### United States Department of Agriculture Agricultural Marketing Service | National Organic Program Document Cover Sheet <https://www.ams.usda.gov/rules-regulations/organic/petitioned-substances>

Document Type:

## ☐ **National List Petition or Petition Update**

A petition is a request to amend the USDA National Organic Program's National List of Allowed and Prohibited Substances (National List).

Any person may submit a petition to have a substance evaluated by the National Organic Standards Board (7 CFR 205.607(a)).

Guidelines for submitting a petition are available in the NOP Handbook as NOP 3011, National List Petition Guidelines.

Petitions are posted for the public on the NOP website for Petitioned Substances.

### ☒ **Technical Report**

A technical report is developed in response to a petition to amend the National List. Reports are also developed to assist in the review of substances that are already on the National List.

Technical reports are completed by third-party contractors and are available to the public on the NOP website for Petitioned Substances.

Contractor names and dates completed are available in the report.

# **Magnesium Sulfate**

**Handling/Processing**

## **Summary of Petitioned Use**



#### **Magnesium sulfate hydration states form different minerals**

- A variety of magnesium sulfate minerals exist, each described by a different hydration state (see *[Table 1](#page-3-0)*,
- below). A common challenge in isolating magnesium sulfate is limiting the potential creation of double
- salts (as evidenced by the formation of distinct crystal lattice), usually with sodium and calcium, which
- makes the isolation of most of these stages challenging and sometimes unfeasible (Lindström et al., 2016; Sadan, 1994).
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- Manufacturers therefore use different sources, conditions, and methods to obtain magnesium sulfate in
- varying hydration states. The most common paths to producing nonsynthetic magnesium sulfate are by:
- open-pit mining of salt efflorescence[1](#page-2-0)
- isolation of the material from salt ponds
- Raw magnesium sulfate primarily appears in the form of (Balboni et al., 2011):
- magnesium sulfate monohydrate (kieserite)
- magnesium sulfate hexahydrate (hexahydrite)
- magnesium sulfate heptahydrate (epsomite)
- Of these, kieserite and epsomite are the most commonly occurring crystalline phases (Kramer, 2001) as the 67 other forms are metastable (Lindström et al., [2](#page-2-1)016; Steiger et al., 2011).<sup>2</sup>
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Other more rare hydration states are (Steiger et al., 2011; Vaniman et al., 2004):

- magnesium sulfate dihydrate (sanderite)
- magnesium sulfate tetrahydrate (starkeyite)
- magnesium sulfate pentahydrate (pentahydrite)
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Different hydration states form due to environmental factors that affect the absorption of water by the

- compound. The formation of the hydrates is dependent on the relative humidity and temperature during
- the evaporation phase, and of the composition of the parent brine (Balboni et al., 2011; Lindström et al.,
- 2016; Linnow et al., 2014). Sadan et. al. (1994) describes applying a minimal amount of pressure to crystal
- clusters as they form, resulting in the hexahydrate or lower hydrated crystals. Additionally, treating raw
- material with higher temperatures and/or subjecting the raw material to longer periods of heating produce
- lower hydration states. Lower hydration phases may be recrystallized to form higher purity products of
- various hydration states (Sadan, 1994).
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 Magnesium sulfate heptahydrate will lose one mole of water on exposure to dry air at room temperature (Merck Research Laboratories Division, 2001). Under dry conditions, the following water loss is observed

- 85 Four moles are lost at 70-80 °C.
- 86 Five moles are lost at 100 °C.
- 87 Six moles are lost at 120 °C.
- 88 Seven moles are lost at ~250 °C.

Conversely, the mineral rapidly absorbs water when exposed to moist air (Merck Research Laboratories

- Division, 2001).
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Efflorescence: Salt deposit formed on a surface via evaporation.

<span id="page-2-1"></span><span id="page-2-0"></span>Metastable: A system with precarious stability that can easily be disturbed.

#### **Table 1. Naturally occurring magnesium sulfate hydrates and their stability. These crystalline phases precipitate from parent brines, namely rock formations, or salt ponds.**

<span id="page-3-0"></span>

 **Sources:** (Balboni et al., 2011; Kramer, 2001; Lindström et al., 2016; National Center for Biotechnology Information, 2023b; Steiger et al., 2011; Vaniman et al., 2004; Warren, 2006)

 \*Most sources state that this hydration state is stable; however, some declare this as a metastable phase that will quickly absorb an additional water molecule and become the more stable heptahydrate phase, at standard conditions 98 ( $\sim$ 50-55% relative humidity at 25 °C).

 Manufacturers produce magnesium sulfate from both liquid brines and solid minerals. These sources are discussed below.

