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.

Calcium Chloride

Handling/Processing

Identification of Petitioned Substance

Chemical Names:
Calcium (II) chloride; Calcium chloride; Calcium dichloride

Other Names:
Antarcticite; $CaCl_2$; E509; Huppert's reagent; Hydrophilite; Liquical; Sinjarite

Trade Names:
Cal-Chlor; Calplus; Dow Flake; Jarcal; LiquiDow; PelaDow; Pickle Crisp; Superflake; Tetra Cor; TETRA Hi-Cal

CAS Numbers:
10043-52-4 (anhydrous); 22691-02-7 (monohydrate); 10035-04-8 (dihydrate); 25094-02-4 (tetrahydrate); 7774-34-7 (hexahydrate)

Other Codes:
E 509
UNII: OFM21057LP (anhydrous)
UNII: LEV48803S9 (monohydrate)
UNII: M4I0D6VV5M (dihydrate)
UNII: 1D898P42YW (hexahydrate)
CHEBI: 3312
EINECS: 233-140-8

Summary of Petitioned Use

This full scope technical report provides information to the National Organic Standards Board (NOSB) to support the sunset review of calcium chloride, listed at 7 CFR 205.605(a)(7). Authors wrote a Technical Advisory Panel (TAP) report about the substance in 1995 (NOSB, 1995), but no technical report has been written on calcium chloride since. This report focuses on calcium chloride, used in organic processing and handling as a nonagricultural (nonorganic) nonsynthetic ingredient.

Calcium chloride was initially reviewed by the NOSB in 1995 (NOSB, 1995). It was included on the National List of Allowed and Prohibited Substances (hereafter referred to as the "National List") with the first publication of the National Organic Program (NOP) Final Rule (65 FR 80548, December 21, 2000). The NOSB recommended its renewal in 2005, 2010, 2015, and 2019 (NOSB, 2005, 2010, 2015, 2019).

Synthetic and nonsynthetic forms of calcium chloride exist. The annotation for nonsynthetic forms of calcium chloride at § 205.605(a)(7) does not prescribe a specific use of the material. Synthetic forms of calcium chloride may also be used as a nutrient, under the listing at 205.605(b)(20), *Nutrient vitamins and minerals*, but not for other uses.

In support of the 2021 sunset review, public commenters stated that calcium chloride is used as a buffering agent in fruit preps, in cheese-making, in olive packing, in dairy analogs, as a disinfectant when used in conjunction with chlorine to mitigate effects on plant tissues, and as a tool to mitigate acrylamide in baking applications (NOSB, 2019).

Characterization of Petitioned Substance

Composition of the Substance:
Calcium chloride is an ionic halide salt composed of one calcium ion and two chloride ions (see *Figure 1*) (Ropp, 2013).

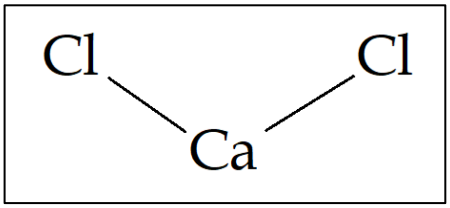

Figure 1: Chemical structure of calcium chloride

Anhydrous calcium chloride rapidly absorbs moisture from the air to form various hydrates, including mono-, di-, tetra-, and hexahydrate species containing 1, 2, 4, and 6 water molecules, respectively (Garrett, 2004). Temperature and the calcium chloride concentration principally govern the crystallization sequence of hydrates in a solution (Garrett, 2004). For example, at room temperature (approximately 20 °C):

- Calcium chloride is fully dissolved in solution up to approximately 44 weight percent (wt%).
- Calcium chloride hexahydrate crystals begin to form between 44-50 wt%, leaving some dissolved calcium and chloride ions in solution.
- A mixture of hexahydrate and tetrahydrate crystals form at up to about 57 wt%, with tetrahydrate and dihydrate forming at up to approximately 76 wt%.
- The dihydrate and monohydrate forms finally occur above 76 wt%, and anhydrous calcium chloride results after nearly complete dehydration.

Several different grades of calcium chloride are available with differing levels of impurities, depending on the manufacturer specifications and physical state (see *Table 1*) (Garrett, 2004). Typical impurities include sodium chloride, magnesium chloride, iron, sulfates, potassium chloride, and calcium bromide (Garrett, 2004; Occidental Chemical Corporation, 2021).

Table 1: Specifications for calcium chloride products from select manufacturers: forms, compositions, and impurities. Adapted from Garrett, 2004.

