12. A "Petition Justification Statement" which provides justification for any of the following actions requested in the petition:
 A. Inclusion of a synthetic on the National List:
 - a) Explain why the synthetic substance is necessary for the production or handling of an organic product:
 - For many fundamental reasons, good soil structure is crucial for meeting the goals of optimization of soil productivity, environmental quality and the success of the organic farmer's operation. Properly functioning soils have the ability to support life by efficiently managing air, water, nutrients, carbon, and energy. These soils are teeming with biological life that is dependent on optimum moisture, oxygen and energy. The right balance of soil moisture and oxygen is determined by the amount of pore space in the soil, which should make up roughly half of the soil volume. Soil aggregation drives this balance and soil chemistry determines soil aggregation. Without balanced soil chemistry and good aggregation, soils are compacted and do not have optimum oxygen or water present; soil biology cannot function well, rainwater runs off or ponds, soils erode, nutrients are lost to the environment and crops struggle, hampering the wellbeing of the organic farming operation.
 - Gypsum (calcium sulfate) is the only tool available to significantly improve soil structure by rebalancing soil chemistry in such a way that leads to attaining the above goals.
 - The material must be of quality and nature that it can be transported, applied and perform reasonably in the soil
 - Therefore, it is critical to have a supply of qualified gypsum available to the organic farmer with no barriers to acquisition and/or use.
 - Barriers to acquisition and/or use include
 - o distance from the gypsum source to the organic farm field
 - quality of material for performance, delivery and spread-ability with available equipment
 - cost of material + delivery + application of required quantities relative to the organic farmer's availability of funds to pay for costs of production, and the farmer's return on the calcium sulfate investment.

(In other words, there is a limit as to how much the organic farmer can pay for material).

- Natural (mined) gypsum in its raw form is not of the quality or nature that it can be transported, applied and perform reasonably in the soil
 - The material must be extracted and processed to reasonable specifications
 - Not all natural gypsum is processed to the specifications needed by agriculture
- Many organic farms are not within a distance from a gypsum mine that allow reasonable means of transportation and delivery of natural gypsum
- Natural gypsum mining, processing and transport is expensive and these costs are reflected in the price of the finished natural gypsum product
- FGD gypsum is of the quality and nature that it can be transported, applied and perform reasonably in the soil
- Many organic farms are within a distance from a FGD gypsum source that allow reasonable means of transportation and delivery
- FGD gypsum is necessary for the production or handling of an organic product by those organic farmers who have barriers to acquisition and/or use of natural gypsum but have no barriers to acquisition and/or use of FGD gypsum
- b) Describe any non-synthetic substances, synthetic substances on the National List or alternative cultural methods that could be used in the place of the petitioned synthetic substance:

Gypsum is a naturally occurring, but unevenly distributed, mineral that can be found in deposits in the United States. As of 2013, mines were the largest single source of gypsum in the United States, according to the USGS mineral commodity summary for gypsum, accounting for over half of the total annual gypsum production (synthetic sources, including FGD, accounted for 43%). At least 47 companies are involved in mined crude gypsum production, operating mines in over 20 states, with Texas, Oklahoma, Nevada, California and Indiana leading the way. The United States has estimated natural gypsum reserves of approximately 700 million tons. Gypsum mines are typically operated at a capacity designed to meet current gypsum demand principally for wallboard, unlike FGD gypsum-producing power plants, which will produce independent of gypsum demand. Therefore, mined gypsum production figures do not represent the total *potential* production rates.

In general, mined gypsum is more expensive than synthetic gypsum and may be more difficult to obtain for agricultural purposes, given that many mine operators are also drywall manufacturers (for example, US Gypsum) and consume their own gypsum. However, mined gypsum for agriculture is not unheard of. There are multiple branded natural gypsum products for this market, including a number that are certified to carry the organic label by the Organic Materials Review Institute (OMRI).

Altogether, there are over 35 branded, mined gypsum-containing products that have

been certified organic by OMRI (several companies produce more than one certified product each). It is difficult to ascertain which of these products are available in the bulk quantities needed for farm-scale uses as well as which are consumer-only products. It is also difficult to establish geographic availability of each product. Gypsum mines are more heavily concentrated in the western United States than elsewhere in the country.

The Midwestern and Southern states tend to have significantly higher concentrations of FGD gypsum producing power plants than they do gypsum mines. Wisconsin, the 7th leading organic state by acreage, does not have any gypsum mines that we have yet identified, but does have significant sources of FGD gypsum.

Natural, mined gypsum could potentially substitute for synthetic gypsum, depending on availability, in regards to its soil remediation and phosphorus abatement properties, but there are also other substances that could supplement soil calcium and sulfur nutrients, such as lime, limestone, bone meal, and elemental sulfur, among others.

There are also cultural practices that can be employed to maintain soil health in similar ways to gypsum, although much recent research has demonstrated that these practices (including gypsum application) work better in combination, rather than independently and may take much longer than gypsum to achieve optimal soil conditions. These cultural practices include:

- No-till or minimal till farming
- Crop rotation
- Buffer strips
- Organic mulch/compost
- Green or animal manure (although animal manure can exacerbate phosphorus runoff)
- c) Describe the beneficial effects to the environment, human health, or farm ecosystem from use of the synthetic substance that support its use instead of the use of a non-synthetic substance or alternative cultural methods:

note: for more information on these topics, citations, and a research bibliography, please refer to the attached literature review.

Gypsum, phosphorus and water pollution

Nutrient runoff from agricultural fields is one source of pollution that impacts the integrity of our waterways and the quality of our critical water resources. Adding nitrogen and phosphorus, among other nutrients, helps to maintain the productivity of farmland and our nation's food security in the current agricultural landscape, but it can also impact the environment once these nutrients leave the field and enter our lakes and rivers. Phosphorus is a primary limiting nutrient for a variety of terrestrial plants

and aquatic algae. In modern agricultural systems, a significant portion of the phosphorus (typically in the form of fertilizers or animal manure) that is applied to fields to support higher crop yields is often transported by rainfall off the fields and into waterways, where it becomes available to aquatic organisms. Under normal or "natural" circumstances, the concentration of available phosphorus in aquatic systems limits the growth of certain organisms, primarily algae. Freed from the constraints of limited phosphorus in freshwater systems, algal "blooms" - rapid increases in the growth and density of algae populations - can occur. Several problems are associated with algal blooms and the increasing frequency of blooms in the United States and elsewhere have made nutrient management a high priority in many areas. Direct economic impacts can be felt as a result of excessive algae, including loss of tourism and recreation income due to degraded waters, higher water treatment costs for drinking water utilities to mitigate toxins that some algae emit, and reduced fishery revenues. Human health concerns include the effects of exposure to toxins in the water. Harmful environmental effects are seen in the disruption of natural systems and the loss of biodiversity due to hypoxia, or the depletion of dissolved oxygen in the water that occurs when unusually large numbers of algae decompose.

Although the effects of high nutrient loads are being observed in freshwater and estuarine systems across the country, the Midwestern United States contains a number of hotspots, due in part to its high percentage of total area under cultivation. In particular, the western end of Lake Erie and the Grand Lake St. Marys watershed in Ohio have been significantly affected. Decades of increasing levels of agricultural phosphorus inputs have severely degraded local conditions. Lake Erie is the shallowest of the Great Lakes, but also the most biologically diverse, and blooms and the hypoxic conditions that follow them threaten the integrity of this valuable natural system. In the fall of 2013, the water system for a town on the shore of Lake Erie was forced to provide bottled water to its customers for several days after levels of the toxin mycrocystin were found to be 3.5 times the safe drinking levels in the water supply. The Grand Lake St. Marys region's tourism and real estate industries suffered huge losses in recent years after the same toxin forced the closure of Grand Lake, a major water body in western Ohio, to practically all recreational activities. Similarly, the 'dead zone' in the Gulf of Mexico is caused by excess nutrient loading transported via the Mississippi River system from Midwestern farm fields.

Naturally, in response to these impacts many local, state, regional and national agencies and stakeholders have made nutrient management from both point and non-point sources a priority. Possible approaches range from tightening controls on the types, amounts, and times at which fertilizers can be applied to fields to various treatment and filtration technologies. The ideal solution would be one or a suite of tools and practices that, at reasonable costs, will allow farmers to support their livelihoods while acting as responsible stewards of the lands and waters their farms impact. FGD gypsum is precisely this type of tool. It is readily available across wide sections of the country, affordable and, in some areas, eligible for nutrient management subsidies, and with a significant and still increasing body of research demonstrating its effectiveness.

Favaretto et al. (2012) found a decrease in dissolved reactive phosphorus in runoff when gypsum was added to agricultural fields. This most likely occurs through the conversion of the phosphorus into less soluble compounds. The concentration of water-soluble phosphorus decreased by 50% in one study (Stout et al., 1998). In research conducted by Dr. Darrell Norton, gypsum application was found to mitigate some of the nutrient loading in runoff caused by the addition of manure to fields (Norton, 2008). Gypsum application on soils where poultry litter was used as fertilizer also significantly reduced soluble phosphorus (Sheng et al., 2012). In research performed in south Florida, dairy manure was the source of phosphorus loading in surface waters, and the application of gypsum resulted in higher retention rates of phosphorus in the soil, thereby reducing soluble phosphorus runoff and are even more effective when gypsum is applied to the buffers. Watts et al. (2009) showed a reduction in soluble phosphorus by up to 40% when gypsum was applied to the grass buffers in Alabama.

Gypsum and Soil Health

When assessing the need for to gypsum application, it is important to understand the stability of the soil by looking at soil aggregates. Aggregates are clusters of soil particles; their size and spacing influences water infiltration. Calcium binds soil particles into more effective aggregates that help with water infiltration (Walworth, 2006). Gypsum particularly improves the physical properties of heavy clay and sodic soils (Chen and Dick, 2011). By improving soil structure, gypsum helps prevent soil particulate dispersion, decreases surface crust formation, aids in seedling emergence, increases water infiltration, and decreases the loss of soil and nutrients due to surface runoff and erosion (Chen and Dick, 2011). When gypsum was applied to fields under no-till practices, it was found to decrease erosion and runoff (Norton, 2011). Due to better infiltration and less surface sealing, the addition of gypsum to soils could help farmers save money on irrigation since more water is available to the crop (Truman et al., 2010).

Gypsum also improves chemical properties of soil such as remedying aluminum toxicity caused by subsoil acidity (Chen and Dick, 2011; Dontsova et al., 2004). Results include better rooting and uptake of water and nutrients, especially during periods of water scarcity (Chen and Dick, 2011). While gypsum addresses subsoil acidity and aluminum toxicity, it is important to note that gypsum is not a liming agent, and does not alter pH levels in the soil (Fisher, 2011).

Appendix 1: Material Safety Data Sheet





Health	1
Fire	0
Reactivity	0
Personal Protection	E

Material Safety Data Sheet Calcium sulfate dihydrate MSDS

Section 1: Chemical Product and Company Identification

Product Name: Calcium sulfate dihydrate

Catalog Codes: SLC1969, SLC5545, SLC4549

CAS#: 10101-41-4

RTECS: WS6920000

TSCA: TSCA 8(b) inventory: No products were found.

Cl#: Not available.

Synonym: Calcium (II) sulfate, dihydrate; precipated calcium sulfate; Sulfuric acid, calcium (2+) salt, dihyydrate

Chemical Name: Calcium Sulfate, Dihydrate

Chemical Formula: CaSO4.2H2O

Contact Information:

Sciencelab.com, Inc. 14025 Smith Rd. Houston, Texas 77396

US Sales: 1-800-901-7247 International Sales: 1-281-441-4400

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call: 1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Calcium sulfate dihydrate	10101-41-4	100

Toxicological Data on Ingredients: Calcium sulfate dihydrate LD50: Not available. LC50: Not available.

Section 3: Hazards Identification

Potential Acute Health Effects:

Slightly hazardous in case of inhalation (lung irritant). Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, .

