Magnesium Chloride

Handling/Processing

Identification of Petitioned Substance

There are two forms of magnesium chloride:

Chemical Names: $MgCl_2 \cdot 6H_2O$
Magnesium chloride hexahydrate
Magnesium chloride
Magnesium dichloride
Magnesium chloride $6H_2O$
Magnesium chloride, 6-hydrate
Magnesium chloride hydrate
Magnesium chloride, hydrous

CAS Number: 7791-18-6

Chemical Names: $MgCl_2$
Magnesium chloride anhydrous
Magnesium chloride
Magnesium dichloride

CAS Number: 7786-30-3

Other Codes: E511, INS511 (both forms)

Summary of Petitioned Use

Magnesium chloride is currently allowed under the National Organic Program regulations at 7 CFR 205.605(b) as a nonagricultural synthetic substance for use as an ingredient in or on processed products labeled "organic" or "made with organic (specified ingredients or food group(s))." The current annotation reads, "derived from sea water." The primary uses of magnesium chloride in organic food processing are as a firming agent in tofu processing and as a source of the essential mineral magnesium in organic infant formula. It is also allowed by the FDA as a flavoring agent, adjuvant, and as a nutrient supplement.

Characterization of Petitioned Substance

Composition of the Substance:

Magnesium chloride is the simple salt of the halogen chlorine and the alkaline earth metal magnesium. As noted in the Identification section above, two forms of magnesium chloride (hexahydrate or anhydrous) are analytically defined and commercially available.

Magnesium chloride hexahydrate is the form of magnesium chloride that is authorized by the FDA for use as a direct food substance (21 CFR 184.1426). It is described in the Merck Index and occurs as colorless, odorless flakes, crystals, granules or lumps (Budavari 1996). The Joint FAO/WHO Expert Committee on Food Additives (JECFA) and the Food Chemicals Codex (FCC) require that the material assays at 99% to 105% $MgCl_2 \cdot 6H_2O$ (JECFA 1980; U. S. Pharmacopeia 2010). The hexahydrate form is far more available and far less expensive than the anhydrous form.

Anhydrous magnesium chloride as described in the Merck Index is prepared from magnesium ammonium chloride hexahydrate in the presence of hydrochloric acid (Budavari 1996). It occurs as soft leaflets and is used as a chemical reagent.

Both forms of magnesium chloride are hygroscopic (absorb water) and deliquescent (absorb enough water to form a solution), so containers of this GRAS ingredient must be closed tightly to avoid moisture pick-up.

The remainder of this report will focus on the hexahydrate form of magnesium chloride used as a food additive.

Source or Origin of the Substance:

The most common sources of magnesium chloride hexahydrate are "derived from sea water" in the very broadest sense. Mineral deposits of magnesium chloride were created thousands to millions of years ago when isolated sea water bodies dried up and their mineral constituents crystallized out (Butts 2004). These mineral deposits are tapped by solution mining, which involves pumping water thousands of feet below the earth's surface to dissolve the minerals and form brines. The brines are pumped to the surface and separated into the component mineral salts. Other important brine sources are active terminal lakes, such as the Great Salt Lake in North America and the Dead Sea in Israel and Jordan (Butts 2004). Underground brine can be found in the remains of ancient terminal lakes that have dried up, such as under Midland, Michigan (Chemical Heritage Foundation 2015). The production of sea salt by solarization has been an important human activity for the last three millennia. Sodium chloride-depleted solar brine is a good source of magnesium chloride, since magnesium chloride makes up 17% of sea water solids (Aikawa 1991). Evaluation Question 1 provides a full description of these natural sources and how the extraction and isolation of magnesium chloride is accomplished.

Magnesium chloride can also be produced by chemical synthesis, which is also described in Evaluation Question 1.

Properties of the Substance

Physical and chemical properties of the substance are summarized in Table 1.

