Magnesium Oxide

Crops

1		Crops
1 2	Iden	tification of Petitioned Substance
3		
4	Chemical Names:	CAS Numbers:
5	Magnesium oxide	1309-48-4
6	Oxomagnesium	1193320-89-6
7		13589-16-7
8	Other Name:	185461-91-0
9	Magnesia	187036-80-2
10	Periclase	227961-49-1
11	Seawater magnesia	52933-73-0
12	Maglite	82375-77-7
13	Oxymag	146024-95-5
14	Calcined magnesia	146024-97-7
15	Magnesia monoxide	148075-95-0
16		148075-92-7
17	Trade Names:	1317-74-4
18	F3 SurfActive	146024-94-4
19	Basfoliar® Mg flo	
20		Other Codes:
		EC No. 215-171-9
		ICSC No. 0504
		RTECS No. OM3850000
21		
22		Summary of Petitioned Use
23		
24	Magnesium oxide is used in organic cro	op production as an additive to modify the physical properties of
25		tions. The United States Department of Agriculture (USDA)
26		approved magnesium oxide as a "synthetic substance allowed for
27		he stipulation that it is "for use only to control the viscosity of a clay
28	suspension agent for humates" in 7 CFl	
29	1 0	
30	This technical report was requested by	the National Organic Standards Board (NOSB) Crops Subcommittee in
31	support of its sunset review of magnesi	
32		
33	Charae	cterization of Petitioned Substance
34		
35	Composition of the Substance:	
36		d formed between magnesium cations (Mg ²⁺) and oxide anions (O ²⁻) an
37		ructure. Magnesium oxide is formed when pure magnesium reacts or is
38		escribed below in Equation 1 (Atkins et al. 2008).
39	-8 F	······································
40		$2 \operatorname{Mg}_{(s)} + O_{2(g)} \rightarrow 2 \operatorname{MgO}_{(s)}$
41		O(v) = -(b) = O(v)
42		Equation 1
43		
44	e .	y of metal ions that can be carried over from mineral and brine
45 46	ě	num, and manganese (de Sousa 2018). The composition and amount oxide are dependent on the source and production conditions. Iron is

of these metals present in magnesium oxide are dependent on the source and production conditions. Iron is
 the most common contaminant in magnesium oxide produced from mineral sources due to its prevalence

Magnesium Oxide

48 in the earth's crust (Atkins et al. 2008, de Sousa 2018). Iron accounts for 0.1-5% of the final mass of 49 magnesium oxide from mineral sources, but it is rarely present in magnesium oxide produced from brine. 50 Calcium makes up most of the impurity when brine is used to produce magnesium oxide, accounting for 51 0.5-3% of the final mass (de Sousa 2018). Mineral sources made of magnesium oxide may also include 52 silicon, depending on the mineral and production conditions used. Magnesium oxide may contain boron if 53 it is produced from some salt lake brine sources (de Sousa 2018). 54 55 Source or Origin of the Substance: Magnesium is an earth abundant element. It is the 8th most abundant element in the earth's crust and the 56 57 3rd most abundant element in the oceans (Atkins et al. 2008, Baird and Cann 2008, USGS 2017, de Sousa 58 2018, Nobre et al. 2020). Magnesium oxide is a commercially available compound that can be produced 59 from mineral and brine (seawater and salt lake) sources. Magnesium oxide exists in mineral form as 60 periclase and can be produced from many magnesium-containing minerals, including brucite (Mg(OH)₂), 61 magnesite (MgCO₃), hydro-magnesite (Mg₅(CO₃)₄(OH)₂), dolomite (CaMg(CO₃)₂), carnallite (KMgCl₃), and olivine (Mg₂SiO₄) (Panda and Mahapatra 1983, USDA 2007, Atkins et al. 2008, USGA 2017, de Sousa 2018, 62 63 Nobre et al. 2020). 64 65 **Properties of the Substance:** The high charge density of magnesium and oxide ions (Mg²⁺, O²⁻) creates strong electrostatic attraction between 66 67 ions, resulting in a high melting point (2852 °C) (Atkins et al. 2008, SA 2020). The rock salt crystalline structure 68 results in poor electrical conductivity, making magnesium oxide a good insulator (Atkins et al. 2008). 69 70 Magnesium oxide is insoluble in water but reacts with water to form magnesium hydroxide (brucite, $[Mg(OH)_2]$), 71 as described below in Equation 2 (PC 14792, USDA 2007, Atkins et al. 2008, de Sousa 2018, SA 2020). The 72 formation of magnesium hydroxide from magnesium oxide and water is a reversible process, and magnesium 73 oxide can be reformed by heating magnesium hydroxide (Atkins et al. 2008, de Sousa 2018, Nobre et al. 2020). 74 75 $MgO_{(s)} + H_2O_{(l)} \rightleftharpoons Mg(OH)_{2(s)}$ 76 77 **Equation 2** 78 79 Magnesium hydroxide is a basic substance that also has low water solubility, with a K_{sp} = 6.3 × 10⁻¹⁰ (Silberberg 80 2003). The basic nature of magnesium hydroxide results in increased solubility in acidic solutions (Silberberg 81 2003, Atkins et al. 2008). 82 83 General properties of magnesium oxide are listed below in Table 1. 84 Table 1. Properties of magnesium oxide 85 86 Property Magnesium oxide White powder, white to translucent crystals Appearance CAS number 1309-48-4 Molecular weight 40.3 g/mol Solubility Insoluble in water and ethanol, soluble in dilute HCl

87 88

89 Specific Uses of the Substance:

Reactivity

Melting point

Boiling point Density

90 Magnesium oxide is used in organic crop production as an additive in mixtures of clay and humates to

Sources: PC 14792, Silberberg 2003, USDA 2007, Atkins et al. 2008, de Sousa 2018, SA 2020