#### **Production from kieserite (MgSO4•H2O)**

Magnesium sulfate monohydrate, also known as the mineral kieserite (Merck Research Laboratories

Division, 2001), occurs in nature as a product of dried saline lake deposits (Deiseroth et al., 2008; Klein &

Hurlbut, 1999). The mineral forms naturally in these marine deposits where seawater concentrates and is

exposed to prolonged evaporation (Rao & Kawamura, 2007). These deposits are primarily found

underground, near the surface and are accessed through open-pit mines (Wu et al., 2021). Although

kieserite is mined in large quantities, most is between 89–93% pure (Sadan, 1994). Kieserite can contain the

- following impurities (Deiseroth et al., 2008):
- 111 halite (NaCl)
- 112 sylvite (KCl)
- 113 polyhalite  $(K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O)$
- 114 langbeinite  $(K_2Mg_2(SO_4)_3)$
- 115 other salt-containing minerals
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 Crude salts are mined from these dried saline deposits, ground, and classified according to grain size (Deiseroth et al., 2008). The solid mixture of salts is treated with an organic conditioning agent, usually a

fatty acid and/or an aromatic carboxylic acid, in order to exploit the differences in solubility and aid in a

- physical separation process (Deiseroth et al., 2008). To avoid dissolution, relative humidity is maintained at
- around 5–10%. The conditioning agent causes the crude kieserite fraction to separate from potassium
- 122 chloride in a dry electrostatic separator (Deiseroth et al., 2008; Nilsen & Piasecki, 2007).<sup>[3](#page-3-1)</sup>
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- In another separation method, the conditioning agent creates one hydrophobic layer and one hydrophilic

layer (Deiseroth et al., 2008). Air is bubbled through the mixture and the hydrophobic particles float to the

- surface where they accumulate as froth and are collected. Different variations of this method exist
- (Deiseroth et al., 2008). One variation uses conditioning agents to select and float potassium chloride,
- attaching the particles to small air bubbles and leaving a crude kieserite salt mixture as the hydrophilic
- layer.
- <span id="page-3-1"></span>

 Electrostatic separation: Common chemical industry method where electromagnetic field generation within a liquid phase causes dispersed material to combine within the dispersant. The dispersed material can then be separated from liquid.

- Regardless of the separation method, the crude kieserite fraction undergoes a water-based hot leaching process where salt impurities are separated based on solubility differences. Once kieserite is isolated, it is
- crystallized, centrifuged, dried, and sieved (Rao & Kawamura, 2007).
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#### **Production from epsomite, Epsom salt (MgSO4•7H2O)**

- Magnesium sulfate heptahydrate, also known as the mineral epsomite or Epsom salt, occurs in nature as
- efflorescence on the rocks of cave walls from deposition from saline springs (Klein & Hurlbut, 1999;
- Wahyudi & Agung, 2006) and in seawater brines (Sadan, 1994). Due to similarities in solubility, epsomite in
- brine is commonly found in sodium (halite) and magnesium double salts (Sadan, 1994). Separating
- epsomite and halite tends to be a costly and extremely complicated process due to the formation of these
- double salts (Sadan, 1994). For this reason, most (but not all) commercial sourcing of natural epsomite is
- from efflorescence. These efflorescence deposits come from saline springs in arid regions and in dry caves,
- and from the deposition of sulfur and magnesium–rich waters in tunnels of sulfide mines (Wahyudi &
- Agung, 2006). The dryness of the caves prevents double salt formation, which in turn keeps magnesium sulfate from joining a mixture in solution.
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- Due to limited quantities of naturally-occurring epsomite, manufacturers also use a liquid brine epsomite-
- halite separation method (Wahyudi & Agung, 2006). To separate the salts, steps are taken to avoid
- formation of double salts in the first place. One common method is to evaporate salt brines to the bittern
- salt stage (see *[Figure 1](#page-5-0)*, at the end of this question). From here, the brine is diluted with fresh water to
- 151 control the precipitation of halite (Bollinger et al., 2015). The remaining brine is cooled to below -5  $^{\circ}C$ ,
- precipitating magnesium sulfate out of the solution. The magnesium sulfate is subsequently re-crystallized.
- This refrigeration process requires a large amount of magnesium-containing brine to produce commercial
- amounts of epsomite, and is not a major processing method (Sadan, 1994).
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- Epsomite is also manufactured through the dissolution of the monohydrate phase (kieserite) in hot water
- followed by a crystallization process in cold water (Rao & Kawamura, 2007). Dissolving kieserite allows for
- subsequent recrystallization of higher hydrated phases, mainly hexa- and heptahydrate forms (Lindström
- et al., 2016). However, the reverse process does not occur. Both epsomite and hexahydrite do not easily
- revert to kieserite upon desiccation in standard conditions (Balboni et al., 2011). The transition between
- 161 hexa- and heptahydrate is reversible and occurs at ~50–55% humidity at room temperature (Vaniman et al., 2004).
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#### **Production of magnesium sulfate from brine precipitation**