Table 1: Physical and Chemical Properties of Magnesium Chloride Hexahydrate (Budavari 1996; U. S. Pharmacopeia 2010; JECFA 1980)

Property	**Value**
CAS Reg. Number	7791-18-6
Chemical formula	$MgCl_2 \cdot 6\ H_2O$
Molar mass	203.30
Appearance	Deliquescent crystals
Solubility, cold water	1 g in 0.6 mL (~ 166 g/100mL)
Solubility, 100°C water	1 g in 0.3 mL (~ 333 g/100mL)
Solubility, alcohol	1 g in 2 mL ethanol (~50 g/100mL)

The two significant characteristics of magnesium chloride hexahydrate that enable its isolation and purification from natural sources are its high water solubility (Lewis 1997b) and its high alcohol solubility.

Specific Uses of the Substance:

The primary use of magnesium chloride hexahydrate in organic food processing is as a firming agent for tofu. Magnesium chloride hexahydrate is also used as a source of the essential mineral magnesium in infant formula (21 CFR 184.1426(c)(2)).

Approved Legal Uses of the Substance:

Magnesium chloride hexahydrate is affirmed by the FDA as Generally Recognized As Safe (GRAS) as a food ingredient (21 CFR 184.1426). It is allowed by the FDA as a flavoring agent, adjuvant, nutrient supplement, and may be used in infant formula.

The EPA regulates magnesium chloride as a pesticide on List D, pesticides of less concern (EPA 1998). Magnesium chloride has also been used to treat bovine hypomagnesemia (low blood magnesium levels) (Budavari 1996).

Action of the Substance:

Magnesium and calcium are coagulating agents that interact with the protein in soymilk to form tofu. Magnesium chloride easily dissolves in water and congeals soymilk quickly, generating smooth or rough textured curd depending on the concentration of magnesium chloride solution (Arii and Takenaka 2013).

Combinations of the Substance:

Magnesium chloride hexahydrate is commercially available as colorless, odorless flakes, crystals, granules or lumps. Both JECFA and FCC require that the material assays at 99% to 105% $MgCl_2 \cdot 6H_2O$. Commercial sources contain no additional or ancillary ingredients (e.g., inert ingredients, stabilizers, preservatives, carriers, anti-caking agents or other materials).

Status

Historic Use:

The practice of making tofu to utilize the protein of the soybean originated about 2,000 years ago. A material called "nigari" is a traditional 'natural' solidifying agent for making tofu in Japan. Nigari consists of the natural components of sea water including magnesium chloride, magnesium sulfate and other elements of sea water that remain after sodium chloride crystallizes from solar brine (Shurtleff and Aoyagi 1975).

Organic Foods Production Act, USDA Final Rule:

The National Organic Standards Board (NOSB) reviewed magnesium chloride hexahydrate in 1995 for inclusion on the National List of Approved and Prohibited Substances for use as a color retention agent, a firming agent for tofu, and a processing aid in sugar beet processing. The Final Rule creating the NOP regulations on December 21, 2000 included a listing of '"magnesium sulfate – derived from sea water" on the National List at §205.605(b) as an allowed synthetic (USDA Agricultural Marketing Service 2000).

Documents from the original NOSB review in 1995 are somewhat unclear regarding the classification of the various source of magnesium chloride as synthetic or nonsynthetic. The Technical Advisory Panel (TAP) review from 1995 indicates that one TAP reviewer categorized all sources of magnesium chloride as synthetic, and the other TAP reviewer categorized magnesium chloride from brine as nonsynthetic (NOSB 1995a). The minutes from the October-November 1995 NOSB Meeting indicate that the NOSB decided to "prohibit non-synthetic magnesium chloride (from sea water)" and "allow only the synthetic form if extracted from sea water" (NOSB 1995b). The NOSB Materials Database document from 1999 acknowledges that magnesium chloride is available from nonsynthetic and synthetic sources (NOSB 1999).