91 influence viscosity. The incorporation of magnesium oxide influences the interactions between clay

2852 °C; 5166 °F 3600 °C; 6512 °F

 3.580 g/cm^3

92 particles and humates by affecting the viscosity of the solution and changing the surface charge of the clay

Reactive with water to form magnesium hydroxide (Equation 2)

- particles to prevent aggregation between the two substances (Reid and Karr 2002, Tombacz 2003, USDA
 2013).
- 95

96 Magnesium oxide has viscosity-related applications in aqueous fluids used for a variety of purposes,

97 including environmental drilling and mining (Hoy 2005). Magnesium oxide has also been used to influence

98 the interactions between suspensions of clays, polymers, and organic matter (including humates) in water

99 purification applications (Bolto et al. 2001 Sabah and Ouki 2017). The addition of magnesium oxide to

100 water purification processes facilitates the removal of organic matter from a solution and adsorption to clay 101 and polymer surfaces; the opposite effect is seen when magnesium oxide is used in organic agriculture

and polymer surfaces; the opposite effect is seen when magnesium oxide is used in organic agriculture
 applications (Bolto et al. 2001, Tombacz 2003, Petzold et al. 2004, Nguyen et al. 2009). In the case of

- applications (Bolto et al. 2001, Tombacz 2003, Petzold et al. 2004, Nguyen et al. 2009). In the case of
 agricultural formulations, magnesium oxide is generally added in the absence of clay and polymer
- flocculants and is added to reach solutions with high ionic strength (high concentration of dissolved ionic
- 105 components) (Tombacz 2003, Nguyen et al. 2009, Zhang et al. 2012). The high ionic strength of the solution
- 106 increases ionic competition for attractive sites on organic material and increases electrostatic repulsions
- 107 between organic material with associated multivalent cations (Wall and Mathews 2005). Magnesium oxide
- also increases the pH of the solution, promoting negative charges on organic carboxylic acids, and
- increasing electrostatic repulsions (Feng et al. 2005, Wall and Mathews 2005, Nguyen et al. 2009).
- 110

111 Magnesium oxide has many uses outside of influencing clay-humate interactions. Magnesium oxide is

- 112 used as a foliar source of the micronutrient Mg^{2+} in conventional crop production and as a soil amendment
- to add magnesium and adjust soil pH (Reid and Karr 2002, CE 2006, Pereira et al. 2015). Magnesium oxide
- 114 has several medicinal applications as an ingredient in antacids, laxatives, and magnesium supplements
- 115 (Flommnebaum et al. 2002, USDA 2007). Magnesium oxide has several applications in industrial

manufacturing as an alternative to lime (calcium oxide [CaO]) in Portland cement, a pH adjuster in tanning

117 processes, and an alternative to titanium oxides in white pigments (Atkins et al. 2008, de Sousa 2018, Nobre

et al. 2020). The high thermal stability and low electrical conductivity of magnesium oxide allow for applications in high temperature environments, including as a component of refractory lining in industrial

- 119 applications in high temperature environments, including as a con 120 furnaces and heating elements (Atkins et al. 2008).
- 121

122 Approved Legal Uses of the Substance:

123 The USDA NOP has approved magnesium oxide as a "synthetic substance allowed for use in organic crop

- 124 production" with the stipulation that it is "for use only to control the viscosity of a clay suspension agent 125 for humates" in 7 CFR 205.601.
- 126

The United States Food and Drug Administration (FDA) allows the use of magnesium as an ingredient in
animal drugs and feeds in 21 CFR 558. Magnesium oxide is an approved ingredient in bambermycins in 21
CFR 558.95, chlortetracycline in § 558.128, fenbendazole in § 558.258, and lasalocid in § 558.311.

- 130
- The FDA has designated magnesium oxide to be generally recognized as safe (GRAS) "when used in
- accordance with good manufacturing or feeding practice" in 21 CFR 582.1431 and § 582.5431. The FDA has
- also granted magnesium oxide GRAS status as a "direct food substance" in § 184.1431. The FDA recognizes
- 134 magnesium oxide as a precursor for GRAS substances magnesium chloride in § 184.1426, magnesium
- hydroxide in § 184.1428, and magnesium sulfate in § 184.1443.
- 136
- 137 The FDA has approved the use of magnesium oxide as an active ingredient in "antacid products for
- 138 over-the-counter (OTC) human use in 21 CFR 331.11 and as an ingredient in over-the-counter "weight
- 139 control drug products" in § 310.545. The FDA has also approved magnesium oxide as an ingredient in
- 140 canned peas in § 155.170.
- 141
- 142 The FDA has approved the use of magnesium oxide as an ingredient for several food additives, adjuvants,
- 143 colorants, production aids, sanitizers, and polymers. These include perfluorocarbon cured elastomers in 21
- 144 CFR 177.2400, components of paper and paperboard in § 176.170, rubber articles in § 176.2600, petroleum
- 145 wax in § 172.886, colorants in § 82.3 and § 178.3297, and sanitizing solutions in § 178.1010.
- 146

The United States Environmental Protection Agency (EPA) has listed magnesium oxide as an "inert
ingredient used pre- and post-harvest" that are "exempt from the requirement of a tolerance" in 40 CFR

149 180.910, and is included on List 4. The EPA has granted magnesium oxide a "tolerance exemption for active

and inert ingredients for use in antimicrobial formulations" in § 180.940. The EPA has also classified

magnesium oxide as an "active ingredient permitted in exempted minimum risk pesticide products" in §
152.25.