Potential Chronic Health Effects:

CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to lungs, upper respiratory tract. Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. WARM water MUST be used. Get medical attention.

Skin Contact:

In case of contact, immediately flush skin with plenty of water. Cover the irritated skin with an emollient. Remove contaminated clothing and shoes. Wash clothing before reuse. Thoroughly clean shoes before reuse. Get medical attention.

Serious Skin Contact:

Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation:

If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention immediately.

Serious Inhalation: Not available.

Ingestion:

Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Non-flammable.

Auto-Ignition Temperature: Not applicable.

Flash Points: Not applicable.

Flammable Limits: Not applicable.

Products of Combustion: Not available.

Fire Hazards in Presence of Various Substances: Not applicable.

Explosion Hazards in Presence of Various Substances:

Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available. Slightly explosive in presence of heat.

Fire Fighting Media and Instructions: Not applicable.

Special Remarks on Fire Hazards:

Calcium Sulfate mixed with phosphorus will ignite at high temperatures. When primed at high temperature with potassium nitrate-calcium silicide mixture, calcium sulfate mixed with excess red phosphorus will burn. When heated to decomposition it emits toxic fumes of oxides of sulfur and calcium.

Special Remarks on Explosion Hazards:

Contact with diazomethane causes an exothermic reaction which may lead to detonation. Many metal oxo-compounds (nitrates, oxides, and particulary sulfates) and sulfides are reduced violently or explosively (undergo a thermite reaction) on heating an intimate mixture with aluminum powder to a suitably high temperture to initiate the reaction. A violent or explosive reaction can occur upon heating when calcium sulfate is mixed with aluminum powder. Containers may explode when heated.

Section 6: Accidental Release Measures

Small Spill:

Use appropriate tools to put the spilled solid in a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and dispose of according to local and regional authority requirements.

Large Spill:

Use a shovel to put the material into a convenient waste disposal container. Finish cleaning by spreading water on the contaminated surface and allow to evacuate through the sanitary system. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions: Do not breathe dust. Keep away from incompatibles such as oxidizing agents, acids.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area. Hygroscopic

Section 8: Exposure Controls/Personal Protection

Engineering Controls:

Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection: Safety glasses. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:

Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:

TWA: 15 (mg/m3) from OSHA (PEL) [United States] Inhalation Total. TWA: 5 (mg/m3) from OSHA (PEL) [United States] Inhalation Respirable. TWA: 10 (mg/m3) from ACGIH (TLV) [United States] TWA: 10 (mg/m3) [United Kingdom (UK)] Inhalation Total. TWA: 4 (mg/m3) [United Kingdom (UK)] Inhalation Respirable.3 Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (hygroscopic crystals; lumps; powder)

Odor: Odorless.

Taste: Not available.

Molecular Weight: 172.17 g/mole

Color: Colorless. White.

pH (1% soln/water): Not available.

Boiling Point: Not available.

Melting Point: Not available.

Critical Temperature: Not available.

Specific Gravity: 2.32 (Water = 1)

Vapor Pressure: Not applicable.

Vapor Density: Not available.

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not available.

Ionicity (in Water): Not available.

Dispersion Properties: Not available.

Solubility:

Very slightly soluble in cold water. Solubility in water: 0.21 g/100 g water @ 20 deg. C; 0.24 g/100 g water @ 25 deg. C. Very soluble in glycerol. Practically insoluble in most organic solvents.

Section 10: Stability and Reactivity Data

Stability: The product is stable.

Instability Temperature: Not available.

Conditions of Instability: Incompatible materials

Incompatibility with various substances: Reactive with oxidizing agents, acids.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity:

Hygroscopic; keep container tightly closed. Loses 1/2 water at 128 C and 2 waters at 163 C. Incompatible with Diazomethane, aluminum, magnesium, phosphorous. The dihydrate form cannot set with water. Hygroscopic; keep container tightly closed.

Special Remarks on Corrosivity: Not available.

Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Inhalation. Ingestion.

Toxicity to Animals:

LD50: Not available. LC50: Not available.

Chronic Effects on Humans: May cause damage to the following organs: lungs, upper respiratory tract.

Other Toxic Effects on Humans: Slightly hazardous in case of skin contact (irritant), of ingestion, inhalation (lung irritant)

Special Remarks on Toxicity to Animals: The probable lethal oral human dose has been estimated to be 0.5 to 5 g/kg

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans:

Acute Potential Health Effects: Skin: May cause skin irritation. Eyes: Causes eye irritation. Inhalation: Causes respiratory tract and mucous membrane irritation. Symptoms may include coughing, rhinitis, epistaxis, sneezing, pneumonia, labored breathing. Ingestion: Because it hardens quickly after absorbing moisture, its ingestion may result in obstruction. Chronic Potential Health Effects: Inhalation: Repeated or prolonged inhalation may cause chronic rhinitis, laryngitis, pharyngitis, impaired sense of smell and taste, bleeding from the nose, and reactions of tracheal and bronchial membranes. t may also cause unspecified effects on the lungs.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not available.

Products of Biodegradation:

Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.

Section 13: Disposal Considerations

Waste Disposal:

Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: Not a DOT controlled material (United States).

Identification: Not applicable.

Special Provisions for Transport: Not applicable.

Section 15: Other Regulatory Information

Federal and State Regulations:

California prop. 65: This product contains the following ingredients for which the State of California has found to cause birth defects which would require a warning under the statute: No products were found. California prop. 65: This product contains the following ingredients for which the State of California has found to cause cancer which would require a warning under the statute: No products were found. Illinois toxic substances disclosure to employee act: Calcium sulfate dihydrate Rhode Island RTK hazardous substances: Calcium sulfate dihydrate

Other Regulations: OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200).

Other Classifications:

WHMIS (Canada): Not controlled under WHMIS (Canada).

DSCL (EEC):

This product is not classified according to the EU regulations. S24/25- Avoid contact with skin and eyes.

HMIS (U.S.A.):

Health Hazard: 1

Fire Hazard: 0

Reactivity: 0

Personal Protection: E

National Fire Protection Association (U.S.A.):

Health: 1

Flammability: 0

Reactivity: 0

Specific hazard:

Protective Equipment:

Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Section 16: Other Information

Other Special Considerations: Not available.

Created: 10/09/2005 04:33 PM

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Appendix 2: Chemical Information Review Document – National Institute of Environmental Health Sciences

Chemical Information Review Document

for

Synthetic and Naturally Mined Gypsum (Calcium Sulfate Dihydrate) [CAS No. 13397-24-5]

Supporting Nomination for Toxicological Evaluation by the National Toxicology Program

January 2006

Prepared by: Integrated Laboratory Systems, Inc. Research Triangle Park, NC Under Contract No. N01-ES-35515

Prepared for: National Toxicology Program National Institute of Environmental Health Sciences National Institutes of Health U.S Department of Health and Human Services Research Triangle Park, NC http://ntp.niehs.nih.gov/

Abstract

Gypsum is the dihydrate form of calcium sulfate. The word "gypsum," however, is used to describe different phases of the same material, including anhydrite (calcium sulfate, with no water of crystallization), selenite, calcined gypsum, and plaster of Paris. It forms as evaporites from marine waters and is usually found collectively with other mineral deposits such as quartz, sulfur, and clavs. Gypsum is also found in lakes, seawater, and hot springs as deposits from volcanic vapors. It is primarily used to manufacture wallboard and plaster for homes, offices, and commercial buildings; it is the most common natural fibrous mineral found indoors. Other applications of gypsum are as a soil additive, as a food and paint filler, and a component of blackboard chalk, medicines, and toothpaste. Humans may therefore be exposed to gypsum via inhalation, ingestion, skin contact, and eye contact. There is concern over the exposure of individuals to gypsum dust in the workplace and home, and this concern has increased in the aftermath of the World Trade Center (WTC) collapse in September 2001. Patients being examined in clinics include office workers, emergency response workers, constructions workers, and public members exposed to dust from the destruction. Analysis of general area and personal breathing zone air samples show that nonasbestos fibers consist mostly of gypsum, fibrous glass, and cellulose. In air and dusts collected from building materials dispersed from the WTC collapse three months later. gypsum was the most common mineral found in outdoor air samples from lower Manhattan. The majority of studies of gypsum workers, however, have reported no lung fibrosis or pneumoconiosis, except when gypsum was contaminated with silica. Gypsum is very soluble in the body. Aerosols of calcium sulfate fibers were quickly cleared from the lungs of rats and guinea pigs via dissolution. Nonpathological findings of subchronic inhalation studies in rats were dependent on the shape of the gypsum fibers. In a chronic inhalation study, calcined gypsum dust produced only minor effects in the lungs of guinea pigs. In carcinogenicity studies, gypsum was weakly tumorigenic. Gypsum induced abdominal cavity tumors in 5% of rats after intraperitoneal injection, carcinomas of the heart and kidney in hamsters after intratracheal administration, and no lung tumors in guinea pigs following inhalation exposure. None of the long-term studies can be considered adequate tests of chronic toxicity or carcinogenicity by modern standards.

Executive Summary

Basis for Nomination

Gypsum (the naturally mined and synthetic form) was nominated by the Mount Sinai-Irving J. Selikoff Center for Occupational and Environmental Medicine and the Operative Plasterers' and Cement Masons' International Association of the United States and Canada for toxicological studies based on widespread human exposure and a lack of well-conducted epidemiology or toxicology studies relevant to assessing the potential for adverse long-term health effects from exposure to gypsum dust. Gypsum is widely used in building materials and human exposure occurs when gypsum is mined, when gypsum is used for manufacturing building materials, when building material is disturbed, especially with power tools for maintenance or renovation, and when buildings are demolished. The nominators state: "Many patients seen in our [New York City] clinic are exposed to gypsum dust in their workplace or in their homes. These patients often have other exposures (asbestos, welding fumes) that make it impossible to attribute any health problems to gypsum by itself. Certain trades are continuously exposed (plasterers, laborers, steamfitters, plumbers, electricians) and have come to us with concern about their exposures. These patients often have other exposures (asbestos, welding fumes) that make it impossible to attribute any health problems to gypsum, by itself. Many office workers, emergency response workers and construction workers and the public were exposed to large amounts of gypsum (as well as other, more toxic substances) in the dust from the burning and collapse of the World Trade Centers [in September 2001]. We see many of these individuals in our clinic, as well."

Nontoxicological Data

Chemical Identification, Physical Properties, and Analysis

The word "gypsum" is used to describe different phases of the same material, including anhydrite (calcium sulfate, with no water of crystallization), selenite, calcined gypsum, and plaster of Paris. According to the National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards, gypsum is the dihydrate form of calcium sulfate. It is a naturally occurring mineral consisting of 79% calcium sulfate and 21% water. Gypsum can be identified and analyzed in dust samples by scanning electron microscopy.

Production and Uses

The United States is the main producer of gypsum; it accounted for $\sim 16.4\%$ of the reported global output in 2003. Commercial quantities of gypsum are available from New York, Michigan, Iowa, Kansas, Arizona, New Mexico, Colorado, Utah, and California. In 2004, the estimated U.S. production of crude gypsum was 18.0 million tons. Synthetic gypsum is mainly produced as a byproduct in flue gas desulfurization (FGD) systems. Calcined gypsum is produced domestically from crude gypsum by heating selenite. In the United States, gypsum is primarily used to manufacture wallboard and plaster for homes, offices, and commercial buildings. Other applications of gypsum are as a soil additive, as a food and paint filler, and a component of blackboard chalk, medicines, dental modes, and toothpaste.