The NOSB has also reviewed magnesium chloride for use in crop production. In 1996, the NOSB reviewed a petition to add magnesium chloride hexahydrate to §205.601 for use as a foliar source of magnesium, as a dust suppressant, as a potential desiccant or defoliant for cotton, and as an herbicide. The NOSB voted to classify magnesium chloride as nonsynthetic when extracted from brine, seawater and salt deposits. Since magnesium chloride is not listed at §205.602 as a prohibited nonsynthetic substance, nonsynthetic sources are considered to be allowed in organic crop production.

International Organic Food Processing Standards

Canadian General Standards Board Permitted Substances List

Magnesium chloride is a permitted processing substance listed in CAN/CGSB-32.311-2015, Table 6.3, "ingredients classified as food additives," with the annotation, "derived from seawater."

CODEX Alimentarius Commission, Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999)

The Codex organic guidelines permit the use of magnesium chloride (INS 511) in food category 06.8, soybean products (excluding soybean products of food category 12.9 and fermented soybean products of food category 12.10); food category 12.9.1, soybean protein products; and food category 12.10, fermented soybean products.

European Economic Community (EEC) Council Regulation, EC No. 834/2007 and 889/2008
The European Community regulation permits the use of the magnesium chloride (or "nigari") in processing organic foods of plant origin as a coagulation agent (EC No. 889/2008 Annex VIII, Section B – Processing Aids).

Japan Agricultural Standard (JAS) for Organic Production
Article 4, Table 1, Food Additives permits the use of food additive INS 511, magnesium chloride, and also "crude seawater magnesium chloride," for processed foods of plant origin as a coagulating agent or for processed bean products.

IFOAM – Organics International
The IFOAM Norms, Appendix 4, Table 1, permit the use of magnesium chloride (INS 511) as an additive and also as a processing and post-harvest handling aid for soybean products only.

Evaluation Questions for Substances to be used in Organic Handling

Evaluation Question #1: Describe the most prevalent processes used to manufacture or formulate the petitioned substance. Further, describe any chemical change that may occur during manufacture or formulation of the petitioned substance when this substance is extracted from naturally occurring plant, animal, or mineral sources (7 U.S.C. § 6502 (21)).

Magnesium chloride from natural sources
Natural commercial sources of magnesium chloride can be classified as (a) sea water; (b) terminal lake brines; (c) subsurface brine deposits; and (d) mineral ore deposits (Butts 2004). Magnesium chloride produced from each of these natural sources is the product of a brine comprising soluble ions of various mineral elements, primarily sodium, potassium, magnesium, calcium, chloride and sulfate.

Sea Water
Sea water is processed in solar ponds to produce concentrated brines from which specific minerals crystallize and are recovered. These specific minerals, called "evaporites," crystallize in a sequence based on the concentrations of anions and cations in the brine and their innate solubility in water (Butts 2004).

Table 2. Important evaporites formed during sea water solarization in their order of formation (Butts 2004)

Mineral name	CAS Registry No.	Other names	Chemical formula
Halite	14762-51-7	salt, sodium chloride	$NaCl$
Epsomite	14457-55-7	Epsom salts, magnesium sulfate	$MgSO_4 \cdot 7H_2O$
Schoenite	15491-86-8	picromerite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
Kainite	1318-72-5		$4KCl \cdot 4MgSO_4 \cdot 11H_2O$
Carnallite	1318-27-0	crackel salt	$MgCl_2 \cdot KCl \cdot 6H_2O$
Bischofite	13778-96-6	magnesium chloride	$MgCl_2 \cdot 6H_2O$

Table 3. Mineral composition of typical sea water and its calculated disposition as evaporites (Lenntech 2005).