- Manufacturers isolate magnesium sulfate by concentrating the hypersaline waters and precipitating the dissolved salts (Loganathan et al., 2017; White et al., 2018). Differences in the solubility of different salts
- cause the dissolved minerals to precipitate out of solution in stages (see *[Figure 1](#page-5-0)*, below) (White et al., 2018):
- 1) Calcium carbonate is the first to precipitate as water evaporates, at around twice the concentration of the parent brine.
- 2) Calcium sulfate, then sodium chloride precipitate at ten to twelve times the concentration of the parent brine.
- 3) The remaining solution, now at 70-90 times the concentration of the parent brine, is a mixture of potassium or magnesium sulfates and chlorides (bittern salts).
- 4) Depending on the environmental factors and the desired product, magnesium sulfate is isolated from this brine via different methods which are explored in more detail below.
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## <span id="page-5-0"></span> **Figure 1: Precipitation sequence of seawater** Precipitation sequence

Order: CaCO<sub>3</sub>  $\rightarrow$  CaSO<sub>4</sub>  $\rightarrow$  NaCl  $\rightarrow$  Bitterns



- <span id="page-5-1"></span>*Synthetic or Nonsynthetic* (NOP, 2016a) is discussed below.
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#### *1. Is the substance manufactured, produced, or extracted from a natural source?*



#### *1. Is the substance a mineral or bacterial culture, as included in the definition of nonagricultural substances at section 205.2 of the USDA organic regulations?*

- When produced from epsomite, kieserite, or brines, magnesium sulfate is a mineral substance. Therefore, magnesium sulfate from these sources is nonagricultural, according to the decision tree.
- When produced from the reaction of magnesium containing material with sulfuric acid, magnesium sulfate is also a mineral. Therefore, these sources are also nonagricultural.
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#### **Evaluation Question #3: If the substance is a synthetic substance, provide a list of nonsynthetic or natural source(s) of the petitioned substance [7 CFR 205.600(b)(1)].**

 Magnesium sulfate occurs in both nonsynthetic and synthetic forms. As stated in *[Evaluation Question](#page-5-1) #2*, food grade magnesium carbonate is produced from nonsynthetic sources. The most common commercial 272 forms of magnesium sulfate are as the nonsynthetic minerals epsomite  $(MgSO_4 \cdot 7H_2O)$  and kieserite (MgSO4•H2O) (Kramer, 2001, p. 9; Zhang et al., 2015). Steiger et. al. (2011) stated that kieserite is not 274 commercially available as a monohydrate, but rather, it is sold in the metastable range MgSO<sub>4</sub>•1.20– 1.27H2O. This is due to its difficult crystallization. Regardless of its true hydration state, kieserite is commercially available from nonsynthetic sources. Magnesium sulfate also naturally occurs in seawater

- and mineral springs (Rao & Kawamura, 2007).
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#### **Evaluation Question #9: Discuss and summarize findings on whether the manufacture and use of the petitioned substance may be harmful to the environment or biodiversity [7 U.S.C. 6517(c)(1)(A)(i) and 7 U.S.C. 6517(c)(2)(A)(i)].**

 **Use**

The hydrated forms of magnesium sulfate are used in food as nutrient sources in salt substitutes and

- dietary supplements, as firming agents, as coagulating agents in tofu production, as flavor enhancers in
- bottled water products, and as fermentation aids in the processing of beer and malt beverages (Food and
- Agriculture Organization of the United Nations & World Health Organization, 2007; Guan et al., 2021; Rao
- & Kawamura, 2007). The quantity of magnesium sulfate used for these purposes is negligible compared to
- other industrial uses. Environmental, chemical, agricultural, and deicing applications made up 75% of
- magnesium compound consumption (including magnesium sulfate) in the U.S. in 2023 (USGS, 2023). The
- U.S. Geological Survey's Mineral Commodity Summary did not cite food processing in the remaining industrial uses. Though these uses are not noted as being specific to one type of food production, it is
- reasonable to expect that magnesium sulfate would be used similarly in organic processing.
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Given the small quantities of magnesium sulfate used as food additives and the ubiquitous nature of

- magnesium and sulfate ions in the environment, food processing applications do not present an area of
- environmental concern. The National Library of Medicine does not list any food uses as sources of artificial
- (human caused) magnesium sulfate pollution (National Center for Biotechnology Information, 2023a).
- Similarly, the EPA (2003) reported on anthropogenic sources of environmental sulfur pollution, noting the
- burning of sulfur-containing fossil fuels, household wastes such as detergents, and effluents coming from
- industries such as steel mills, tanneries, sulfate-pulp mills, and textile plants, but did not cite the use of
- magnesium sulfate in food processing as a source of sulfur pollution (U.S. EPA, 2003).