Environmental Occurrence and Persistence

Naturally Occurring Gypsum

Gypsum is formed as evaporites from marine waters. It occurs in various forms in nature—gypsite (an impure form in the earth), selenite (flattened and twinned crystals and transparent cleavable masses), alabaster (a translucent and fine grain), and satin spar (a silky and fibrous transparent crystal form)—and in various purities. It is usually found collectively with other mineral deposits such as quartz, halite, sulfur, pyrites, carbonates, and clays. Gypsum is also found in lakes, seawater, and hot springs as deposits from volcanic vapors and sulfate solutions in veins. In the United States, gypsum sources are centered near California, the Great Lakes, and the Texas-Oklahoma area.

Gypsum in Air and Dusts from the World Trade Center (WTC) Collapse

At the WTC disaster site, assessment of general area and personal breathing zone air samples showed that most exposures, including asbestos, did not exceed the NIOSH recommended exposure limits (RELs) or Occupational Safety and Health Administration (OSHA) permissible exposure levels (PELs) [see below]. In samples with concentrations ≥ 0.1 fibers/cm³ of air, most nonasbestos fibers were found to be gypsum, fibrous glass, and cellulose. Fallen samples collected one and two days after the attack from areas within 0.5 mile of Ground Zero contained particulate matter with <2.5 µm mass median aerodynamic diameter (PM_{2.5}) that consisted mostly of calcium-based compounds, including gypsum.

When air and dusts from building materials dispersed from the WTC collapse were collected from November 4 to December 11, 2001, in and around 30 residential buildings in lower Manhattan and from four residential buildings above 59th Street (approximately five miles northeast of the WTC site), gypsum was the most common mineral found in lower Manhattan outdoor air samples. Concentrations found in 40 of 114 respirable fraction PM₄ were estimated at 3 to 14 μ g/m³. Above 59th Street, gypsum concentrations in air were $\leq 5 \mu$ g/m³. Gypsum concentrations in outdoor settled dusts in lower Manhattan were about 0.03 to 27%. In the residential building common areas, gypsum concentrations in settled dusts ranged from about 0.07 to 20%, while in 45 of 57 residences in these buildings, levels ranged from about 0.05 to 30%.

Gypsum in Indoor Environments

Gypsum is stated to be the most common natural fibrous mineral found indoors (20:1 gypsum fibers to asbestos) mainly because of its use in plaster in buildings. In a German study of fibrous dusts from installed mineral wool products in living rooms and workrooms, 134 measurements revealed an average air pollution of 3184 gypsum fibers/m³.

Human Exposure

Humans may be exposed to gypsum via inhalation, ingestion, skin contact, and/or eye contact. According to the NIOSH National Occupational Exposure Survey (NOES), conducted between 1981 and 1983, an estimated 7,865 workers (1,279 females) were potentially exposed to gypsum dust in eight industries. In a postmortem analysis of subjects in Rome, Italy, with no occupational exposure to mineral dusts, fibrous particles (generally asbestos fibers and small amounts of talc, rutile [aluminum oxide], and calcium sulfate [7778-18-9]) were detected in lung tissue in 16% of subjects. Mineral particle concentrations ranged from 0.7×10^5 to 1.7×10^5 particles/mg, indicating significant accumulations of mineral particles in lungs of persons living in urban areas. In a study of personal exposure to respirable inorganic and organic fibers geometric mean concentrations ranging from 600 to 4700 fibers/m³ of gypsum fibers were found in European taxi drivers, office workers, retired persons, and schoolchildren.

Regulatory Status

The NIOSH REL for gypsum is 10 mg/m³ (total dust—air) and 5 mg/m³ (respirable fraction—air) as a ten-hour time-weighted average (TWA). The OSHA PELs are 15 and 5 mg/m³ as an eight-hour TWA, respectively. The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) for gypsum (as total dust containing no asbestos and <1% crystalline silica) is 10 mg/m³ as TWA. In 1992, the Environmental Protection Agency (EPA) established that phosphogypsum (byproduct from a manufacturing process such as for phosphoric acid) must not have a certified average ²²⁶Ra concentration >370 becquerel/kg (Bq/kg), restricting its use in most applications.

Toxicological Data

Data from reproductive or developmental toxicity, initiation/promotion, anticarcinogenicity, genotoxicity, or immunotoxicity studies were not available for gypsum dust or fibers.

Human Data

Gypsum is a skin, eye, mucous membrane, and respiratory system irritant. Early studies of gypsum miners did not relate pneumoconiosis with chronic exposure to gypsum. Other studies in humans (as well as animals) showed no lung fibrosis produced by natural dusts of calcium sulfate except in the presence of silica. However, a series of studies reported chronic nonspecific respiratory diseases in gypsum industry workers in Gacki, Poland.

Absorption, Distribution, Metabolism, and Excretion

Unlike other fibers, gypsum is very soluble in the body; its half-life in the lungs has been estimated as minutes. In four healthy men receiving calcium supplementation with calcium sulfate ($CaSO_4 \cdot 1/2H_2O$) (200 or 220 mg) for 22 days, an average absorption of 28.3% was reported.

Health Effects from Occupational Exposures

In a study of 241 underground male workers employed in four gypsum mines in Nottinghamshire and Sussex for a year (November 1976-December 1977), results of chest X-rays, lung function tests, and respiratory systems suggested an association of the observed lung shadows with the higher quartz content in dust rather than to gypsum; the small round opacities in the lungs were characteristic of silica exposure. Prophylactic examinations of workers in a gypsum extraction and production plant (dust concentration exceeded TLV 2.5- to 10-fold) reported no risk of pneumoconiosis due to gypsum exposure, while another study of gypsum manufacturing plant workers reported that chronic occupational exposure to gypsum dust had resulted in pulmonary ventilatory defect of the restrictive form.

Three cases of idiopathic interstitial pneumonia with multiple bullae throughout the lungs were seen in Japanese schoolteachers (lifetime occupation) exposed to chalk; 2/3 of the chalk was made from gypsum and small amounts of silica and other minerals.

Skin Irritation

Coal miners using anhydrite (containing traces of calcium fluoride and hydrofluoric acid) have complained of skin irritation. In ten volunteers, five applications of anhydrite paste (100 mg) or hemihydrate paste (100 mg) to the forearm under occlusion for 24 hours produced mean blood flow values of 18.0 and 14.0%, respectively; controls had a value of 12.1%. The increased blood flow indicated increased irritancy; however, there was no clinical sign of irritation in any subject.

Chemical Disposition, Metabolism, and Toxicokinetics

In rats exposed to an aerosol of anhydrous calcium sulfate fibers (15 mg/m^3) or a combination of milled and fibrous calcium sulfate (60 mg/m³) six hours per day, five days per week for three weeks, gypsum dust was quickly cleared from the lungs of via dissolution and mechanisms of particle clearance.

In guinea pigs given intraperitoneal (i.p.) injections of gypsum (doses not provided), gypsum was absorbed followed by the dissolution of gypsum in surrounding tissues. In another study, after i.p. injection of gypsum (2 cm^3 of a 5 or 10% suspension in saline) into guinea pigs, which were sacrificed at intervals up to 180 days, most of the dust was found distributed in the peritoneum of the anterior abdominal wall. Gypsum dust produced irregular and clustered nodules, which decreased in size over time.

Several feeding studies in pigs on the bioavailability of calcium in calcium supplements, including gypsum, have been conducted. The bioavailability of calcium in gypsum was similar to that for calcitic limestone, oyster shell flour, marble dust, and aragonite, ranging from 85 to 102%.

Acute Exposure

In mice, the i.p. and intragastric LD_{50} values were 6200 and 4704 mg/kg, respectively, for phosphogypsum (98% CaSO₄·H₂O). For plaster of Paris, the values were 4415 and 5824, respectively. In rats, an intragastric LD_{50} of 9934 mg/kg was reported for phosphogypsum.

Direct administration of WTC $PM_{2.5}$ [mostly composed of calcium-based compounds, including calcium sulfate (gypsum) and calcium carbonate (calcite)] (10, 32, or 100 µg) into the airways of mice produced mild to moderate lung inflammation and airway hyperresponsiveness at the high dose. [It was noted that WTC $PM_{2.5}$ is composed of many chemical species and that their interactions may be related with development of airway hyperresponsiveness.] In female SPF Wistar rats intratracheally (i.t.) instilled with anhydrite dust (35 mg) and sacrificed three months later, an increase in total lipid or hydroxyproline content in the lungs was not observed compared to controls.

Short-term and Subchronic Exposure

In inhalation (nose-only) experiments in which male F344 rats were exposed to calcium sulfate fiber aerosols (100 mg/m³) for six hours per day, five days per week for three weeks, there were no effects on the number of macrophages per alveolus, bronchoalveolar lavage fluid (BALF) protein concentration, or BALF γ -glutamyl transpeptidase activity (γ -GT). Following three weeks of recovery, nonprotein thiol levels (NPSH), mainly glutathione, were increased in animals. In follow-up experiments, rats were exposed to an aerosol of anhydrous calcium sulfate fibers (15 mg/m³) or a combination of milled and fibrous calcium sulfate (60 mg/m³) for the same duration. Calcium levels in the lungs were similar to those of controls; however, gypsum fibers were detected in the lungs of treated animals. Significant increases in NSPH levels in BALF were observed in rats killed immediately after exposure at both doses and in recovery group animals at the higher dose. At 15 mg/m³, almost all NPSH was lost in macrophages from all treated animals (including those in recovery), but a significant decrease in extracellular γ -GT activity was seen only in recovery group animals. Overall, the findings were "considered to be non-pathological local effects due to physical factors related to the shape of the gypsum fibers and not to calcium sulphate *per se*."

Intratracheal administration of man-made calcium sulfate fiber (2.0 mg) once per week for five weeks resulted in no deaths or significant body weight changes in female Syrian hamsters compared to controls. Inflammation (specifically, chronic alveolitis with macrophage and neutrophil aggregation) was observed in the lung.

Chronic Exposure

In guinea pigs, inhalation of calcined gypsum dust $(1.6 \times 10^4 \text{ particles/mL})$ for 44 hours per week in 5.5 days for two years, followed with or without a recovery period of up to 22 months, produced only minor effects in the lungs. There were 12 of 21 deaths over the entire experimental period. These were due to pneumonia or other pulmonary lesions; however, no significant gross signs of pulmonary disease or nodular or diffuse pneumoconiosis became significant. Beginning near 11 months, pigmentation and atelectasis were seen. During the recovery period, four of ten guinea pigs died; two died of pneumonia. Pigmentation continued in most animals but not atelectasis. Low-grade chronic inflammation, occurring in the first two months, also disappeared.

Synergistic/Antagonistic Effects

In rats, i.t. administration of anhydrite (5-35 mg) successively and simultaneously with quartz reduced the toxic effect of quartz in lung tissue. This protective effect on quartz toxicity was also seen in guinea pigs; calcined gypsum dust prevented or hindered the development of fibrosis. Natural anhydrite, however, increased the fibrogenic effect of cadmium sulfide in rats. Additionally, calcined gypsum dust had a stimulatory effect on experimental tuberculosis in guinea pigs.

Cytotoxicity

In Syrian hamster embryo cells, gypsum (up to 10 μ g/cm²) did not induce apoptosis. Negative results were also found in mouse peritoneal macrophages (tested at 150 μ g/mL gypsum dust) and in Chinese hamster lung V79-4 cells (tested up to 100 μ g/mL).

Carcinogenicity

In female Sprague-Dawley rats, i.p. injection of natural anhydrite dusts from German coal mines (doses not provided) induced granulomas; whether gypsum was the causal factor was not established. In Wistar rats, four i.p. injections of gypsum (25 mg each) induced abdominal cavity tumors, mostly sarcomatous mesothelioma, in 5% of animals; first tumor was seen at 546 days. In a subsequent experiment using the same procedure, female Wistar rats exhibited the first tumor at 579 days after the last injection. Mean survival of the tumor-bearing rats (5.7% of test group) was 583 days, while mean survival of the test group was 587 days. Tumor types seen were a sarcoma having cellular polymorphism, a carcinoma, and a reticulosarcoma.