Ionic species	Typical sea water, per liter			sediment	halite	epsomite	carnallite	bischofite
Anions	**mg**	**%,w/w**	**mEq**	**mEq**	**mEq**	**mEq**	**mEq**	**mEq**
Chloride (Cl^-)	18,980	55.0%	535		-459		-30	-46
Sulfate (SO_4^{2-})	2,649	7.7%	55	-18		-37		

Bicarbonate (HCO_3^-)	140	0.4%	2	-2				
Bromide (Br^-)	65	0.2%	1					
Borate (BO_3^{3-})	26	0.1%	1					
Fluoride (F^-)	1	0.0%	0					
Silicate (SiO_3^{2-})	1	0.0%	0					
Iodide (I^-)	< 1	0.0%	0					
Total anions			595					
Cations								
Sodium (Na^+)	10,556	30.6%	459		-459			
Magnesium (Mg^{2+})	1,262	3.7%	104			-37	-20	-47
Calcium (Ca^{2+})	400	1.2%	20	-20				
Potassium (K^+)	380	1.1%	10				-10	
Strontium (Sr^{2+})	13	0.0%	0					
Total cations			593					
Total solids	34,483	(100%)						

Solar evaporation of over 90+% of the water in sea water creates a saturated solution of sodium chloride. During this phase of solarization, calcium carbonate and calcium sulfate crystallize and become sediment in the initial solar pond. Further evaporation of water leads to crystallization of relatively pure sodium chloride as the mineral "halite." Sodium chloride represents 76.5% of the mass of typical sea water minerals. "Sea salt," the commercial product produced by solar evaporation of the sea water, contains as much sodium chloride (> 98.5%) as mined "salt" does. Salt production from solar ponds represents 14% of the total salt produced in the United States (Butts 2004).

Crystallization of sodium chloride from sea water creates magnesium-rich solar brine. As more water is evaporated from solar brine, magnesium combines with any remaining sulfate to form epsomite (crystalline magnesium sulfate), or with potassium to form a double sulfate evaporite called schoenite.

The final evaporites formed depend on the ionic composition of the brine. Potassium and magnesium form a double chloride salt, called carnallite. If the formation of carnallite removes all the potassium from the solar brine, and magnesium is the only remaining cation, magnesium chloride in the form of the mineral bischofite is the last mineral to crystallize since it is the most water-soluble evaporite. Bischofite is the natural mineral form of magnesium chloride hexahydrate.

Terminal lake brines

A terminal lake is a lake where water is flowing in but no water flows out, so that the dissolved salts concentrate and form brine as the water evaporates. The Great Salt Lake in Utah is a familiar example. Great Salt Lake brine is the primary source of magnesium chloride in North America. The Great Salt Lake contains sodium-magnesium-chloride-sulfate brine with low alkalinity (Domagalski, Orem, and Eugester 1989). Like solarization of seawater, the first evaporite of Great Salt Lake brine to form is halite (sodium chloride), followed by schoenite (magnesium-potassium sulfate), kainite (potassium chloride-magnesium sulfate double salt), and carnallite (potassium-magnesium chloride), resulting in a magnesium chloride brine (Neitzel 1971). Evaporating the water in this magnesium chloride brine creates crude solid magnesium chloride.

The Dead Sea is also a terminal lake. Magnesium chloride is produced in Israel and Jordan from Dead Sea brine. Magnesium chloride accounts for about half of Dead Sea solids. The major minerals in Dead Sea brine are magnesium chloride and potassium chloride, which crystallize as the double salt carnallite (Sadan 1979). Carnallite is then treated with water to isolate the magnesium chloride, taking advantage of the fact that magnesium chloride is over three times more soluble in water than is potassium chloride.

The sequence of crystallization of the dissolved salts in natural brines during isothermal (solar) evaporation produces the same minerals found in mineral deposits in prehistoric sea beds (Fezei, Hammi, and M'nif 2012). Successive evaporation sequences lead to precipitation of sodium chloride (halite) and then the potassium chloride–magnesium sulfate double salt (kainite). Thereafter, in traditional solarization, the mother liquor is cooled to remove magnesium sulfate heptahydrate (epsomite). This step is essential before precipitating the potassium chloride magnesium chloride double salt (carnallite). Fezei et al. (Fezei, Hammi, and M'nif 2012) developed a process to ameliorate brine containing excessive sulfate. Sulfate can be quantitatively removed prior to epsomite formation by adding calcium chloride to form insoluble calcium sulfate (gypsum). Avoiding loss of magnesium in the form of epsomite and increasing the chloride content of the brine increases the yield of magnesium chloride. The sulfate–free solution is suitable to be used for the production of magnesium chloride hexahydrate with purity greater than 90%. This brine is not the source of large amounts of magnesium chloride, but the chemistry is an example of optimizing magnesium chloride yields. The chemistry of this intervention is as follows:

$$MgSO_4 \text{ (in the brine)} + CaCl_2 \text{ (solution)} \rightarrow CaSO_4 \text{ (solid)} + MgCl_2 \text{ (in the brine)}$$

Magnesium chloride can also be extracted from any of these brines in a two-step process that bypasses the lengthy solar evaporation steps. Adding calcium hydroxide to magnesium chloride-containing brine precipitates magnesium as magnesium hydroxide. This precipitate is mixed with concentrated brine (now containing calcium and chloride) and a source of carbon dioxide to regenerate a pure magnesium chloride liquor (Butts 2004). The chemistry of the process is as follows:

$$MgCl_2 \text{ (liquid)} + Ca(OH)_2 \text{ (solid)} \rightarrow Mg(OH)_2 \text{ (solid)} + CaCl_2 \text{ (in the brine)}$$
$$Mg(OH)_2 \text{ (solid)} + CaCl_2 \text{ (in the brine)} + CO_2 \rightarrow MgCl_2 + H_2O + CaCO_3 \text{ (solid)}$$

Subsurface brine deposits

Brine deposits in Midland, Michigan, have been a source of magnesium chloride since the 1890s. The Dow company originally obtained its bromine, chlorine, sodium, calcium and magnesium from the brine of ancient seas under Midland (Chemical Heritage Foundation 2015).

Mined mineral deposits

The two major mined mineral sources of magnesium chloride are bischofite and carnallite, both of which were formed during prehistoric solar evaporation of sea water (Butts 2004). Solution mining of these ore bodies creates a brine that is processed on the surface.

Bischofite ore is found as a sea salt concentrate dated from the Permian Period (nearly 200 million years ago), with one such zone extending through northern Europe, from the British Isles into Russia. MagnesiumUSA, Inc. has a bischofite mine located in Poltava, Ukraine, that is considered to be a region that contains some of the largest, purest, deepest and oldest deposits of bischofite in the world. Their mine has a bischofite deposit that is estimated to be more than 300 million years old, and supplies Natural Bischofite Solution, Magnesium Chloride Crystals, and other magnesium products. Natural Bischofite Solution also is extracted with water and produced at a depth of 2,650 meters (8,700 feet) (MagnesiumUSA 2016). Nedmag Industries facilities are located above a 250 million year old Zechstein deposit of bischofite and carnallite salts in Northern Europe. At a depth of approximately 1,500 meters below the surface, unique bischofite salt layers consist of very pure magnesium chloride. Bischofite brine is extracted through solution mining by injecting water into the salt layers. The water dissolves the magnesium chloride, forming a magnesium chloride brine, which is pumped up to the surface where it is processed to be sold in liquid or dry form. Bischofite is also found in salt deposits in the originally discovered bischofite deposit in Stassfurt, Saxony-Anhalt, Germany, in Atyrau, Atyrau Province, Kazakhstan, and in Peru (Hudson Institute of Mineralogy).

Magnesium chloride is isolated from bischofite and carnallite ore deposits by solution mining, similar to how sodium bicarbonate is extracted from trona ore in Wyoming. Water is pumped into the ore body to dissolve these soluble minerals, forming a brine which is pumped to the surface. Most of the patented processes for purification and concentration of these brines rely on water and evaporation, without any additional chemicals (Jones, Grover, and Silsbee 1917; Neitzel 1971; Dillard, Davis, and Every 1976;

Groenhof 1982; Nylander 1972). However, because magnesium chloride is soluble in alcohol while potassium chloride is not, several patented processes for separating pure magnesium chloride from carnallite employ a low molecular weight alcohol, such as methanol, to recover pure magnesium chloride (Chassagne 1974; Lambly, Leibson, and Chassagne 1976; Fox, Degen, and Leibson 1977). At the end of the extraction process, the magnesium chloride has not been changed into a different substance, and any alcohol used as an extraction aid has been removed from the final substance.