# **Manufacturing**

- The environmental impacts related to the food additive, magnesium sulfate, come primarily from its sourcing and manufacturing.
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Magnesium sulfate deposits exist in the Western United States; however, the material is not mined from

- domestic sources and is instead imported primarily from China, India, Germany, and Canada (Kramer,
- 2001; Merrill, 2022). Currently, the largest importing source of the material for the United States is China
- (Merrill, 2022). China is currently the largest producer and exporter of magnesium compounds in the
- world, including magnesium sulfate (Wu et al., 2021). Most of this magnesium sulfate comes from salt

- lakes in the northern part of the Tibet Autonomous Region and Qaidam Basin of the Qinghai Province. Because magnesium sulfate is not as readily available as other magnesium compounds, literature about
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- mining activities for this specific material is limited. Wu et. al. (2021) notes that magnesium mining
- activities in China are not well-managed, resulting in heavy damage to surface vegetation through large-scale open-pit mining. The equipment itself also causes serious water and air pollution (Wu et al., 2021).
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- International studies primarily in Australia have also identified a need for more research and data
- 
- regarding the effects (if any) of magnesium sulfate contamination stemming from mining operations (Canham et al., 2020; van Dam et al., 2010). The focus of existing studies shows that low-hardness waters
- 322 (i.e., soft waters with low concentrations of  $Ca^{2+}$  and/or  $Mg^{2+}$ ) are susceptible to adverse effects stemming
- from discharges from mining operations.
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Although van Dam et al. (2010) report magnesium sulfate to be of generally low toxicity and low

- significance as an environmental contaminant, it is potentially toxic to aquatic life. Its main toxic effect on
- aquatic life is cellular damage caused by osmo-regulatory stress due to elevated ion concentrations
- (Kleinhenz et al., 2019). Sulfate contributes slightly to toxicity; it is the magnesium ion that primarily causes
- toxicity to invertebrate organisms (van Dam et al., 2010). Magnesium sulfate's potential for aquatic toxicity
- comes from its high solubility and its role as a physiologic calcium blocker. (National Center for
- Biotechnology Information, 2023b; van Dam et al., 2010). An ionic compound, magnesium sulfate is highly
- soluble in water (710 mg of the compound will solubilize in 1000 mL of water) (National Center for
- Biotechnology Information, 2023b). Magnesium ions compete with (and inhibit) the uptake of calcium ions
- in biological systems (van Dam et al., 2010).
- 

Direct toxicity through non-osmoregulatory mechanisms can also occur. Magnesium ions are also a known

- disrupter of numerous calcium-dependent processes. One study showed that organisms in surface waters with low calcium concentrations are more susceptible to small elevations of magnesium concentration (van
- Dam et al., 2010). When elevated magnesium concentrations accompany elevated calcium concentrations,
- there is a reduction of risk effects to certain aquatic species. The same researchers also observed two plant
- species, one with a high calcium requirements and one with low requirements. The researchers showed
- 342 that the magnesium toxicity to algae species (*Chlorella spp*.) is extremely low ( $LC_{50}$ = 6014 mg/L), as this
- algal species has fewer calcium-dependent mechanisms. However, some species are at a higher risk of
- toxicity and may not be protected by calcium amelioration (Kleinhenz et al., 2019).
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 Kleinhenz et. al (2019) focused on the tropical freshwater mussel *Velesunio sp.* and discussed the effects of high magnesium ion environments during a critical life stage. This species occurs in naturally low- hardness waterways throughout the northern Australian tropics. The researchers observed the species' growth and survival, first from larvae to juvenile, and then the first two weeks of the juvenile stage when an adult shell begins forming. The researchers found that *Velesunio sp.* is moderately sensitive to

magnesium toxicity when compared to other freshwater species such as:

- the crayfish *Austropotamobius palippes spp.* and *Orconectes limosus*
- the water flea *Daphna magna*
- the worm *Caenorhabditis elegans*
- 

356 Of these, the mussels response to magnesium sulfate were more comparable to  $A$ . *palippes*, with an  $LC_{50}$  range of 270–480 mg/L. *C. elegans* was the least sensitive species mentioned in the study, with an LC50 of 4389 mg/L.

#### **Report Authorship**

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 All individuals are in compliance with Federal Acquisition Regulations (FAR) Subpart 3.11—Preventing Personal Conflicts of Interest for Contractor Employees Performing Acquisition Functions.