Intratracheal administration of man-made calcium sulfate fiber (2.0 mg) once per week for five weeks produced tumors in three of 20 female Syrian hamsters observed two years later. An anaplastic carcinoma was found in the heart, and one dark cell carcinoma was seen in the kidney. Two tumors of unspecified types were observed in the rib.

In guinea pigs, inhalation of gypsum (doses not provided) for 24 months produced no lung tumors.

Other Data

In rats, i.t. administration of gypsum (doses not provided in abstract) from FGD for up to 18 months produced no arterial blood gas changes or indications of secondary heart damage as compared to controls. In another study, a single i.t. dose (25 mg) of flue gas gypsum dust did not produce a pathological reaction when observed for up to 18 months. There were also no signs of developing granuloma of fibrosis of the lungs. Lead quickly accumulated in the femur after injection but was eliminated during the observation period. In the Ames test, the flue gas gypsum dust was negative.

Recently implemented mercury emissions controls on coal-fired power plants have increased the likelihood of the presence of mercury in synthetic gypsum formed in wet FGD systems and the finished wallboard produced from the FGD gypsum. In a study at a commercial wallboard plant, the raw FGD gypsum, the product stucco (beta form of $CaSO_4 \cdot 1/2H_2O$), and the finished dry wallboard each contained about 1 µg Hg/g dry weight. Total mercury loss from the original FGD gypsum content was about 0.045 g Hg/ton dry gypsum processed.

Structure-Activity Relationships

Calcium sulfate (up to 2.5%) was negative in *Salmonella typhimurium* strains TA1535, TA1537, and TA1538 and in *Saccharomyces cerevisiae* strain D4 with and without metabolic activation. In pregnant mice, rats, and rabbits, daily oral administration of calcium sulfate (16-1600 mg/kg bw) beginning on gestation day 6 up to 18 produced no effects on maternal body weights, maternal or fetal survival, or nidation; developmental effects were also not seen.

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1.0 Basis for Nomination

Gypsum (the naturally mined and synthetic form) was nominated by the Mount Sinai-Irving J. Selikoff Center for Occupational and Environmental Medicine and the Operative Plasterers' and Cement Masons' International Association of the United States and Canada for toxicological studies based on widespread human exposure and a lack of well-conducted epidemiology or toxicology studies relevant to assessing the potential for adverse long-term health effects from exposure to gypsum dust. Gypsum is widely used in building materials and human exposure occurs when gypsum is mined, when gypsum is used for manufacturing building materials, when building material is disturbed, especially with power tools for maintenance or renovation, and when buildings are demolished. The nominators state: "Many patients seen in our [New York City] clinic are exposed to gypsum dust in their workplace or in their homes. These patients often have other exposures (asbestos, welding fumes) that make it impossible to attribute any health problems to gypsum by itself. Certain trades are continuously exposed (plasterers, laborers, steamfitters, plumbers, electricians) and have come to us with concern about their exposures. These patients often have other exposures (asbestos, welding fumes) that make it impossible to attribute any health problems to gypsum, by itself. Many office workers, emergency response workers and construction workers and the public were exposed to large amounts of gypsum (as well as other, more toxic substances) in the dust from the burning and collapse of the World Trade Centers [in September 2001]. We see many of these individuals in our clinic, as well."

2.0 Introduction

Gypsum [13397-24-5]

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ChemIDplus (2004) identifies gypsum as calcium sulfate (according to the database, also called plaster of Paris) and phosphogypsum. According to the National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards, gypsum is the dihydrate form of calcium sulfate and plaster of Paris [CAS No. 26499-65-0] is the hemihydrate form (NIOSH, undated-c,d). This is the naming followed by the U.S. EPA ([SRS] undated), Registry (2005), and ChemFinder (2004). Phosphogypsum is given as a synonym for gypsum (RTECS, 2000). It usually designates the byproduct produced from a manufacturing process such as for phosphoric acid (Health Physics Society, 2001; Reed, 1975). Additionally, plaster of Paris is given a separate CAS Registry Number, 26499-65-0 (NIOSH, undated-c; RTECS, 1998; Registry, 2005).

The word "gypsum" is used to describe different phases of the same material, including anhydrite (calcium sulfate, with no water of crystallization), selenite, calcined gypsum, and plaster of Paris (Reed, 1975; Health Council of the Netherlands, Committee on Updating of Occupational Exposure Limits, 2002). This review presents data for gypsum dust and fibers; the terminology used in the original sources was employed. Information and study data relating to oral exposure to gypsum or anhydrous calcium sulfate (including dietary supplements) and the use of gypsum in bone implants is generally not included in this review.

2.1 Chemical Identification and Analysis

2.1.1 Gypsum [13397-24-5]

Gypsum (9CI) (CaSO₄·2H₂O; mol. wt. = 174.19) is also called:

Calcium(II) sulfate dihydrate CoCoat T Crystacal R Duracal Cement G 6 (refractory) G 16 (gypsum) G 75 (mineral) GIPS Gypsite Gypsum stone Gypsum sulfate Hydrated calcium sulfate Hydrocal Hydroperm Landplaster Mineral white New Diastone PE 20A Phosphogypsum Primoplast SK (mineral) Tiger Kencoat

Sources: ChemFinder (2004); NIOSH (undated-c); Registry (2005); RTECS (2000); U.S. EPA SRS (undated)

PubChem CID = 24948InChI: 1/Ca.H2O4S.2H2O/c;1-5(2,3)4;;/h;(H2,1,2,3,4);2*1H2/q+2;;;/p-2/fCa.O4S.2H2O/qm;-2;;

2.1.2 Plaster of Paris [26499-65-0]

Plaster of Paris (CaSO₄· $1/2H_2O$; mol. wt. = 145.2) is also called:

Calcium sulfate hemihydrate Crystacal Dried calcium sulfate Densite Densite (gypsum) FGR Gypsum hemihydrate Hemihydrate gypsum PH 200 Sakura Plaster of Paris B Grade TA 20 Tiger Stone

Sources: NIOSH (undated-c); Registry (2005); RTECS (1998)

2.1.3 Calcium sulfate [7778-18-9]

Calcium sulfate (CaSO₄; mol. wt. = 136.14) is also called:

Anhydrite Anhydrous calcium sulfate (1:1) Anhydrous gypsum Anhydrous sulfate of lime Drierite Gibs Karstenite Muriacite Natural anhydrite Sulfuric acid, calcium salt Terra Alba Thiolite

Sources: ChemFinder (2004); ChemIDplus (2004); Registry (2005)

2.1.4 Analytical Methods

Ambient nanometer-sized airborne particles, including sulfur-bearing particles, can be identified and analyzed by a new technique called energy-filtered transmission electron microscopy (EFTEM) (Chen et al., 2005). Gypsum was one of the minerals identified in bulk dust samples collected from Danish offices and analyzed by scanning electron microscopy (Molhave et al., 2000). The components of several crystals (silica, gypsum, brushite, etc.) in urinary stones were identified by polarization microscopy, infrared spectroscopy, X-ray diffraction, electron microscopy, and chemical analysis (Kim, 1982). Suspensions of total dust samples from Portland cement (PC) are quantitatively analyzed by measuring the intensities of X-ray fluorescence for Ca, Si, Fe, and Sr in samples deposited onto Ag membrane filters as well as the attenuation of X-rays from the fluorescing Ag membrane filter. The common crystalline solid phases in dust from PC bulk material and air samples are compared using X-ray diffraction for qualitative confirmation (OSHA, 1991).

Property	Information	Reference(s)		
Gypsum [13397-24-5]				
Physical State	white crystalline powder or lumps	IPCS (2004a)		
Odor	odorless	NIOSH (undated-c)		
Melting Point (°C)	100	Registry (2005)		
Density (g/cm ³)	2.3	IPCS (2004a); Registry (2005)		
Specific Gravity	2.32	NIOSH (undated-d)		
Water Solubility	0.24 g/100 mL @ 25 °C	IPCS (2004a)		
Vapor Pressure (mm Hg)	0	NIOSH (undated-d)		
Plaster of Paris [26499-65-0]				
Physical State	fine hygroscopic yellow or white powder	IPCS (2004b); NIOSH (undated-d)		
Odor	odorless	NIOSH (undated-d)		
Melting Point (°C)	163	IPCS (2004b); Registry (2005)		
Density (g/cm ³)	2.76 (_ hemihydrate); 2.63 (_ hemihydrate)	IPCS (2004b)		
Specific Gravity	2.5	NIOSH (undated-d)		
Water Solubility	0.30 g/100 mL @ 25 °C	IPCS (2004b)		
Vapor Pressure (mm Hg)	~0	NIOSH (undated-d)		
	Calcium Sulfate [7778-18-9]			
Physical State	white hygroscopic powder or crystal	ChemFinder (2004)		
Odor	odorless	ChemFinder (2004)		
Melting Point (°C)	1450	Registry (2005) ChemFinder (2004)		

2.2 Physical-Chemical Properties

Density (g/cm ³)	2.960	Registry (2005) ChemFinder (2004)
Water Solubility	slightly soluble	ChemFinder (2004)

Gypsum is a naturally occurring mineral consisting of 79% calcium sulfate and 21% water (Reed, 1975). The white color of pure gypsum changes to gray, brown, or pink as impurities are added. When heated, gypsum loses 75% of its water, becoming hemihydrate gypsum (CaSO₄·1/2H₂O), which is easily grounded to a powder commonly called plaster of Paris. When mixed with water, forming a paste or slurry, it dries and sets as a very hard solid. Additionally, as the plaster-water mixture dries, water will chemically recombine with hemihydrate gypsum, and the material will revert back to the original composition of gypsum (Founie, 2003). Further heating to above ~180 °C will produce the anhydrous form, called anhydrous calcium sulfate or anhydrite (Wikipedia, 2005).

Phosphogypsum (byproduct of manufacturing processes) is relatively acidic, contains a small amount of fluoride, and is slightly radioactive. The radium content of phosphogypsum is 20 to 30 picoCuries ²²⁶Ra per gram (pCi/g), whereas the radium content of natural gypsum and of most soils and rocks is 1 to 2 pCi/g or less (Florida State University, undated).

2.3 Commercial Availability

Commercial quantities of gypsum are available from New York, Michigan, Iowa, Kansas, Arizona, New Mexico, Colorado, Utah, and California in the United States and in England and Canada (Wikipedia, 2005). In 2003, crude gypsum was mined by 22 companies in the United States at 45 mines in 17 states. Companies that produced ~77% of the total U.S. crude gypsum were U.S. Gypsum Corporation (9 mines), National Gypsum Company (6 mines), Georgia-Pacific Corporation (6 mines), BPB America Inc. (5 mines), and American Gypsum Company (3 mines). Calcining plants that produced ~92% of the national calcined gypsum output were U.S. Gypsum (21 plants), National Gypsum (15 plants), Georgia-Pacific (14 plants), and BPB (6 plants) (Founie, 2003). Calcined gypsum is marketed as plaster or prefabricated products; the plaster is packed in 100-lb bags and sold under various trade names (Reed, 1975).

3.0 Production Processes

Gypsum is produced from deposits found worldwide and is consumed within the country in which it is mined. Synthetic gypsum is mainly produced as a byproduct in flue gas desulfurization (FGD) systems; smaller amounts originate from chemical processes such as acid neutralization processes, citric acid production, sugar production from sugar beets, and titanium dioxide production. Calcined gypsum is produced domestically from crude gypsum (Founie, 2003). It is produced by heating selenite at ~350 °F for one hour. Upon addition of water, plaster of Paris is formed, which then quickly sets and hardens as selenite again. Gypsum for use in cement is crushed to -1/2 inch; it is ground to about 100 mesh for agricultural or filler use (Reed, 1975).

Phosphogypsum is an industrial byproduct from the manufacture of fertilizer (Founie, 2003).