152

154 Action of the Substance:

155 Magnesium oxide is used in organic crop production as a viscosity control additive to clay-humate

156 mixtures (USDA 2013). Humates are mixtures of organic material that have been partially decomposed,

157 primarily through oxidative processes. The oxidation of the organic components results in carboxylic acids

and phenols making up most functional groups (Baird and Cann 2008, Sabah and Ouki 2017). These

159 functional groups result in the formation of negatively charged carboxylate and phenolate anions that are

stable across acidic, neutral, and basic pH (del Mar Ramos-Tejada et al. 2003, Feng et al. 2005, Nguyen et al.
2009).

161 162

163 Humates often adsorb to the surfaces of clay particles in aqueous environments due to ligand exchange

164 interactions, metal bridging, and van der Waals interactions (Tombacz 2003, Petzold et al. 2004, Feng et al.

165 2005, Baird and Cann 2008, Zhang et al. 2012, Sabah and Ouki 2017). Clay-humate interactions are

166 dependent on clay composition and surface structure and the pH and ionic strength of the aqueous

167 environment. Humate adsorption onto clay surfaces increases with decreased pH and increased ionic

strength (Bolto et al. 2001, del Mar Ramos-Tejada et al. 2003, Tombacz 2003, Feng et al. 2005, Zhang et al.

169 2012, Sabah and Ouki 2017).

170

171 Magnesium oxide has the potential to affect the surface of clay particles and the pH of the aqueous

solution. Magnesium oxide is incorporated into the pores of clay particles, displacing other substances in a

173 process referred to as exfoliation (Pereira et al. 2015). When the exfoliation process replaces trivalent ions

174 (e.g., Al^{3+} , Fe^{3+}) with magnesium ions (Mg²⁺), the clay particle exhibits a greater negative surface charge

175 (Tombacz 2003, Zhang et al. 2012). Increased negative surface charges on clay particles exfoliated with

176 magnesium oxide, and the negative surface charges of humates, increases electrostatic repulsions in

solution and prevents aggregation of clay and humate particles (Reid and Karr 2002, Tombacz 2003, USDA2013).

179

180 Magnesium oxide can also affect the pH of the aqueous solution, which decreases humate adsorption

181 (Bolto et al. 2001, del Mar Ramos-Tejada et al. 2003, Tombacz 2003, Feng et al. 2005, Zhang et al. 2012,

182 Sabah and Ouki 2017). As described in the "Properties of the Substance" section, magnesium oxide reacts

183 with water to form the base magnesium hydroxide (Equation 2). Furthermore, the solubility of magnesium

184 hydroxide improves in acidic solutions, increasing solution pH more dramatically in acidic solutions

185 (Silberberg 2003). As described above, the surface charge of humates is dependent on pH, with a greater

186 negative surface charge possible under basic conditions, whose high pH promotes the formation of

187 carboxylate and phenolate ions (del Mar Ramos-Tejada et al. 2003). Therefore, adsorption of humates to

clay surfaces is decreased at high pHs due to the increased electrostatic repulsions between the negatively

189 charged clay and humate surfaces (Feng et al. 2005, Nguyen et al. 2009).

190

Magnesium oxide has also been reported to facilitate aggregation between individual humate particles and humates and clay particles (Bolto et al. 2001, Feng et al. 2005, Nguyen et al. 2009, Zhang et al. 2012, Zhang et al. 2020). Magnesium oxide is insoluble in water and remains solid in aqueous mixtures. Magnesium oxide surfaces promote the adsorption of humates through ligand exchange, which refers to interactions between carboxylate groups on the humate surface with the hydroxides present due to magnesium

196 oxide-water interactions (Equation 2) (Zhang et al. 2020). Hydroxide-carboxylate interactions between

197 magnesium oxide and humate surfaces are further enhanced by van der Waals interactions between the

198 two substances (Zhang et al. 2020).

199

200 The incorporation of magnesium ions to the surface of clays may result in enhanced interactions between

clay and humate particles. Improved adsorption following magnesium oxide exfoliation has been

202 connected to improved ligand exchange interactions with the hydroxides that form at the interface of magnesium ion and the aqueous solution (Bolto et al. 2001, Feng et al. 2005, Zhang et al. 2012). Metal 203 204 bridging between cations and carboxylate groups may also facilitate increased adsorption. Metal bridging 205 occurs by chelate interactions (multiple points of interaction) between metals and carboxylate ions (Bolto et 206 al. 2001, Feng et al. 2005). 207 208 **Combinations of the Substance:** 209 As described above in the "Specific Uses of the Substance" and "Action of the Substance" sections, 210 magnesium oxide is used in combination with clays and humates in organic crop production. Clays and 211 humates are classified as non-synthetic substances, which are allowed in organic production (NOP 5034-1). 212 213 Status 214 215 **Historic Use:** 216 Magnesium oxide does not have a historical use within organic crop production, and it was recently added 217 to the National List in 2018 (AMS-NOP-14-0079). For conventional agriculture, magnesium oxide is used as 218 a source of magnesium micronutrients in foliar fertilizers and as a soil amendment micronutrient and pH 219 adjuster (Reid and Karr 2002, CE 2006, Pereira et al. 2015). 220 221 **Organic Foods Production Act, USDA Final Rule:** 222 Magnesium oxide is not listed in the Organic Foods Production Act of 1990 (OFPA). 223 224 The USDA NOP has approved magnesium oxide as a "synthetic substance allowed for use in organic crop 225 production" with the stipulation that it is "for use only to control the viscosity of a clay suspension agent 226 for humates" in 7 CFR 205.601. 227 228 International: 229 Describe the status of the substance among international organizations. Specifically, the report should 230 address whether the petitioned substance is allowed or prohibited for use in other international organic 231 standards such as: 232 233 The Canadian General Standards Board Permitted Substances List (updated November 2015) 234 The CAN/CGSB-32.311-2015 lists magnesium oxide as a "mineral" for use in "feed, feed additives and feed 235 supplements" and in "health care products and production aids." 236 237 CODEX Alimentarius Commission, Guidelines for the Production, Processing, Labelling and Marketing 238 of Organically Produced Foods (GL 32-1999) 239 Magnesium oxide is not listed in the CODEX GL 32-1999. 240 241 European Economic Community (EEC) Council Regulation, EC No. 834/2007 and 889/2008 Magnesium oxide is listed in ED No. 889/2008 as a "feed material of mineral origin." Magnesium oxide is 242 243 not listed in EC. No 834/2007. 244 245 Japan Agricultural Standard (JAS) for Organic Production 246 Magnesium oxide is not listed in the JAS for organic production. 247 248 International Federation of Organic Agriculture Movements (IFOAM) 249 Magnesium oxide is not included in the IFOAM Norms for organic production and processing. 250 251 Evaluation Questions for Substances to be used in Organic Crop or Livestock Production 252 253 Evaluation Question #1: Indicate which category in OFPA that the substance falls under: (A) Does the 254 substance contain an active ingredient in any of the following categories: copper and sulfur compounds,