Magnesium chloride formed by chemical synthesis

Several synthetic processes that create magnesium chloride use hydrochloric acid. Three are described by the FDA at 21 CFR 184.1426:

- reaction of magnesium oxide with hydrochloric acid,
- treatment of magnesium ammonium chloride hexahydrate with hydrochloric acid, and
- dissolution of magnesium oxide, hydroxide, or carbonate in aqueous hydrochloric acid.

Other synthetic pathways include:

- action of hydrochloric acid on magnesium oxide or hydroxide, especially the hydroxide, when precipitated from seawater or Great Salt Lake brine by addition of calcium (Lewis 1997a), and
- as a by-product in the manufacture of titanium (Jackson et al. 2000).

Evaluation Question #2: Discuss whether the petitioned substance is formulated or manufactured by a chemical process, or created by naturally occurring biological processes (7 U.S.C. § 6502 (21)). Discuss whether the petitioned substance is derived from an agricultural source.

Two magnesium chloride-containing evaporites, carnallite and bischofite, are created by the solarization of sea water or natural brines, which is a naturally occurring process. Carnallite and bischofite also occur as mineral deposits that formed naturally over millions of years in salt lakes. Solar evaporation and crystallization are considered physical (not chemical) processes.

The process by Fezei et al. that removes sulfate from terminal lake brines by adding calcium chloride to precipitate calcium sulfate is a chemical process that produces additional magnesium chloride.

The two-step process of extracting magnesium chloride from terminal lake brines involves adding lime (calcium hydroxide) to precipitate magnesium hydroxide, and then mixing the solid magnesium hydroxide with the brine and carbon dioxide to generate pure magnesium chloride liquor. This process is similar to how citric acid produced by microbial fermentation is isolated. Calcium hydroxide is added to the citric acid-containing culture to precipitate citric acid as calcium citrate. Citric acid is recovered by reacting calcium citrate with sulfuric acid. Calcium precipitates as calcium sulfate and citrate is converted to citric acid. Citric acid produced in this manner is classified as a nonsynthetic substance at §205.605(a).

Several patented processes for purifying magnesium chloride sourced from solution mining rely on synthetic alcohols, such as methanol, to take advantage of the high alcohol solubility of magnesium chloride (Chassagne 1974; Lambly, Leibson, and Chassagne 1976; Fox, Degen, and Leibson 1977).

Synthesis of magnesium chloride by the reaction of a magnesium compound such as the oxide, hydroxide, or carbonate with hydrochloric acid is a chemical process, which involves chemical reaction of an acid and an alkali to form a salt.

Agricultural vs. Nonagricultural sources

Magnesium chloride made directly or indirectly from sea water, brine, or mineral ore is considered to be derived from nonagricultural sources.

<u>Evaluation Question #3:</u> 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 chloride produced by reacting a magnesium compound or mineral with hydrochloric acid is considered synthetic. This is because the substance undergoes a chemical change so that it is chemically or structurally different from how it naturally occurs in the source material.

Natural sources of magnesium chloride are described in Evaluation Question 1, and the substance can be extracted by various means which may affect the classification of the final substance as synthetic or nonsynthetic. Evaporation and crystallization are physical processes which do not result in chemical change. Magnesium chloride extracted from brine by the two-step process involving calcium hydroxide and carbon dioxide is not chemically or structurally different from how it naturally occurs in the source material.

<u>Evaluation Question #4:</u> Specify whether the petitioned substance is categorized as generally recognized as safe (GRAS) when used according to FDA's good manufacturing practices (7 CFR § 205.600 (b)(5)). If not categorized as GRAS, describe the regulatory status.