4.0 **Production and Import Volumes**

In 2003, the latest figures showed that the United States was the lead world producer of gypsum, accounting for $\sim 16.4\%$ of the reported global output (Founie, 2003). During the period between 2001 and 2003, U.S. production of crude gypsum remained fairly constant; values ranged from

15.7 to 16.7 million tons. This was a decrease from the production of 22.4 and 19.5 million tons in 1999 and 2000, respectively. However, estimates for 2004 show an increase with a value of 18.0 million tons. Manufacture of synthetic gypsum has steadily increased: in 1999, 5.2 million tons were produced, while in 2004, an estimated 11.0 million tons were produced. Also in 2004, an estimated 25.5 million tons of calcined gypsum were produced. Imports of crude gypsum [including anhydrite] steadily decreased (9.3 million tons in 1999 to 8.3 million tons in 2003); 10.4 million tons was estimated for 2004. U.S. exports, however, were low with only 130,000 metric tons sent abroad (Founie, 2005; Olson, 2004). Additionally, in 2003, 18 U.S. coal-fired electrical plants produced ~12.0 million tons of synthetic gypsum from FGD system (Founie, 2003).

Since the mid-1980s, the annual production rate of phosphogypsum has ranged from 40 to 47 million metric tons per year; 4.5 tons of phosphogypsum results from the production of a ton of phosphoric acid. As of 1989, the phosphoric acid industry consisted of 21 active facilities that used the wet-acid production process; the majority of these facilities are located in Florida (12), Louisiana (3), and North Carolina (1) (U.S. EPA, 2004).

5.0 Uses

In the United States, gypsum is primarily used to manufacture wallboard and plaster (construction material) for homes, offices, and commercial buildings (Founie, 2003). In 2003, ~90% of U.S. consumption was comprised of these products (Olson, 2004). Gypsum is added to cement to delay setting time. Worldwide, gypsum is used in portland cement, which is employed in concrete for bridges, buildings, highways, and many other structures. It is also used as a soil additive or conditioner for large areas of land in suburban and agricultural regions. High-purity gypsum is used in various industrial operations, including the production of foods, glass, paper, and pharmaceuticals (Founie, 2003). In foods (e.g., tofu and breads), it is a source of calcium; we consume 28 lb of gypsum in our lifetime (Snyder and Russel, undated). It is especially found in traditional (i.e., Chinese herbal) medicines (e.g., Yuan et al., 1999). Gypsum is also used in blackboard chalk, dental modes, surgical casts, paint filler, toothpaste, and molds for casting metals (Wikipedia, 2005).

Synthetic gypsum is used as a substitute for mined gypsum, principally for wallboard manufacturing, agricultural purposes, and cement production (Founie, 2003).

6.0 Environmental Occurrence and Persistence

Naturally Occurring Gypsum

Gypsum is formed as evaporites from marine waters; they are found as orderly stratigraphic beds with limestone and salt (Reed, 1975). Gypsum occurs in various forms in nature—gypsite (an impure form in the earth), selenite (flattened and twinned crystals and transparent cleavable masses), alabaster (a translucent and fine grain), and satin spar (a silky and fibrous transparent crystal form)—and in various purities. It is usually found collectively with other mineral deposits such as quartz, halite, sulfur, pyrites, carbonates, and clays. Gypsum is also found in lakes, seawater, hot springs, deposits from volcanic vapors, and sulfate solutions found in narrow channels in rock or earth (Oakes et al., 1982; Wikipedia, 2005). For example, in the interaction of lava from Hawaii's Kilauea volcano with sea water, which yields large clouds of mist known as LAZE, airborne fibers were detected in one of five LAZE plume (beach) samples at a

concentration of 0.16 fibers/cm³. These fibers were composed largely of hydrated calcium sulfate, similar in morphology to gypsum [exact identification could not be made in all cases] (Kullman et al., 1994).

At the base of the Guadalupe Mountains in Texas are white dunes of gypsum, formed from the evaporation of seas (Miller, 2005). These dunes of gypsum are also found in neighboring New Mexico; gypsum beds up to 100 feet thick were reported. In the United States, gypsum sources are centered near California, the Great Lakes, and the Texas-Oklahoma area, although gypsum beds are also found in other states such as Iowa and Utah, up to 200 feet thick (Reed, 1975).

Gypsum in Air and Dusts from the World Trade Center (WTC) Collapse

At the WTC disaster site, assessment of general area and personal breathing zone air samples showed that most exposures, including asbestos, did not exceed the NIOSH recommended exposure limits (RELs) or Occupational Safety and Health Administration (OSHA) permissible exposure levels (PELs) [see Section 8.0]. In samples (n=25) with concentrations ≥ 0.1 fibers/cm³ of air, most nonasbestos fibers were found to be gypsum, fibrous glass, and cellulose (McKinney et al., 2002). Fallen samples collected one and two days after the attack from areas within 0.5 mile of Ground Zero contained particulate matter with <2.5 µm mass median aerodynamic diameter (PM_{2.5}) that were alkaline and mostly of calcium-based compounds, including calcium sulfate (gypsum) and calcium carbonate (calcite), arising from crushed building materials such as cement and wallboard (Gavett, 2003; McGee et al., 2003).

When air and dusts from building materials dispersed from the WTC collapse were collected from November 4 to December 11, 2001, in and around 30 residential buildings in lower Manhattan and from four residential buildings above 59th Street (approximately five miles northeast of the WTC site), gypsum was the most common mineral found in lower Manhattan outdoor air samples. Concentrations found in 40 of 114 respirable fraction PM₄ (particulate matter of mass median diameter 4 µm) were estimated at 3 to 14 µg/m³. (The X-ray diffraction method used to determine a broad range of constituents gave only semiquantitative results for gypsum; thus, values were reported as estimates.) Frequencies of gypsum occurrence were 33 of 105 PM₁₀ samples and 24 of 101 PM₁₀₀ samples. Above 59th Street, gypsum concentrations in air were $\leq 5 \mu g/m^3$ (WTC Environmental Assessment Working Group, 2002; see also Jeffery et al., 2003).

Gypsum concentrations in outdoor settled dusts in lower Manhattan were about 0.03 to 27%. In the residential building common areas (23 of 26 samples), gypsum concentrations in settled dusts ranged from about 0.07 to 20%. In 45 of 57 residences in these buildings, gypsum dust concentrations ranged from about 0.05 to 30%. The estimated maximum gypsum concentration above 59th Street was 4% (WTC Environmental Assessment Working Group, 2002).

Gypsum in Indoor Environments

Gypsum is stated to be the most common natural fibrous mineral found indoors (20:1 gypsum fibers to asbestos) mainly because of its use in plaster in buildings (Hoskins, 2001). In a German study of fibrous dusts from installed mineral wool products in living rooms and workrooms, 134 measurements revealed an average air pollution of 3184 gypsum fibers/m³; 20% of those with a diameter of >1 μ m were from construction materials (Anonymous, 1994).

7.0 Human Exposure

Humans may be exposed to gypsum via inhalation, ingestion, skin contact, and/or eye contact (NIOSH, undated-c). The same exposure routes exist for plaster of Paris (NIOSH, undated-d). It was estimated that healthy individuals exposed to ~425 μ g WTC PM_{2.5}/m³ air [see Section 6.0] for eight hours would receive a dose comparable to that of mice receiving 100 μ g [see Section 9.1.3], which could lead to lung inflammation, airway hyperresponsiveness, and cough (Gavett, 2003; Gavett et al., 2003).

According to the NIOSH National Occupational Exposure Survey (NOES), conducted between 1981 and 1983, an estimated 7,865 workers (1,279 females) were potentially exposed to gypsum dust in eight industries (NIOSH, undated-a). For plaster of Paris, an estimated 60,066 employees (7,948 females) were exposed in 16 industries (NIOSH, undated-b). Analysis by specific occupations is also available.

When fragments of lung tissue were taken postmortem from the upper lobe of the right lung of 60 subjects who had resided in Rome, Italy, with no occupational exposure to mineral dusts, fibrous particles (generally asbestos fibers and small amounts of talc, rutile [aluminum oxide], and calcium sulfate [7778-18-9]) were detected in 16% of subject. Mineral particle concentrations ranged from 0.7×10^5 to 1.7×10^5 particles/mg, indicating significant accumulations of mineral particles in lungs of persons living in urban areas (Albedi et al., 1990). In a study of personal exposure to respirable inorganic and organic fibers, geometric mean concentrations of 597, 1046, 1965, and 3722 fibers/m³ of gypsum fibers (length >5 µm) were found in European taxi drivers, office workers, retired persons, and schoolchildren, respectively. Levels of gypsum fiber with a length between 2.5 and 5 µm were higher: 1729, 1406, 3010, and 4725 fibers/m³, respectively (Schneider et al., 1996).

8.0 Regulatory Status

The NIOSH REL for gypsum and plaster of Paris is 10 mg/m^3 (total dust—air) and 5 mg/m^3 (respirable fraction—air) as a ten-hour time-weighted average (TWA). The OSHA PELs are 15 and 5 mg/m³ as an eight-hour TWA, respectively (NIOSH, undated-c,d; RTECS, 2000). The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) for gypsum and plaster of Paris (as total dust containing no asbestos and <1% crystalline silica) is 10 mg/m³ as TWA (IPCS, 2004a,b).

In 1992, the Environmental Protection Agency (EPA) established that phosphogypsum not have a certified average ²²⁶Ra concentration >370 becquerel/kg (Bq/kg); this restricted its use in most applications including agricultural and construction purposes. It is therefore stockpiled in stacks (Health Physics Society, 2001; U.S. EPA, 2004).

9.0 Toxicological Data

9.1 General Toxicology

Both gypsum and plaster of Paris are skin, eye, mucous membrane, and respiratory system irritants. Other symptoms humans may exhibit from exposure are coughing, sneezing, or rhinorrhea (NIOSH, undated-c,d). Early studies of gypsum miners did not relate pneumoconiosis with chronic exposure to gypsum (Forbes et al., 1950; Gardner, 1938; Riddell,

1934; Schepers and Durkan, 1955; all cited by Oakes et al., 1982). Other studies in humans (as well as animals) showed no lung fibrosis produced by natural dusts of calcium sulfate except in the presence of silica (e.g., Burilkov and Michailova-Dotschewa, 1990, and Einbrodt, 1988). However, a series of studies reported chronic nonspecific respiratory diseases in gypsum industry workers in Gacki, Poland (Owsinski and Dolezal, 1972). Results of more recent human exposure studies to gypsum dust/fiber are presented below.

9.1.1 Human Data

Absorption, Distribution, Metabolism, and Excretion

Unlike other fibers, gypsum is very soluble in the body with an estimated half-life in the lungs in the range of several minutes (Hoskins, 2001). In healthy men receiving calcium sulfate supplementation (CaSO₄·1/2H₂O; 220 mg orally), average absorption was 28.3% (Rao and Rao, 1974).

Health Effects from Occupational Exposures

Plasterers and Construction Workers

Numerous case-control studies have been conducted regarding a possible association between cancer risk and occupations, including plasterers and construction workers (exposures to crystalline silica, man-made mineral fibers, polycylic aromatic hydrocarbons, etc.) (e.g., Arndt et al., 1996, Bruske-Hohlfeld et al., 2000, and Milne et al., 1983). A statistically significant increase in risks for lung cancer, asbestosis, other non-malignant respiratory diseases, and benign neoplasms was observed among plasterers potentially exposed to toxic materials such as plaster of Paris, silica, fiberglass, talc, and 1,1,1-trichloroethylene. Plasterers were also found to have the highest risk of liver cancer (Bouchardy et al., 2002; Okuda et al., 1989; Stern et al., 2001; Zahm et al., 1989).

Workers in the Gypsum Industry

In a study of 241 underground male workers employed in four gypsum mines in Nottinghamshire and Sussex for a year (November 1976-December 1977), results of chest X-rays, lung function tests, and respiratory systems suggested an association of the observed lung shadows with the higher quartz content in dust rather than to gypsum. The small round opacities in the lungs were characteristic of silica exposure (Oakes et al., 1982).