- 254 substance contain an active ingredient in any of the following categories: copper and sulfur cont 255 toying derived from bacteria, pheromones, soang, bertigultural ails, fish emulsions, treated soand
- 255 toxins derived from bacteria; pheromones, soaps, horticultural oils, fish emulsions, treated seed,

256 257 258 259 260 261	vitamins and minerals; livestock parasiticides and medicines and production aids including netting, tree wraps and seals, insect traps, sticky barriers, row covers, and equipment cleansers? (B) Is the substance a synthetic inert ingredient that is not classified by the EPA as inerts of toxicological concern (i.e., EPA List 4 inerts) (7 U.S.C. § 6517(c)(1)(B)(ii))? Is the synthetic substance an inert ingredient which is not on EPA List 4, but is exempt from a requirement of a tolerance, per 40 CFR part 180?
262 263 264 265 266 267	A) Magnesium oxide does not contain any of the listed categories as an active ingredient. However, magnesium oxide is an ionic compound that is found naturally in mineral form as periclase and may be produced from other mineral magnesium sources, as described in the "Source or Origin of the Substance" section (Baird and Cann 2008). Most commercially available magnesium oxide is derived by treatment of saltwater brines, but it may still be considered mineral in form.
268 269 270 271 272 273 274	B) Magnesium oxide is included in the EPA List 4 of inerts. Additionally, the EPA has listed magnesium oxide as an "inert ingredient used pre- and post-harvest" that are "exempt from the requirement of a tolerance" in 40 CFR 180.910. The EPA has granted magnesium oxide a "tolerance exemption for active and inert ingredients for use in antimicrobial formulations" in § 180.940, and classified magnesium oxide as an "active ingredient permitted in exempted minimum risk pesticide products" in § 152.25.
275 276 277 278 279	<u>Evaluation Question #2</u> : 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)).
280 281 282 283 284 285	As described in the "Source or Origin of the Substance" section, magnesium oxide is commercially produced from both mineral and brine (seawater and salt lake) sources. There are multiple mineral sources for magnesium oxide production, although magnesite (magnesium carbonate [MgCO ₃]) is the most used mineral (de Sousa 2018, Nobre et al. 2020). While magnesium oxide may also be produced from brines, mineral sources are used for most commercial production since they offer a less energy-intensive means of production (de Sousa 2018).
286 287 288 289 290 291 292	Calcination of magnesium salt is the most common method for producing magnesium oxide. Calcination is the process of "heat[ing] a solid to a high temperature to dive off volatile substances" or "heat[ing] a metal to a high temperature to form the oxide of the metal" (Goldman 1982). The common magnesium compounds and production methods of magnesium oxide from mineral and brine sources are discussed below.
292 293 294	Calcination of magnesium carbonates (magnesite)
295 296 297 298 299 300	The calcination of magnesite is the most common method of producing magnesium oxide (Atkins et al. 2008, Baird and Cann 2008, de Sousa 2018, Nobre et al. 2020). The calcination of magnesite produces solid magnesium oxide while liberating carbon dioxide gas, as described below in Equation 3. To remove carbon dioxide from the carbonate ion, magnesite is heated to between 600 °C and 700 °C (Panda and Mahapatra 1983, Nobre et al. 2020).
301	$MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_{2(g)}$
302 303 304	Equation 3
305 306 307 308 309 310	While 600 °C represents the lower limit for the calcination process, different calcination conditions (temperature, residence times) may be used to alter the physical properties of the magnesium oxide product. The specific calcination processes allow the manufacturer to control the structural characteristics, specifically the surface area and porosity of the magnesium oxide product (de Sousa 2018, Nobre et al. 2020). These characteristics are influenced by the temperature and residence times of the calcination process, which determine the nature of the expulsion of carbon dioxide gas from the solid (de Sousa 2018).