Magnesium chloride hexahydrate is affirmed as GRAS at 21 CFR 184.1426, and is allowed by the FDA as a flavoring agent and adjuvant and as a nutrient supplement.

<u>Evaluation Question #5:</u> Describe whether the primary technical function or purpose of the petitioned substance is a preservative. If so, provide a detailed description of its mechanism as a preservative (7 CFR § 205.600 (b)(4)).

Magnesium chloride does not function as a preservative.

<u>Evaluation Question #6:</u> Describe whether the petitioned substance will be used primarily to recreate or improve flavors, colors, textures, or nutritive values lost in processing (except when required by law) and how the substance recreates or improves any of these food/feed characteristics (7 CFR § 205.600 (b)(4)).

Magnesium chloride is not used to recreate or improve characteristics lost in processing. Magnesium chloride is used to create and modify the texture of the soy bean curd product, tofu. Magnesium chloride is a salt of the essential nutrient magnesium, and is specifically permitted as a nutrient supplement at 21 CFR 184.1426. Nutritionally complete products intended as the sole item in the diet of human infants frequently contain magnesium chloride as a source of both magnesium and chloride as required at 21 CFR 107.100.

<u>Evaluation Question #7</u>*:* Describe any effect or potential effect on the nutritional quality of the food or feed when the petitioned substance is used (7 CFR § 205.600 (b)(3)).

Adding magnesium chloride to any food or feed will increase the amounts of the essential mineral nutrients magnesium and chloride. Severe magnesium deficiency is rare in the United States, but habitually low intakes are commonplace. Magnesium depletion has cardiovascular effects, including increased blood pressure, atrial fibrillation, ventricular tachycardia and fibrillation, and increased risk of cardiac ischemia.

<u>Evaluation Question #8:</u> List any reported residues of heavy metals or other contaminants in excess of FDA tolerances that are present or have been reported in the petitioned substance (7 CFR § 205.600 (b)(5)).

Magnesium chloride hexahydrate for food processing meets the Food Chemicals Codex heavy metal specification for lead of not more than 4 parts per million (U. S. Pharmacopeia 2010). The JECFA specification for lead in magnesium chloride hexahydrate is not more than 2 ppm (JECFA 2004).

<u>Evaluation Question #9:</u> 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)).

The historical process of solar evaporation of sea water to obtain salt and additional minerals such as magnesium chloride creates saline ponds and infertile soil. Solar salt ponds have been reused for several millennia in the Eastern Mediterranean so that the environmental damage is localized. With respect to terminal lakes such as the Great Salt Lake, the major environmental threat here is not related to mineral extraction operations; it is the reduction of water flow into this terminal lake caused by agricultural and other diversions (Wurtsbaugh et al. 2016). Winds blowing over dry lake beds cause dust storms and urban pollution.

An environmental risk with solution mining is surface subsidence, as the underlying mineral is dissolved and removed, effectively creating a cavern.

Several patented processes for the separation of sea minerals employ volatile synthetic low molecular weight alcohols (primarily methanol) to extract magnesium chloride. Solution mining with water containing methanol would result in release of methanol to the environment. However, a comprehensive review of chemical production from natural brines (Butts 2004) makes no mention of methanol or other alcohols in solution mining, suggesting that these processes have little or no commercial application.

Methanol is released to the environment during industrial uses and naturally from volcanic gases, vegetation, and microbes. Exposure may occur from ambient air and during the use of solvents. Acute (short-term) or chronic (long-term) exposure of humans to methanol by inhalation or ingestion may result in blurred vision, headache, dizziness, and nausea. No information is available on the reproductive, developmental, or carcinogenic effects of methanol in humans. Birth defects have been observed in the offspring of rats and mice exposed to methanol by inhalation. The EPA has not classified methanol with respect to carcinogenicity (EPA 2000).