Prophylactic examinations of workers in a gypsum extraction and production plant (dust concentration exceeded TLV 2.5- to 10-fold) reported no risk of pneumoconiosis due to gypsum exposure. Occupational dust bronchitis was observed in four cases; death due to chronic non-specific lung disease was 5.3%, not exceeding the average for the corresponding age and sex collective in the general population (Burilkov and Michailova-Dotschewa, 1990). In another study of gypsum manufacturing plant workers (n=50), chronic occupational exposure to gypsum dust resulted in pulmonary ventilatory defect of the restrictive form (Moustafa et al., 1994 abstr.).

<u>Schoolteachers</u>

Three cases of idiopathic interstitial pneumonia with multiple bullae throughout the lungs were seen in Japanese schoolteachers (lifetime occupation) exposed to chalk; 2/3 of the chalk was made from gypsum and small amounts of silica and other minerals (Ohtsuka et al., 1995).

Skin Irritation

Coal miners using anhydrite (containing traces of calcium fluoride and hydrofluoric acid) for filling in gaps between rocks and beams have complained of skin irritation. When the hemihydrate was used as a substitute, which was less alkaline than anhydrite paste, a significant decrease in the condition was reported. In ten volunteers, five applications of anhydrite paste (100 mg) or hemihydrate paste (100 mg) to the forearm under occlusion for 24 hours produced mean blood flow values of 18.0 and 14.0%, respectively; controls had a value of 12.1%. The increased blood flow indicated increased irritancy; however, there was no clinical sign of irritation in any subject (Lachapelle et al., 1984).

9.1.2 Chemical Disposition, Metabolism, and Toxicokinetics

In rats exposed to an aerosol of anhydrous calcium sulfate fibers (15 mg/m³) or a combination of milled and fibrous calcium sulfate (60 mg/m³) six hours per day, five days per week for three weeks, gypsum dust was quickly cleared from the lungs via dissolution and mechanisms of particle clearance (Clouter et al., 1997, 1998; both cited by Health Council of the Netherlands, Committee on Updating of Occupational Exposure Limits, 2002).

In guinea pigs given intraperitoneal (i.p.) injections of gypsum (doses not provided), gypsum was absorbed followed by the dissolution of gypsum in surrounding tissues (Greim, 1996; cited by Health Council of the Netherlands, Committee on Updating of Occupational Exposure Limits, 2002). In another study, after i.p. injection of gypsum (2 cm³ of a 5 or 10% suspension in saline) into guinea pigs, which were sacrificed at intervals up to 180 days, most of the dust was found distributed in the peritoneum of the anterior abdominal wall. Gypsum dust produced irregular and clustered nodules, which decreased in size over time, leaving brown pigment which ultimately disappeared (Miller and Sayers, 1936, 1941).

Several studies in pigs on the bioavailability of calcium in calcium supplements, including gypsum, have been conducted. The animals were fed calcium-supplemented diets for up to 42 days. The bioavailability of calcium in gypsum was similar to that for calcitic limestone, oyster shell flour, marble dust, and aragonite, ranging from 85 to 102% (e.g., see Ross et al., 1984, and Fialho et al., 1992).

9.1.3 Acute Exposure

In mice, the i.p. and intragastric (gavage) LD_{50} values were 6200 and 4704 mg/kg, respectively, for phosphogypsum (98% CaSO₄·H₂O). For plaster of Paris, the values were 4415 and 5824, respectively. In rats, an intragastric LD_{50} of 9934 mg/kg was reported for phosphogypsum (Khodykina et al., 1996).

In mice, direct administration of WTC $PM_{2.5}$ [mostly composed of calcium-based compounds, including calcium sulfate (gypsum) and calcium carbonate (calcite); see Section 6.0] (100 µg) into the airways produced mild to moderate lung inflammation and airway hyperresponsiveness to methacholine that was similar to that from a standard ambient air PM sample and greater than that from toxic residual oil fly ash sample. Lower doses (10 and 32 µg) did not induce significant inflammation or hyperresponsiveness; inhalation of WTC $PM_{2.5}$ (11 mg/m³) also had no such effects (Gavett, 2003; Gavett et al., 2003). [It was noted that WTC $PM_{2.5}$ is composed of

many chemical species and that their interactions may be related with development of airway hyperresponsiveness (McGee et al., 2003).]

In female SPF Wistar rats intratracheally (i.t.) instilled with anhydrite dust (35 mg) and sacrificed three months later, an increase in total lipid or hydroxyproline content in the lungs was not observed compared to controls (Breining et al., 1990).

9.1.4 Short-term and Subchronic Exposure

In inhalation (nose-only) experiments in which male F344 rats were exposed to calcium sulfate (fiber) aerosols (100 mg/m³) for six hours per day, five days per week for three weeks, there were no effects on the number of macrophages per alveolus, bronchoalveolar lavage fluid (BALF) protein concentration, or BALF γ -glutamyl transpeptidase activity (γ -GT). Following three weeks of recovery, nonprotein thiol levels (NPSH), mainly glutathione, were increased in animals (Clouter et al., 1996; cited by Health Council of the Netherlands, Committee on Updating of Occupational Exposure Limits, 2002). In follow-up experiments, rats were exposed to an aerosol of anhydrous calcium sulfate fibers (15 mg/m^3) or a combination of milled and fibrous calcium sulfate (60 mg/m^3) for the same duration. Calcium levels in the lungs were similar to those of controls; however, gypsum fibers were detected in the lungs of treated animals. Significant increases in NSPH levels in BALF were observed in rats killed immediately after exposure at both doses and in the three-week recovery group animals at the higher dose. At 15 mg/m³, almost all NPSH was lost in macrophages from all treated animals (including those in recovery), but a significant decrease in extracellular y-GT activity was seen only in recovery group animals. At 60 mg/m³, γ -GT activity in lung macrophages was significantly increased; this was hypothesized as a "compensatory response" to the loss of NPSH. Overall, the findings were "considered to be non-pathological local effects due to physical factors related to the shape of the gypsum fibers and not to calcium sulphate per se" (Clouter et al., 1997, 1998; both cited by Health Council of the Netherlands, Committee on Updating of Occupational Exposure Limits, 2002).

Intratracheal administration of man-made calcium sulfate fiber (2.0 mg) once per week for five weeks resulted in no deaths or significant body weight changes in female Syrian hamsters compared to controls. Inflammation (specifically, chronic alveolitis with macrophage and neutrophil aggregation) was observed in the lung (Adachi et al., 1991).

9.1.5 Chronic Exposure

In guinea pigs, inhalation of calcined gypsum dust aerosol (average size=5 μ m [range 1-40 μ m]; dose=1.6 x 10⁴ particles/mL) for 44 hours per week in 5.5 days for two years, followed with or without a recovery period of up to 22 months, produced only minor effects in the lungs. There were 12 of 21 deaths over the entire experimental period. These were due to pneumonia or other pulmonary lesions; however, no significant gross signs of pulmonary disease or nodular or diffuse pneumoconiosis became significant. Beginning near 11 months, pigmentation and atelectasis (and later diffuse cellular reaction without fibrosis) were seen. During the recovery period, four of ten guinea pigs died; two died of pneumonia. Pigmentation continued in most animals but not atelectasis, although diffuse cellular proliferation was seen. Low-grade chronic inflammation, occurring in the first two months, also disappeared (Schepers et al., 1955).

9.1.6 Synergistic/Antagonistic Effects

In rats, i.t. administration of anhydrite (5-35 mg) successively and simultaneously with quartz reduced the toxic effect of quartz in lung tissue—specifically, total lipid and hydroxyproline content. With increasing anhydrite concentration, a decrease in foam cell content with an increase in the number of histiocytic nodules was observed (Breining et al., 1990; Rosmanith and Breining, 1988). This antagonistic (protective) effect on quartz toxicity was also seen in guinea pigs; calcined gypsum dust prevented or hindered the development of fibrosis (Schepers et al., 1955).

Natural anhydrite, however, increased the fibrogenic effect of cadmium sulfide in rats (Brammertz and Breining, 1992). Additionally, calcined gypsum dust had a stimulatory effect on experimental tuberculosis in guinea pigs (Schepers et al., 1955).

9.1.7 Cytotoxicity

In Syrian hamster embryo cells, gypsum (up to $10 \ \mu g/cm^2$) did not induce apoptosis (Dopp et al., 1995; cited by Health Council of the Netherlands, Committee on Updating of Occupational Exposure Limits (2002). Negative results were also found in mouse peritoneal macrophages (tested at 150 $\mu g/mL$ gypsum dust) and in Chinese hamster lung V79-4 cells (tested up to 100 $\mu g/mL$) (Chamberlain et al., 1982).

9.2 Reproductive and Teratological Effects

No data were available.

9.3 Carcinogenicity

In female Sprague-Dawley rats, i.p. injection of natural anhydrite dusts from German coal mines (doses not provided) induced granulomas; whether gypsum (or other unknown components) was the causal factor was not established (Greim, 1996; cited by Health Council of the Netherlands, Committee on Updating of Occupational Exposure Limits, 2002). In Wistar rats, four i.p. injections of gypsum (25 mg each) induced abdominal cavity tumors, mostly sarcomatous mesothelioma, in 5% of animals; first tumor was seen at 546 days (Pott et al., 1974). In a subsequent experiment using the same procedure, female Wistar rats exhibited the first tumor at 579 days after the last injection. Mean survival of the tumor-bearing rats (5.7% of test group) was 583 days, while mean survival of the test group was 587 days. Tumor types seen were a sarcoma having cellular polymorphism, a carcinoma, and a reticulosarcoma (Pott et al., 1976).

Intratracheal administration of man-made calcium sulfate fiber (average diameter=1.0 μ m, average length=17.8 μ m; dose=2.0 mg/animal) once per week for five weeks produced tumors in three of 20 female Syrian hamsters observed two years later. An anaplastic carcinoma was found in the heart, and one dark cell carcinoma was seen in the kidney. Two tumors of unspecified types were observed in the rib (Adachi et al., 1991).

In guinea pigs, inhalation of gypsum (doses not provided) for 24 months produced no lung tumors (Schepers, 1971).

9.4 Initiation/Promotion Studies

No data were available.

9.5 Anticarcinogenicity

No data were available.

9.6 Genotoxicity

No data were available.

9.7 Cogenotoxicity

No data were available.

9.8 Antigenotoxicity

No data were available.

9.9 Immunotoxicity

No data were available.

9.10 Other Data

Flue Gas Gypsum

In rats, i.t. administration of gypsum (doses not provided in abstract) from FGD by the limestone and lime hydrate process for up to 18 months produced no arterial blood gas changes or indications of secondary heart damage as compared to controls (Einbrodt et al., 1988). In another study, a single i.t. dose (25 mg) of flue gas gypsum dust did not produce a pathological reaction when observed for up to 18 months. There were also no signs of developing granuloma of fibrosis of the lungs. Concentrations of aluminum, chromium, and nickel were not increased in the lungs, kidneys, or livers. Lead quickly accumulated in the femur after injection but was eliminated during the observation period. In the Ames test, the flue gas gypsum dust was negative (Bartmann, 1986 diss.).

Recently implemented mercury emissions controls on coal-fired power plants increased the likelihood of the presence of mercury in synthetic gypsum formed in wet FGD systems and the finished wallboard produced from the FGD gypsum. Mercury emissions during the wallboard production thermal processes of drying and calcining are also expected. In a study at a commercial wallboard plant, the raw FGD gypsum, the product stucco (beta form of CaSO₄·1/2H₂O), and the finished dry wallboard each contained about 1 μ g Hg/g dry weight. Total mercury loss from the original FGD gypsum content was about five percent or about 0.045 g Hg/ton dry gypsum processed (Marshall et al., 2005).