- 311 High temperatures and long residence times promote particle growth and the formation of regular crystal 312 lattices, which reduce porosity and surface area in the magnesium oxide product (de Sousa 2018, Nobre et 313 al. 2020).
- 314

315 Magnesium oxide calcination products are classified by their reactivity, which is a kinetic measure of their

316 neutralization of an acid source (de Sousa 2018, Nobre et al. 2020). The acid source used for these

317 determinations is variable, although citric acid and acetic acid are commonly used (Nobre et al. 2020). The

- 318 rate of acid neutralization is reportedly connected to hydration of magnesium oxide to form the base
- 319 magnesium hydroxide (Mg[OH]₂, described in Equation 2), which neutralizes the acid. The rate of
- 320 magnesium oxide hydration is based on the surface area and crystal structure of the solid, with solids with higher surface areas and greater porosity having faster rates of hydration, therefore, faster rates of acid 321
- 322 neutralization (Atkins et al. 2008, de Sousa 2018, Nobre et al. 2020).
- 323

324 Specific calcination conditions and the reactivity of magnesium oxide solids are defined by their 325 temperature ranges and are displayed below in Table 2. High temperature calcination conditions, also

326 known as "dead-burned" in the literature, are the most common commercial conditions used in the

production of magnesium oxide from mineral sources (de Sousa 2018). 327

- 328
- 329 330

Table 2. Calcination conditions for magnesium carbonate minerals

Method	Temperature range (°C)	Relative surface area	Reactivity
Caustic-calcined or light-burned	700 – 1000	Highest	Reactive
Hard-burned	1000 - 1500	High	Less reactive
Periclase or dead-burned	1400 - 2000	Low	Low reactivity
Fused	2800+	Lowest	Inert, unreactive
Sources: de Sousa 2018, Nobre et al. 2020.			

331

332 Calcination of magnesium hydroxide

333 334

335 Magnesium hydroxide from mineral sources

336 Magnesium hydroxide is found in mineral form as brucite but may also be isolated from chemical 337 treatment of other magnesium-containing minerals (i.e., magnesium silicates) (de Sousa 2018, Nobre et al. 338 2020). Magnesium silicates can be digested with hydrochloric acid (HCl) to produce water soluble magnesium chloride (MgCl₂), according to Equation 4 shown below. (Baird and Cann 2008, Nobre et al. 339 340

 $Mg_3Si_2O_5(OH)_{4(s)} + 6 HCl_{(aq)} \rightarrow 3 MgCl_{2(aq)} + 2 SiO_{2(s)} + 5 H_2O_{(l)}$

Equation 4

2020). Magnesium chloride can be isolated from the silicon dioxide solid via filtration.

341 342

343

344

345

346 Magnesium chloride can be converted to magnesium hydroxide, which can be precipitated as a solid due 347 to its low water solubility (Atkins et al. 2008, de Sousa 2018, Nobre et al. 2020). The conversion of 348 magnesium chloride to magnesium hydroxide occurs through a metathesis reaction where the chloride ions (Cl-) are exchanged for hydroxide ions (OH-) (Atkins et al. 2008). The most common hydroxide sources 349 for the magnesium metathesis are from sodium hydroxide (NaOH) or the *in situ* formation of hydroxide 350 351 from lime (calcium oxide [CaO]) or dolomitic lime (calcium magnesium oxide [CaMgO₂]), as described in 352 Equations 5, 6, and 7, respectively (Nobre et al. 2020). Dolomitic lime is the most common input due to its 353 reduced cost compared to sodium hydroxide and increased efficiency compared to lime. However, sodium 354 hydroxide is used to prepare magnesium oxide products with reduced levels of calcium impurities (Nobre 355 et al. 2020). 356

- 357
- 358

 $MgCl_{2(aq)} + 2 NaOH_{(aq)} \rightarrow Mg(OH)_{2(s)} + 2 NaCl_{(aq)}$

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359	Equation 5
360 361	$M\alpha C_{1} + C_{2}O_{1} + H_{2}O_{2} + M\alpha (OH)_{2} + C_{2}C_{1} + C_{3}$
362	$MgCl_{2 (aq)} + CaO_{(s)} + H_2O_{(l)} \rightarrow Mg(OH)_{2 (s)} + CaCl_{2 (aq)}$
363	Equation 6
364 365	$MgCl_{2 (aq)} + CaMgO_{2 (s)} + 2 H_2O_{(l)} \rightarrow 2 Mg(OH)_{2 (s)} + CaCl_{2 (aq)}$
366	
367 368	Equation 7
 369 370 371 372 373 374 	Once magnesium hydroxide has been isolated as a solid, it is calcined to produce magnesium oxide by liberating water vapor, as shown below in Equation 8. The calcination of magnesium hydroxide occurs at lower temperatures than that of magnesium carbonate (350 °C), although temperatures of 1000 °C or higher may be required to liberate water molecules that have been incorporated into the ionic crystal structure (Nobre et al. 2020).
375	$Mg(OH_2)_{(s)} \rightarrow MgO_{(s)} + H_2O_{(g)}$
376 377	Equation 8
378	
379	Magnesium hydroxide from brine Magnesium is a major commencer of accurator, realized on the third most shundows along out (Nakur et al.
380 381	Magnesium is a major component of seawater, ranking as the third most abundant element (Nobre et al. 2020). Most magnesium present in brine exists as the soluble ionic compound magnesium chloride. When
382	brines are used to produce magnesium oxide, the first step is to concentrate the brine, usually via solar
383	evaporation (Panda and Mahapatra 1983). Once concentrated, the brine may be converted to magnesium
384	oxide through two differing methods, described in more detail below.
385	
386	Direct conversion to magnesium hydroxide
387	
388	Once concentrated, the brine may undergo direct conversion to form magnesium hydroxide with the
389	addition of sodium hydroxide, lime, or dolomitic lime, as described in Equations 5, 6, and 7, respectively.
390 391	As with mineral sources, dolomitic lime is the most common additive to facilitate the magnesium
391 392	metathesis (Panda and Mahapatra 1983). As with the mineral form, the isolated magnesium hydroxide is calcined to produce magnesium oxide, as described in Equation 8 (Panda and Mahapatra 1983, de Sousa
393	2018).
394	2010).
395	Purification to remove calcium and other metals
96	
397	Rather than undergoing direct conversion of brine to magnesium hydroxide, additional purification steps
398	may be added. These steps help to reduce the concentrations of calcium and other multivalent metal ions i
399	the magnesium oxide product and to make the production process more efficient (Atkins et al. 2008, Nobr
00	et al. 2020). The purification process occurs with the initial acidification of the brine solution to pH 4, which
01 02	removes carbonates found primarily as calcium bicarbonate (CaHCO ₃). The acidification process reduces the calcium concentration in the brine by the precipitation of water insoluble calcium sulfate, as shown
-02	below in Equation 9.
-04	celon in Equation 7.
05	$Ca(HCO_3)_{2 (aq)} + H_2SO_{4 (aq)} \rightarrow CaSO_{4 (s)} + 2 CO_{2 (g)} + 2 H_2O_{(l)}$
06	
07	Equation 9
08	
-09	Once the brine has been filtered to remove the calcium sulfate solids, the pH is raised and magnesium
10	hydroxide is formed with the addition of sodium hydroxide, lime, or dolomitic lime, as described above in
11	Equations 5, 6, and 7, respectively. As with the direct conversion of brine and the mineral production of
12 13	magnesium hydroxide, dolomitic lime is more often used than lime due to its higher efficiency. Sodium hydroxide is used in the magnesium metathesis to produce magnesium hydroxide with higher purity and
13	nyaroxide is used in the magnesium metathesis to produce magnesium nyaroxide with higher purity and