Manufacturer	Product	CaCl2 specifications	Impurities
Tetra Chemicals	$CaCl_2$ liquid	28-42%	<0.1% NaCl <0.1% $MgCl_2$ <1% others
Tetra Chemicals	$CaCl_2$ liquid, food grade	32-41%	<5% NaCl and $MgCl_2$ <0.3% $Ca(OH)_2$ <0.004% fluoride <0.002% heavy metals <0.0005% Pb
Dow Chemical Co.	$CaCl_2$ flake	77%	<0.2% NaCl 0.5% $MgCl_2$ <1% others
Hill Brothers Chemical Co.	$CaCl_2$ flake	77-80%	<4.3% NaCl <0.07% $MgCl_2$ <0.85% others <0.1% $Ca(OH)_2$ <0.04% $CaCO_3$ <0.04% SO_4 <0.005% Fe <0.002% heavy metals
Tetra Chemicals	$CaCl_2$ pellets	94-97%	<2% NaCl <0.1% $MgCl_2$ <1% others <20 ppm Fe <250 ppm SO_4 <2000 ppm $CaCO_3$
Tetra Chemicals	$CaCl_2$ food grade	94-97%	<1% NaCl <0.1% $MgCl_2$ <0.1% others <20 ppm Fe <250 ppm SO_4 <2000 ppm $CaCO_3$

Source or Origin of the Substance:

Calcium chloride is found in small amounts in seawater (about 0.15%) and mineral springs, and in higher concentrations in naturally occurring brines (Kemp & Keegan, 2003; Patnaik, 2003). Although two naturally occurring calcium chloride minerals occur, they are exceedingly rare. The minerals are sinjarite and antarcticite, and occur rarely, associated with dry lakes or brines as the dihydrate ($CaCl_2 \cdot 2H_2O$) and hexahydrate ($CaCl_2 \cdot 6H_2O$) varieties, respectively (Kemp & Keegan, 2003; Ropp, 2013). Calcium chloride also occurs with the minerals tachyhydrite ($MgCl_2 \cdot CaCl_2 \cdot 12H_2O$), chlorocalcite ($KCaCl_3$), and carnallite ($KMgCl_3 \cdot 6H_2O$) (Kemp & Keegan, 2003).

Almost all naturally occurring calcium chloride exists as subsurface brines, most often associated with potash or halite (NaCl) deposits (Garrett, 2004). Surface lakes with appreciable calcium chloride concentrations are extremely rare, but several lakes or springs occur with dilute calcium chloride concentration (Garrett, 2004).[1] Strongly concentrated calcium chloride brines only occur within porous rock strata above, below, or aside other evaporite salt deposits, typically becoming more dilute as they approach the surface due to infiltration of rainwater (meteoric water) (Garrett, 2004).

Calcium chloride brines form as part of the complex sequence of mineral crystallization and dissolution resulting from the evaporation of saltwater (Garrett, 2004). Calcium carbonate (calcite) crystallizes first, followed by calcium sulfate (gypsum) and sodium chloride salt. Potash crystallizes next as the mixed water-soluble salts of potassium chloride, potassium sulfate, magnesium chloride, and magnesium sulfate. Further evaporation or exposure to other brines generally results in the double-salt potash mineral carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$). Carnallite is easily leached by infusions of more dilute brine resulting in crystallized sylvite (potassium chloride) deposits and concentrated magnesium chloride brine. As the concentrated magnesium chloride brine seeps through the deposit, it reacts with the calcite minerals from the first precipitation event to yield dolomite limestone ($CaCO_3 \cdot MgCO_3$) and concentrated calcium chloride brine. This is known as the dolomitization reaction (Garrett, 2004).

Properties of the Substance:

Calcium chloride is a white, odorless, crystalline salt in solid form, but is often sold in liquid solution or as pressed flakes (see *Table 2*). Calcium chloride is highly soluble in water and readily absorbs moisture (Ropp, 2013).

Calcium chloride and solutions of calcium chloride absorb moisture from the air to form different hydrates, dependent on calcium chloride concentration, relative humidity of the surrounding air, vapor pressure of moisture in the air, surface area of the exposed material, and air circulation conditions (Patnaik, 2003). The solid material can absorb so much moisture from the air that it becomes a liquid solution simply by exposure to atmospheric humidity (Garrett, 2004). Highly water-soluble crystalline substances may become liquids when the ambient relative humidity surpasses a certain threshold value (Mauer & Taylor, 2010). Beyond this threshold, the aqueous phase is more thermodynamically stable (Mauer & Taylor, 2010). Calcium chloride expresses this property, *deliquescence*, at relatively low humidity levels compared to many other commonly used food ingredients (Garrett, 2004; Mauer & Taylor, 2010).

The dissolution of calcium chloride in water is a strongly exothermic process (releasing heat), and quickly produces temperatures of approximately 60 °C (140 °F) (Ropp, 2013). This exothermic property and calcium chloride's effect of depressing the freezing point of water are commonly exploited for deicing roadways (Ropp, 2013).

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[1] Two commercial sources of calcium chloride come from Bristol and Cadiz lakes. These "lakes" are dry lake beds with subsurface saltwater. They are more accurately known as alkali flats or playas.