10.0 Structure-Activity Relationships

In the PubChem database, anhydrite [CID = 115280] is listed as a similar compound to gypsum. Anhydrite (i.e., calcium sulfate without water of crystallization) was reviewed by the Health Council of the Netherlands, Committee on Updating of Occupational Exposure Limits in 2002. Calcium sulfate (up to 2.5%) was negative in *Salmonella typhimurium* strains TA1535, TA1537, and TA1538 and in *Saccharomyces cerevisiae* strain D4 with and without metabolic activation. In pregnant mice, rats, and rabbits, oral administration of calcium sulfate (16-1600 mg/kg bw) daily beginning on gestation day 6 up to 18 produced no effects on maternal body weights, maternal or fetal survival, or nidation; developmental effects were also not seen (Health Council of the Netherlands, Committee on Updating of Occupational Exposure Limits, 2002).

11.0 Online Databases and Secondary References

11.1 Online Databases

National Library of Medicine Databases (TOXNET) ChemIDplus EMIC and EMICBACK HSDB IRIS

STN International Files	
AGRICOLA	IPA
BIOSIS	MEDLINE
BIOTECHNO	NIOSHTIC
CABA	NTIS
CANCERLIT	Registry
EMBASE	RTECS
ESBIOBASE	TOXCENTER

TOXCENTER includes toxicology data from the following files:

Aneuploidy	ANEUPL*
BIOSIS Previews [®] (1969-present)	BIOSIS [*]
CAplus (1907-present)	CAplus
International Labour Office	CIS [*]
Toxicology Research Projects	CRISP [*]
Development and Reproductive Toxicology	DART ^{®*}
Environmental Mutagen Information Center File	EMIC [*]
Epidemiology Information System	EPIDEM [*]
Environmental Teratology Information Center File	ETIC [*]
Federal Research in Progress	FEDRIP [*]
Health Aspects of Pesticides Abstract Bulletin	HAPAB
Hazardous Materials Technical Center	HMTC [*]
International Pharmaceutical Abstracts (1970-present)	IPA [*]
MEDLINE (1951-present)	MEDLINE
Pesticides Abstracts	PESTAB [*]
Poisonous Plants Bibliography	PPBIB [*]
Swedish National Chemicals Inspectorate	RISKLINE
Toxic Substances Control Act Test Submissions	TSCATS [*]

*These are also in TOXLINE. Missing are TOXBIB, NIOSHTIC[®], NTIS.

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In-House Databases Current Contents on Diskette[®] The Merck Index, 1996, on CD-ROM

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Appendix A: Units and Abbreviations $^{\circ}C = degrees Celsius$ $\mu g/L = microgram(s)$ per liter $\mu g/m^3 = microgram(s)$ per cubic meter $\mu g/mL = microgram(s)$ per milliliter $\mu M = micromolar$ BALF = bronchoalveolar lavage fluid EPA = Environmental Protection Agency FGD = flue gas desulfurization g = gram(s)g/mL = gram(s) per milliliter γ -GT = γ -glutamyl transpeptidase h = hour(s)i.p. = intraperitoneal(ly)i.t. = intratracheal(ly)kg = kilogram(s)L = liter(s)lb = pound(s)LC = liquid chromatography LC_{50} = lethal concentration for 50% of test animals LD_{50} = lethal dose for 50% of test animals LD = low doseM = male(s)MD = mid dosemg/kg = milligram(s) per kilogram $mg/m^3 = milligram(s)$ per cubic meter mg/mL = milligram(s) per milliliter min = minute(s)mL/kg = milliliter(s) per kilogram mm = millimeter(s)mM = millimolarmmol = millimole(s)mmol/kg = millimoles per kilogram mo = month(s)mol = mole(s)mol. wt. = molecular weight NIOSH = National Institute for Occupational Safety and Health n.p. = not providedNPSH = nonprotein thiol levels NTP = National Toxicology Program OSHA = Occupational Safety and Health Administration PEL = permissible exposure limit $PM_{2.5}$ = particulate matter with <2.5 µm mass median aerodynamic diameter PM_4 = particulate matter of mass median diameter 4 µm PM_{10} = particulate matter of mass median diameter 10 µm PM_{100} = particulate matter of mass median diameter 100 µm

ppb = parts per billion ppm = parts per million REL = relative exposure limit TWA = time-weighted average WTC = World Trade Center

Appendix B: Description of Search Strategy and Results

A preliminary PubMed (free MEDLINE) search was done on July 27, 2004, using the search statement: gypsum OR calcium(w)(sulfate OR sulphate) OR plasterer*. A total of 98 records were retrieved.

Simultaneous searches of files MEDLINE, CANCERLIT, NIOSHTIC, AGRICOLA, CABA, BIOTECHNO, EMBASE, ESBIOBASE, BIOSIS, IPA, TOXCENTER, and NTIS on STN International were done on August 25 and 31, 2005. The history of the online search session is reproduced below.

L1	6566	S 7778-18-9
L2	11577	S 13397-24-5 OR 26499-65-0
L3	8365	S (CA OR CALCIUM)(W)(SULFATE OR SULPHATE)
L4	2769	S (CA OR CALIUM)(6A)(SULFATE? OR SULPHATE?)
L5	18010	S (CA OR CALCIUM) (6A) (SULFATE? OR SULPHATE?)
L6	14981	S (CA OR CALCIUM)(3A)(SULFATE? OR SULPHATE?)
L7		S GYPSUM
L8	3273	S PHOSPHOGYPSUM OR ANHYDRITE
L9	175	S PLASTERER?
L10		S L1 OR L2 OR L3 OR L7 OR L8 OR L9
L11		S (L10 AND (DENTAL OR DENTIST? OR BONE? OR IMPLANT?)) AND TOXIC?
		SET DUPORDER FILE
L12	41	DUP REM L11 (18 DUPLICATES REMOVED)
L13		SORT L12 1-41 TI
		SAVE L13 X270BONESTOX/A
L14	29165	S L10 NOT L11
L15		S L14 NOT (RADON OR RA(W) 226 OR 226(W) RA OR 222(W) RN)
L16		S L15 NOT (RADIATION OR EMANAT? OR IRRADIAT?)
L17		S LIG NOT IRRADN
L18		S L17 NOT (FISH OR DAPHNIA OR MOLLUS? OR CRUSTACEA?)
L19		S L18 NOT (AQUATIC (6A) (BIOTA OR FLORA OR FAUNA))
L20		S L19 AND ((AIR OR ATMOSPHER?) (6A) (POLLUT? OR MONITOR? OR EMISSION?)
L21		S L19 AND BREATH
L22		S L19 AND BREATH S L19 AND (CHRONIC? OR SUBCHRONIC? OR (14 OR 102 OR 104 OR 13)
L23		S L19 AND (CHROMIC: OR SOBERROWIC: OR (14 OR 102 OR 104 OR 13) S L19 AND (MONTH? OR YEAR? OR 90 (W) DAY?)
L23 L24		S L19 AND (LUNG OR LUNGS OR PULMONARY OR FIBROTIC OR FIBROSIS
L24 L25		S L19 AND (LONG OR LONGS OR FOLMONARI OR FIGHOFIC OR FIGHOSIS S L19 AND (BRONCH? OR ALVEOL? OR RESPIR? OR CLARA OR COPD OR EPIDEMIOL?)
L26		S L19 AND (METAB? OR URIN? OR EXCRET? OR CLEARANCE OR BIOAVAIL?)
L27		S L19 AND (CYTOTOX? OR PROLIFER? OR VITRO OR INCUBAT? OR CULTUR?)
L28		S L19 AND (BLOOD? OR PLASMA? OR IMMUN? OR SERUM OR LYMPH?)
L29		S L19 AND (HYPERSENSITIV? OR ALLERGEN? OR HAPTEN?)
L30		S L19 AND (REPRODUCTI? OR DEVELOPMENTAL? OR TERAT?)
L31		S L19 AND (PREGNAN? OR FETAL? OR FOETAL? OR FETUS? OR FOETUS?)
L32		S L19 AND (EMBRYO? OR PLACENTA? OR GESTAT?)
L33		S L19 AND (MUTANT? OR MUTAT? OR MUTAGEN? OR GENOTOX? OR GENETIC(6A)TOXIC)
L34		S L19 AND (CARCINO? OR CANCER? OR TUMOR? OR TUMOUR? OR PATHO?)
L35		S L19 AND (PRENEOPLAS? OR HYPERPLAS? OR NEOPLAS?)
L36		S L19 AND (EPIDEMIOL? OR HUMAN? OR MINER? OR WORKER? OR HYGIENE)
L37		S L19 AND (SALMONELLA AND AMES AND HPRT AND MICRONUCLE? OR COMET(W)ASSAY)
L38		S L19 AND (SALMONELLA OR AMES OR HPRT OR MICRONUCLE? OR COMET(W)ASSAY OR UDS OR SCE)
L39		S L19 AND (CASE(W)CONTROL OR PROSPECTIVE)
L40		S L19 AND (ENZYM? OR CARDIOVASCULAR OR CARDIAC OR HEART OR ARTER?)
L41		S L20 OR L21 OR L22 OR L23 OR L24 OR L25 OR L26 OR L27
L42		S L20-L35
L43		S L42 OR L38-L40
L44		S EPIMIOL? AND L19
L45		S EPIDEMIOL? AND L19
L46		S HUMAN? AND L19
L47		S MINER? AND L19
L48	33	S (MINER OR MINERS) AND L19
-> ~	110 2000 000	
=> S L19 AND OCCUPATIONAL(W) DISEASE?		
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Appendix 3: Scientific Literature Summary and Review



November, 2013 Greenleaf Advisors, LLC

Gypsum for Agricultural Use: The State of the Science

Abstract

Soil health is an issue of global concern that influences, among other things, food security and water quality. Certain farming practices, when properly applied, can protect and improve soil health. Research studies and farm management experiences in the U.S. indicate that gypsum is an effective and valuable soil amendment for certain soil types (Chen and Dick, 2011; Chen, Kost, Dick, 2008; Dontsova et al., 2004; Fisher, 2011; Stout et al., 1998; Walworth, 2006; Wolkowski et al., 2000). Gypsum, or calcium sulfate dihydrate (CaSO₄•2H₂O), has been mined for use as an agricultural amendment for centuries. More recently, it has been produced as a by-product from emission scrubbers in coal-fired power plants, and is known as Flue Gas Desulfurization (FGD) Gypsum. FGD gypsum has fewer impurities than mined gypsum. It is a direct source of macronutrients (calcium and sulfur) for plants, and improves soil physical and chemical properties that promote nutrient uptake from soil minerals into plants. By enhancing soil composition and improving water infiltration, gypsum can contribute to enhanced crop growth, improve water conservation, and reduce the loss of soil and nutrients into area waterways.

Introduction

The need to increase crop yields to meet global population growth has led to intensive farming practices, which have depleted soils around the world. Nearly all U.S. agricultural soil is somewhat

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degraded and much of the soil in the Midwest is classified as very degraded ("Land Degradation", 2010). Poor soil conditions inhibit plant uptake of important nutrients, like phosphorus and nitrogen, reducing yields and producing less healthy plants. To compensate, farmers often over-apply fertilizers and pesticides, which further stress soils and load nearby waterways with excess nutrients. This causes toxic algal blooms, eutrophication, loss of aquatic diversity, water quality degradation and public health concerns. Furthermore, degraded soils retain less water, making farmlands less resilient during drought conditions.

Gypsum

Research indicates that certain soil amendments can aid in remediating soils, resulting in higher yields and reduced sediment runoff (Chen and Dick, 2011; Stout et al., 1998). One promising amendment is gypsum, a sulfate mineral that has



FGD gypsum being spread on a cover crop

been used as a fertilizer for centuries (Chen and Dick, 2011). It is found naturally in sedimentary rocks around the world, including the United States, which has several active gypsum mines. However, mined gypsum is not an economical solution in many locations, in part due to transportation costs (Rhoton, 2011).