- 414 lower calcium content (Nobre et al. 2020). Once the purified magnesium salts have been converted to 415 magnesium hydroxide, the substance is calcined to form purified magnesium oxide, as described above in 416 Equation 8 (Nobre et al. 2020). 417 418 Evaluation Question #3: Discuss whether the petitioned substance is formulated or manufactured by a 419 chemical process, or created by naturally occurring biological processes (7 U.S.C. § 6502 (21)). 420 421 Magnesium oxide is a naturally occurring compound that is found in the mineral periclase. However, as 422 discussed above in the "Source of Origin of the Substance" section and Evaluation Ouestion 2, the majority 423 of commercially available magnesium oxide is formed through the calcination of magnesium carbonate-424 containing minerals (e.g., magnesite, hydro-magnesite), as shown in Equation 3. Magnesium can also be 425 sourced from other mineral sources in the form of magnesium chlorides and silicates, which can be converted to magnesium hydroxide via acid-base and metathesis reactions described in Evaluation 426 427 Question 2 and Equations 4–7. Magnesium hydroxide sourced as brucite or by the chemical processing of 428 other magnesium-containing minerals is calcined to form magnesium oxide, as shown in Equation 8. 429 430 Magnesium oxide is also produced from seawater and salt lake brine sources, as described above in the "Source of Origin of the Substance" section and Evaluation Question 2. While magnesium is a common 431 432 elemental component of brine, magnesium oxide is not present in brine sources due to its water 433 insolubility. Magnesium chloride is the primary source of magnesium within brine and is converted to 434 magnesium hydroxide using the same reactions used to process mineral sources of magnesium chloride 435 described by Equations 5, 6, and 7. Additionally, brine may be treated with sulfuric acid to remove carbonates, reducing the amount of calcium in the final product, as described in Equation 9. Magnesium 436 437 oxide from brine is also obtained by calcination of magnesium hydroxide, as described in Evaluation Question 2 and Equation 8. 438 439 440 NOP guidelines classify substances produced by the "heating or burning of non-biological matter (e.g., minerals) to cause a chemical reaction" as synthetic (NOP 5033). Based on this classification, all commercial 441 442 sources of magnesium oxide are considered synthetic, formed by calcination (heating) to liberate carbon 443 dioxide (Equation 3) or water (Equation 8). 444 445 Evaluation Question #4: Describe the persistence or concentration of the petitioned substance and/or its 446 by-products in the environment (7 U.S.C. § 6518 (m) (2)). 447 448 At the time of publication, the author of this report found no studies on the environmental persistence of 449 magnesium oxide. Magnesium oxide is likely to have a long persistence due to its water insolubility. The 450 water insoluble nature of the substance makes it unlikely to enter water systems, and it is likely to have 451 low bioavailability in terrestrial systems (USDA 2007). 452 453 The production of magnesium oxide from both brine and mineral sources results in the formation of 454 magnesium and calcium salts, as described in Evaluation Ouestion 2. These salt substances are prevalent in 455 nature in seawater and in mineral forms, and therefore, the contributions from magnesium oxide 456 production are difficult to quantify (Atkins et al. 2008, Baird et al. 2008, USGS 2017). 457 458 Evaluation Ouestion #5: Describe the toxicity and mode of action of the substance and of its breakdown 459 products and any contaminants. Describe the persistence and areas of concentration in the environment 460 of the substance and its breakdown products (7 U.S.C. § 6518 (m) (2)). 461 At the time of publication, the author of this report found no studies on the environmental persistence or 462 toxicity of magnesium oxide. Magnesium oxide, its production byproducts, and its breakdown products 463 464 are ionic compounds that are commonly found in seawater and minerals (USDA 2007, Atkins et al. 2008, Baird and Cann 2008, USGS 2017). As described in the "Properties of the Substance" section and Evaluation 465
- 466 Question 4, magnesium oxide is insoluble in water, making it unlikely to contaminate water systems and
- 467 giving it low bioavailability in terrestrial systems (USDA 2007).
- 468