<u>Evaluation Question #10:</u> Describe and summarize any reported effects upon human health from use of the petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (i), 7 U.S.C. § 6517 (c) (2) (A) (i)) and 7 U.S.C. § 6518 (m) (4)).

Magnesium chloride is used in medicine (e.g., parenteral solutions) as a source of soluble magnesium ions, which are essential for many cellular activities. It has also been used as a cathartic. JECFA has established an Acceptable Daily Intake (ADI) for magnesium chloride as "no limit" (JECFA 1980).

<u>Evaluation Question #11:</u> Describe any alternative practices that would make the use of the petitioned substance unnecessary (7 U.S.C. § 6518 (m) (6)).

Use of a coagulant is necessary for tofu processing. Tofu comprises the curdled globular proteins of soybeans. Soybeans are made into soymilk and the coagulant is added to curdle the globulins. Potential alternative practices, including use of dairy cultures and animal enzymes, such as rennet, that curdle the proteins of ruminant milk, have no effect on soy globulins (Institute of Food Technologists 2010) and would not be suitable for vegans or vegetarians.

<u>Evaluation Question #12:</u> Describe all natural (non-synthetic) substances or products which may be used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)).

Magnesium chloride is a prime candidate mineral salt for supplementing a human food with soluble magnesium. Few food grade magnesium salts possess good solubility and acceptable taste profiles and are included on the National List. A human requirement for preformed sulfate has not been established, whereas chloride is known to be an essential nutrient (Institute of Medicine 2005), so magnesium chloride is a more acceptable source of this nutrient for formulated products than is magnesium sulfate.

A natural mineral that provides nutritionally available magnesium is dolomite, a calcium carbonate-magnesium carbonate. Dolomite is insoluble in water so it is unsuitable for nutritional fortification of liquid products and for making tofu, but it can be useful in some solid and dry food products.

For tofu processing, four basic types of coagulants are used: chloride types (such as magnesium chloride and calcium chloride), sulfate types (such as calcium sulfate and magnesium sulfate), glucono delta-lactone, and acidic agents (such a citrus juices, vinegar, or lactic acid sources) (Shurtleff and Aoyagi 2000). Each of these has unique effects on the texture of tofu (deMan, deMan, and Gupta 1986). Calcium chloride, calcium sulfate, glucono delta-lactone, and lactic acid and citric acid are all classified as nonsynthetic on §205.605(a).

Calcium sulfate, calcium chloride, magnesium chloride, and glucono-delta-lactone are the most frequently used coagulants for precipitating soy protein curd to make tofu (Arii and Takenaka 2013; Shurtleff and Aoyagi 1975). Glucono delta-lactone is an effective coagulant used to make tofu, especially "silken" tofu. The Japanese typically use "nigari," the solids remaining in salt water after sea salt and magnesium sulfate crystallize, which contains as much as 90% magnesium chloride, as one component of the coagulants. They then use calcium chloride or calcium sulfate as a second component, since too much calcium and too much magnesium each can adversely impact tofu texture (Arii and Takenaka 2013). Magnesium sulfate has a bitter, saline taste that limits its use as a total replacement for magnesium chloride.

Various acidic substances can curdle soy protein. Jeong et al. (Jeong et al. 2004) developed a method for preparing bean curd containing lactic acid for the Korean market by preparing bean soup using soybeans, cooling the bean soup, and adding a lactic acid-containing bacterial culture to the bean soup to curdle the bean protein, thus forming bean curd. Citrus juices, particularly lemon juice, are effective coagulants. Tofu made with lemon juice may be too tart for some tastes (Chang 2006), but it is great tasting for others (Obatolu 2008).

<u>Evaluation Information #13:</u> Provide a list of organic agricultural products that could be alternatives for the petitioned substance (7 CFR § 205.600 (b) (1)).

Juice from organic lemons can be used as a coagulant for tofu (Sanjay et al. 2008). However, each coagulant has unique effects on tofu taste and texture. Tofu made with lemon juice may be too tart for some tastes (Chang 2006), but it is great tasting for others (Obatolu 2008).

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