Gypsum is also produced when sulfur dioxide is scrubbed from coal-fired power plant exhaust stacks. This type of gypsum, flue gas desulfurization (FGD) gypsum, contains fewer impurities than



mined gypsum, with 90 to 99% purity concentration compared to 66 to 98% concentration for mined gypsum (Chen and Dick, 2011). FGD gypsum has been recognized as a beneficial additive for agricultural application, equivalent to or better than mined gypsum. Compared to mined gypsum, FGD gypsum has more desirable spreading characteristics, which allow it to be applied easily (Dontsova et al., 2004). With more coal fired power plants installing pollution scrubbers to comply with air quality standards, FGD gypsum production has increased and will likely double in the next decade while remaining economical (Wolkowski et al., 2010).

Improved soil composition

In assessing the need for to gypsum application, it is important to understand the stability of the soil by looking at soil aggregates. Aggregates are clusters of soil particles; their size and spacing influences water infiltration. Calcium binds soil particles into more effective aggregates that help with water infiltration (Walworth, 2006). Gypsum particularly improves the physical properties of heavy clay and sodic soils (Chen and Dick, 2011). By improving soil structure, gypsum helps prevent soil particulate dispersion, decreases surface crust formation, aids in seedling emergence, increases water infiltration, and decreases the loss of soil and nutrients due to surface runoff and erosion (Chen and Dick, 2011). When gypsum was applied to fields under no-till practices, it was found to decrease erosion and runoff (Norton, 2011). Due to better infiltration and less surface sealing, the addition of gypsum to soils could help farmers save money on irrigation since more water is available to the crop (Truman et al., 2010).

Gypsum also improves chemical properties of soil such as remedying aluminum toxicity caused by subsoil acidity (Chen and Dick, 2011; Dontsova et al., 2004). Results include better rooting and uptake of water and nutrients, especially during periods of water scarcity (Chen and Dick, 2011). While gypsum addresses subsoil acidity and aluminum toxicity, it is

Improved water quality and quantity

Gypsum can also amend problems associated with excess phosphorus. High phosphorus levels pose a threat to waterways. The calcium in gypsum lowers the amount of phosphorus released in surface runoff. Additionally, gypsum aggregation of soils also reduces the amount of surface runoff.

Favaretto et al. (2012) found a decrease in dissolved reactive phosphorus in runoff when gypsum was added. This most likely occurs through the conversion of the phosphorus into less soluble compounds. The concentration of water-soluble phosphorus decreased by 50% in one study (Stout et al., 1998). In research conducted by Dr. Darrell Norton, gypsum application was found to mitigate some of the nutrient loading in runoff caused by the addition of manure to fields (Norton, 2008). Gypsum application on soils where poultry litter was used as fertilizer also significantly reduced soluble phosphorus (Sheng et al., 2012). In research performed in south Florida, dairy manure was the source of phosphorus loading in surface waters, and the application of gypsum resulted in higher retention rates of phosphorus in the soil, thereby reducing soluble phosphorus in waterways (Andersen et al., 1995). Grass buffers can also reduce soluble phosphorus runoff and are even more effective when gypsum is applied to the buffers. Watts et al. (2009) showed a reduction in soluble phosphorus by up to 40% when gypsum was applied to the grass buffers in Alabama.

Improved Crops

Improved soil conditions increase crop yields (Chen and Dick, 2011). The sulfur and calcium in gypsum also contribute to crop yields. Calcium is important for strengthening cell walls and membranes and for developing root tips (Fisher, 2011). Gypsum may improve the yields and quality of calcium-



dependent crops, such as peanuts, tomatoes and cantaloupes (Baligar et al., 2011). Sulfur is also an essential element. Corn yields, for example, are often limited by inadequate sulfur, which is needed to balance soil nitrogen in producing protein. In fact, sulfur is an often forgotten essential nutrient for plant growth and is rapidly being depleted in soils (Chen and Dick, 2011). A Wooster, Ohio study found that in addition to nitrogen fertilizers, adding sulfur in the form of FGD gypsum boosts corn yields (Chen, Kost, Dick, 2008). The gypsum contributed to the increased uptake of these important elements – nitrogen and sulfur.



Gypsum application can produce healthier, more resilient crops

The application of gypsum reduces the amount of nitrogen fertilizer needed for producing higher corn yields, making gypsum economically advantageous while reducing the amount of fertilizer run off (Chen, Kost, Dick, 2008). A Texas study indicated gypsum provided at least three times more available calcium than other tested treatments. A higher level of application was more effective than the lower level (Brauer et al., 2005). Gypsum applications in Kansas increased wheat yields an average of 10 bushels over a five year period (Lamond, 1992).

It should also be noted that Gypsum application in California avocados groves resulted in a decrease in *Phytophthora cinnamomi* infection; however, it is not fully understood how gypsum reduced the incidence of infection, so further research is needed (Messenger et al., 2000). In California orchards and vineyards, studies have shown gypsum to reduce crop failure associated with the calcium leaching properties of the snow melt (Rouppet, 2008). These cases indicate gypsum is effective in boosting crop yields and acting as a catalyst for nutrient uptake in plants.

Whole systems approach

Gypsum is a proven beneficial soil amendment across the United States and the world for a variety of crops (Fisher, 2011; Brauer, 2005; Peacock; Rouppet, 2008; Miller et al., 1998). While gypsum has a number of benefits when used, best results are achieved when used with other sustainable farming practices such as no tillage, cover crops, and crop rotation (Fisher, 2011). Farmers in the Midwest have been using gypsum for decades with positive results; including better water infiltration and higher yields (Fisher, 2011).

Application

Some factors should be taken into account when considering gypsum use; the rate and season to best apply gypsum will vary by location and soil type (Dontsova et al., 2004; Peacock). Over-application of gypsum may result in seedling damage and nutrient imbalance. Additionally, when purchasing the FGD gypsum it is important that it has been washed in the manufacturing process to remove potentially high levels of boron that can be toxic to certain crops, such as corn (Dontsova et al., 2004). Low concentrations of trace metals may be found in gypsum, generally at lower concentrations than government regulations, but it is best to test samples before applying (Dontsova et al., 2004). As previously mentioned, gypsum does not remedy all soil problems. Location and soil composition influence gypsum's effectiveness and thus is not suitable for all crops (Franzen, 2008).

Other environmental benefits

In addition to water quality and agronomic benefits, use of FGD gypsum as a soil amendment benefits the environment by avoiding the need to landfill



excess material and minimizing the mining and associated impacts of extracting virgin gypsum deposits (Chen and Dick, 2011). Gypsum can also reduce nitrous oxide (N₂O) emissions, a potent greenhouse gas. In 2010, agricultural soil management practices made up 68% of N₂O emissions in the U.S. (EPA, 2012). Several farming practices contribute directly to N₂O emissions, including the application of synthetic fertilizer, which alone accounts for 18% of the N₂O contributed by agricultural soil management practices. Indirect contributions also include surface leaching and runoff, making up 12% of N₂O due to agricultural soil management practices. Synthetic fertilizer and surface leaching and runoff, which gypsum reduces, together make up 20% of total U.S. N₂O emissions (EPA, 2012).

Conclusions

Overall, gypsum is an effective soil amendment, improving soil conditions and their effective nutrient processing capabilities for certain soil types. It helps to restore degraded soils by enhancing water infiltration and improving soil composition, contributing to less erosion and nutrient loading in area waterways. For some crops, gypsum can help increase the available nutrients to crops, allowing for greater yields. Gypsum is most effective as one part of a whole systems farming approach that takes into consideration soil type, crop, and hydrology. Not only does a reduction in nitrogen fertilizer benefit the environment, it may also benefit farmers economically (Chen, Kost, Dick, 2008). Gypsum can be an important tool for maintaining healthy, functioning soils, contributing to healthy crops and healthy waterways.



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May 28, 2014

National Organic Standards Board C/O National List Manager USDA/AMS/NOP, Standards Division 1400 Independence Ave, SW Room 2648-So., Ag Stop 0268 Washington, DC 20250-0268

Dear members of the National Organic Standards Board,

Gypsum contributes to a healthy environment in many ways. Studies at the USDA-ARS National Soil Erosion Research Laboratory at Purdue University have demonstrated that applying gypsum improves water infiltration so soil absorbs rainwater quickly. This minimizes surface runoff and contributes to less soil erosion and loss of applied nutrients.

In addition to soil and water quality benefits, the beneficial reuse of gypsum enables utilities and other processing plants to reduce their dependence on landfilling. Recycling gypsum is a sustainable practice that positively impacts our environment and agricultural production.

At trade shows and other venues, GYPSOIL has found strong interest in synthetic gypsum from the organic farming community and we are ready to be a reliable source of this high-quality product to organic growers should the petition be approved by the NOSB. We support this petition because of our understanding of how valuable a tool synthetic gypsum is, not only directly to farmers, but to the people and natural areas that their farms impact.

Sincerely,

BENEFICIAL REUSE MANAGEMENT/GYPSOIL

Robert C. Spoerri President

Verne Armstrong Armstrong Farms 3351 Airport Rd Pierre, SD 57501

National Organic Standards Board C/O National List Manager USDA/AMS/NOP, Standards Division 1400 Independence Ave, SW Room 2648-So., Ag Stop 0268 Washington, DC 20250-0268

Dear members of the National Organic Standards Board,

As an organic farmer who is looking to use calcium sulfate (gypsum) as a soil amendment, I would like to add my support to the petition to include synthetic calcium sulfate to the National List of Synthetic Substances Allowed for Use in Organic Production.

As you may know, gypsum has the following benefits when used for agriculture:

- Improvements to soil structure and water infiltration •
- Remediation of clay-containing soils
- Remediation of sodic soils
- Reduction of phosphorous runoff into lakes and rivers •
- As a source of calcium and sulfur for plant growth

The environmental and soil health benefits of gypsum use are strongly aligned with the goals and purpose of organic certification. It can lead to more resilient and secure organic food production while supporting farmers' abilities to be good stewards of the lands and waters their farms impact.

Although alternatives exist, they are not available in my area and are too expensive to import. Also, they are potentially less effective and have fewer benefits than synthetic calcium sulfate.

Thank you for considering allowing this valuable tool to be used on my farm and those of other likeminded farmers.

Sincerely,

Verne Armstrong

Richard Lange 1214 Southwest Rd. Platteville, WI 53818

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Sincerely,

Richard Large

Richard Lange

Ed Runde 2069 Model Rd. Cuba City, WI 53818

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EdRunde

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Tim Vosberg 3308 County H. Cuba City, WI 53818

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Sincerely,

Im Vosbery

Tim Vosberg

Joe Placke 9071 Fever Hill Rd. Cuba City, WI 53807

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Sincerely,

Joseph (Placke

Joe Placke

Keith Wilson 10700 S. Galena Rd. Cuba City, WI 53807

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Thank you for considering allowing this valuable tool to be used on my farm and those of other likeminded farmers.

Sincerely,

feith Wilson

5-9-14

Keith Wilson

Simon Runde 2504 Highview Rd Cuba City, WI 53807

National Organic Standards Board C/O National List Manager USDA/AMS/NOP, Standards Division 1400 Independence Ave, SW Room 2648-So., Ag Stop 0268 Washington, DC 20250-0268

Dear members of the National Organic Standards Board,

As an organic farmer who is looking to use calcium sulfate (gypsum) as a soil amendment, I would like to add my support to the petition to include synthetic calcium sulfate to the National List of Synthetic Substances Allowed for Use in Organic Production.

As you may know, gypsum has the following benefits when used for agriculture:

- Improvements to soil structure and water infiltration
- Remediation of clay-containing soils
- Remediation of sodic soils
- Reduction of phosphorous runoff into lakes and rivers
- As a source of calcium and sulfur for plant growth

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Simon Runde