- As described in the "Properties of the Substance" section, magnesium oxide reacts with water in a
 reversible manner to produce magnesium hydroxide. Magnesium hydroxide also has low water solubility,
 making it unlikely to contaminate water systems or be readily bioavailable in terrestrial systems (Silberberg
 2003, USDA 2007).
 Evaluation Question #6: Describe any environmental contamination that could result from the
 petitioned substance's manufacture, use, misuse, or disposal (7 U.S.C. § 6518 (m) (3)).
- As described in Evaluation Questions 4 and 5, magnesium oxide and its breakdown and byproducts are
 prevalent in minerals, seawater and salt lakes and unlikely to contribute to environmental contamination.
 When used as approved within organic agriculture, magnesium oxide is applied in limited quantities as a
- When used as approved within organic agriculture, magnesium oxide is applied in limited quantities as a viscosity control additive, making it unlikely to contribute to environmental contamination (NOSB 2013).
- 481
- Given the ubiquitous nature of magnesium salts in terrestrial and aquatic systems, the most likely cause of
 environmental contamination is linked to mining minerals and the production of magnesium oxide.
 Mining operations may result in contamination through the release of naturally occurring contaminants
 released from mineral sources and accidental spills. Mining operations may also result in changes to
- 486 ground water, which may be rerouted, affecting the water table (USGS 2001).
- 487
- As described above in Evaluation Question 2, the most common method of magnesium oxide production is
- the calcination of magnesium carbonate. As shown in Equation 3, the calcination of magnesium carbonate
- directly contributes to carbon dioxide formation, which is a known greenhouse gas (Baird and Cann 2008,
- 491 Nobre et al. 2020). The calcination process is energy intensive, and the energy consumption to facilitate this
- 492 process may also contribute to additional carbon dioxide emissions if the power comes from the
- 493 combustion of fossil fuels (Nobre et al. 2020). While magnesium oxide production from brine does not
- 494 directly contribute to carbon dioxide emissions, it requires larger amounts of energy than mineral
- 495 production methods and may contribute to carbon dioxide concentrations through energy consumption496 (de Sousa 2018, Nobre et al. 2020).
- 497

498Evaluation Question #7: Describe any known chemical interactions between the petitioned substance499and other substances used in organic crop or livestock production or handling. Describe any

- 500 environmental or human health effects from these chemical interactions (7 U.S.C. § 6518 (m) (1)).
- 501

As described in the "Properties of the Substance" section, magnesium oxide is insoluble in water but will react with water to form magnesium hydroxide (Equation 2). Magnesium hydroxide also has low water solubility, although its basic nature gives it higher solubility in acidic environments (Silberberg 2003). The basic nature of magnesium hydroxide will result in the neutralization of acidic compounds present in terrestrial or water systems within the agro-ecosystem. Reactions between magnesium hydroxide and acidic soils may result in increased soil pH.

508

509 <u>Evaluation Question #8:</u> Describe any effects of the petitioned substance on biological or chemical 510 interactions in the agro-ecosystem, including physiological effects on soil organisms (including the salt 511 index and solubility of the soil), crops, and livestock (7 U.S.C. § 6518 (m) (5)).

- 512
- At the time of publication, the author of this report found no studies on the environmental persistence ortoxicity of magnesium oxide, or its effects on soil organisms.
- 515
- 516 As described in the "Properties of the Substance" section and Evaluation Question 7, magnesium oxide
- 517 reacts with water to form the basic substance magnesium hydroxide. The basic nature of magnesium
- 518 hydroxide results in increased solubility in acidic environments, driven by the neutralization of acidic
- 519 compounds. The introduction of magnesium oxide may result in increased soil pH.
- 520
- 521 As described in the "Action of the Substance" section, magnesium oxide may interact with both clays and
- 522 humates. Magnesium oxide may alter the surface of clays through exfoliation processes, which may result
- 523 in changes to the surface chemistry and surface charge of clay particles in terrestrial and aquatic systems

- (Nguyen et al. 2009, Pereira et al. 2015). Magnesium oxide can adsorb humates through ligand exchange
 and van der Waals interactions (Zhang et al. 2020).
- 527 Additionally, magnesium oxide can influence interactions between clay particles and humates in terrestrial 528 and water systems, as discussed in the "Action of the Substance" section. The effect of magnesium oxide is
- dependent on the clay component, as well as the environmental conditions in terms of pH and ionic
- 530 strength (Bolto et al. 2001, del Mar Ramos-Tejada et al. 2003, Tombacz 2003, Feng et al. 2005, Nguyen et al.
- 531 2009, Zhang et al. 2012, Sabah and Ouki 2017). The presence of magnesium oxide may increase clay-
- humate aggregation by facilitating ligand exchange and metal bridging interactions (Bolto et al. 2001, Feng
- et al. 2005, Zhang et al. 2012). Magnesium oxide may also decrease aggregation by increasing electrostatic
- repulsions between negatively charged clay and humate surfaces through clay exfoliation increasing the
- pH (Bolto et al. 2001, del Mar Ramos-Tejada et al. 2003, Tombacz 2003, Feng et al. 2005, Nguyen et al. 2009,
 Zhang et al. 2012, Sabah and Ouki 2017).
- 537

538 <u>Evaluation Question #9:</u> Discuss and summarize findings on whether the use of the petitioned 539 substance may be harmful to the environment (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) 540 (i)).

541

542 At the time of publication, the author of this report found no studies on the environmental persistence or

- toxicity of magnesium oxide. As described in Evaluation Questions 4–8, the insoluble nature of magnesium
- oxide makes it unlikely to contaminate water systems, and its insolubility results in low bioavailability
- 545 within terrestrial environments. Moreover, when used as approved within organic agriculture, magnesium
- oxide is applied in limited quantities as a viscosity control additive, making environmental contaminationunlikely (NOSB 2013).
- 548

549Evaluation Question #10: Describe and summarize any reported effects upon human health from use of550the 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. § 6518551(m) (4)).

552

Magnesium oxide has been classified as GRAS by the FDA and is a common ingredient for medicinal applications as a laxative, antacid, and magnesium supplement (Flommnebaum et al. 2002, USDA 2007). The Food and Agriculture Organization of the United Nations (FAO) has classified magnesium oxide as a substance with "no toxicological grounds to limit use in accordance with good manufacturing practices" (FAO 1967). The International Programme on Chemical Public Safety (IPCS) has not provided a hazard classification for magnesium oxide (IPCS 2010).

559

Magnesium oxide has been reported to be a respiratory irritant if airborne particles (i.e., magnesium oxide fume) are inhaled (NIOSH 1994, NJ DOH 2003, IPCS 2010). Inhalation of magnesium oxide fume may result in mechanical irritation and flu-like symptoms, including headache, fever and chills, aches, and cough (NJ DOH 2003, IPCS 2010). Health effects of magnesium oxide are not known to be chronic in nature, rather, they have been reported to be short term, lasting hours to days (NIOSH 1994, NJ DOH 2003, IPCS 2010). To prevent respiratory irritation, respirators should be worn when exposed to magnesium oxide fume (NIOSH 1994, NJ DOH 2003, IPCS 2010).

567

568Evaluation Question #11: Describe all natural (non-synthetic) substances or products which may be569used in place of a petitioned substance (7 U.S.C. § 6517 (c) (1) (A) (ii)). Provide a list of allowed570substances that may be used in place of the petitioned substance (7 U.S.C. § 6518 (m) (6)).

571

572 As described in the "Source or Origin of the Substance" section, magnesium oxide is a naturally occurring 573 substance that can be found in mineral form. Non-synthetic mineral forms of magnesium oxide offer a 574 potential alternative to synthetic versions in the form of the mineral periclase. However, the mineral forms

- of magnesium oxide are likely to have greater concentration of other ions, which may make them less
- 676 effective in the approved application of viscosity control of clay–humate mixtures.
- 577

578 Calcium oxide in the form of ovstershell lime has been classified by the NOP as non-synthetic if it does not 579 undergo calcination (NOP 5034-1). Calcium oxide, like magnesium oxide, forms rock salt crystals and reacts with water to form hydroxides (Atkins et al. 2008). Calcium oxide and hydroxide are basic, with 580 581 calcium hydroxide classified as a strong base, which would result in increased pH (Silberberg 2003). 582 However, calcium oxide and calcium hydroxide are more water soluble than the analogous magnesium 583 compounds, which would result in increased ionic strength of the aqueous mixtures compared to 584 magnesium oxide (Silberberg 2003, Atkins et al. 2008). Increased ionic strength of the solution promotes 585 aggregation of clay and humate particles, as the increased charge in solution stabilizes the negative surface 586 charges and reduces electrostatic repulsions (Tombacz 2003, Feng et al. 2005, Nguyen et al. 2009, Zhang et 587 al. 2012, Sabah and Ouki 2017). Moreover, oystershell lime is likely to include other mineral salts, which may result in reduced efficacy compared to synthetic calcium oxide that has undergone purification 588 589 processes. 590 591 As described in the "Action of the Substance" section, aggregation of clay and humate particles can be 592 influenced by the pH and ionic strength of the mixture. Humate adsorption onto clay surfaces decreases 593 with increased pH and decreased ionic strength (Bolto et al. 2001, del Mar Ramos-Tejada et al. 2003, 594 Tombacz 2003, Feng et al. 2005, Zhang et al. 2012, Sabah and Ouki 2017). The addition of basic substances 595 increases the pH of the clay-humate mixture, maximizing negative surface charges to prevent aggregation. 596 Calcium carbonate (limestone) offers a potential alternative to magnesium hydroxide as a basic compound

- with limited solubility to avoid dramatic increases in ionic strength (Silberberg 2003, Hoy 2005, Atkins et al.
 2008, USDA 2018). Calcium hydroxide (listed as hydrated lime) is a synthetic substance that is approved
- for use in organic crop production in 7 CFR 205.601. However, as discussed above in the context of
- 600 oystershell lime, calcium hydroxide is a strong base that is soluble and would also result in increased ionic
- strength, which may reduce efficacy of viscosity control for clay-humate mixtures.
- 602

603Evaluation Question #12: Describe any alternative practices that would make the use of the petitioned604substance unnecessary (7 U.S.C. § 6518 (m) (6)).

605 Magnesium oxide is used as an additive to control mixture viscosity by preventing the aggregation of clay 606 607 and humate particles. However, literature reports also state that the stabilization of colloidal clay suspensions can be facilitated by the adsorption of humates to the surface of clay particles (del Mar Ramos-608 609 Tejada et al. 2003, Tombacz 2003, Petzold et al. 2004, Baird and Cann 2008, Nguyen et al. 2009, Zhang et al. 610 2012, Pereria et al. 2015, Sabah and Ouki 2017). When humates adsorb onto the surface of clays, their negative surface charge prevents aggregation with other clay particles. In addition to electrostatic 611 612 repulsions, humates provide steric repulsions due to their size, which further prevents aggregation (del 613 Mar Ramos-Tejada et al. 2003, Tombacz 2003, Baird and Cann 2008, Sabah and Ouki 2017). Given the ability of clay-humate aggregates to stabilize colloidal mixtures, the correct ratio of clay to humate particles 614 may alleviate the necessity for magnesium oxide or other additives to control the viscosity of the mixtures. 615 616

Report Authorship

The following individuals were involved in research, data collection, writing, editing, and/or final approval of this report:

- Philip Shivokevich, Visiting Assistant Professor of Chemistry, University of Massachusetts Amherst
- Catherine Canary, Technical Editor, Savan Group

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