Table 2: Chemical and physical properties of calcium chloride

Property	**Value**[a]
Physical state or appearance	Cubic crystals, powder, flakes, liquid solution
Color	White
Odor	Odorless
Taste	Salty, saline
Molecular weight (g/mol)	110.99
Density (g/cm^3 at 25 °C)	2.16
pH	7
pK$_a$	8-9
Solubility (g/100 mL at 20 °C)	74.5 (water);
Boiling Point (°C)	1935
Melting Point (°C)	773
Heat of fusion (cal/g)	61.5
Stability	Readily absorbs moisture from the air to form mono-, di-, tetra-, and hexahydrates
Reactivity	May emit hydrogen chloride upon heating and decomposition

[a]*Sources:* (National Center for Biotechnology Information, 2023; Ropp, 2013)

Specific Uses of the Substance:

Calcium chloride has a wide range of non-food uses including (Garrett, 2004; Kemp & Keegan, 2003):

- road deicing
- dust control
- chemical manufacturing
- metallurgy
- waste water treatment
- concrete additive
- oil and gas drilling
- tire ballast

Calcium chloride brine has a low freezing point and is an effective heat transfer media (Kemp & Keegan, 2003). For this reason, processors use calcium chloride brine as a refrigerant for the production of frozen desserts (Verma, 2011) and for immersion freezing of fish (Park et al., 2014). Calcium chloride also has a variety of uses as an ingredient and processing aid within foods (see *Table 3*). Some uses are complimentary to each other. In fruit and vegetable processing, calcium chloride is primarily considered a firming agent, but it also functions as an antimicrobial agent and texturizer (Irfan et al., 2013). In dairy and soy products, it can be both a coagulation aid and a nutrient supplement (Acosta et al., 2020; Chen et al., 2021).

Table 3: Specific uses of calcium chloride in processed foods

Use	**Type of Food Products**	**Reference(s)**
Antimicrobial agent	Cured meats, groundnuts, postharvest whole figs	(Garrett, 2004; Irfan et al., 2013; Raccach & Henningsen, 1997)
Curing or pickling agent	Cucumber pickles, fish, olives	(García-Serrano et al., 2020; Garrett, 2004; USDA-ARS, 2014)
Firming agent	Fish, mushrooms, processed whole and cut fruits and vegetables	(Garrett, 2004; Martín-Diana et al., 2007; Wuest et al., 1987)
Flavor enhancer	Beer, canned breadnut seeds, cucumber pickles, processed meat products	(Garrett, 2004; Horita et al., 2011; Howe, 2020; Pérez-Díaz et al., 2015)
Nutrient supplement	Dairy products, nutrition beverages, tofu	(Acosta et al., 2020; Barone et al., 2022; Palacios et al., 2021; Ropp, 2013)
pH control agent	Beer	(Krottenthaler & Glas, 2009)
Processing aid	Bakery products, beer, cheese, tofu	(Gresser, 2009; Harboe et al., 2010; Lei et al., 2023; Sarion et al., 2021)
Stabilizer and thickener	Fruit jams and jellies	(Ruiz, 1958; Suutarinen et al., 2002)
Synergist in combination with sodium alginate	Dressings, fruit snack foods, sauces, soups	(Hefft & Adeutnji, 2024; Maleki et al., 2020)
Texturizer	Beef, Chicken, Goose, Lamb, Rabbit	(Garrett, 2004; Gerelt et al., 2002; St. Angelo et al., 1991)

Anticaking agent

Calcium chloride is allowed as an anticaking agent, humectant, and surface-active agent (see *Approved Legal Uses of the Substance*). However, we found no evidence in the literature suggesting that these are applications currently in practice within the food industry.

Curing or pickling agent

Processors use calcium chloride in a variety of combinations and concentrations for pickling and curing brines. Consumer demand for pickled products with lower sodium chloride content continues to drive research to optimize calcium chloride brines specific to the end product (García-Serrano et al., 2020).

Coagulant

Processors add calcium chloride in a concentration range of 0.4-0.5% to coagulate soymilk in the process of making soft or pressed tofu (L. Zheng et al., 2020).

Calcium chloride serves as a coagulation aid in cheese production. Cheese producers add it prior to the coagulant. The addition of calcium chloride to milk for cheese-making reduces the amount of rennet required (Ernstrom et al., 1958). This can be advantageous to producers seeking to increase cheese yields, but also those working with fluctuations in milk composition associated with seasonal factors or late lactation (Guinee & O'Brien, 2010; Ong et al., 2017). The addition of calcium chloride at 0.2 g/L is common in commercial practice (Guinee & O'Callaghan, 2010). Calcium chloride also decreases the pH of milk for cheese-making and decreases the time required for curd formation (Harboe et al., 2010).

Firming agent

Processors commonly use calcium chloride as a firming agent for whole and cut fruits and vegetables. Calcium is an important component in the crosslinking of pectin in the plant cell wall (see *Action of the Substance* below for further information). The calcium-pectin crosslinking influences firmness of the crop and its pathogen resistance. Research also demonstrates that this material plays an important role in food preservation, but the biological mechanism that regulates this is still unclear (Gao et al., 2020). Dipping cut tomatoes in a calcium chloride solution is a common practice to obtain the firming effects. Barrett et al. (1998) demonstrated in the laboratory that ½ inch diced tomatoes dipped in a 0.5% calcium chloride solution resulted in a 50% increase in firmness compared to a raw tomato control. They found no benefit to increasing the solution concentration to 1%. Generally, the concentration of calcium chloride can range between 0.5-3% for wash treatments for postharvest whole and minimally processed crops (Martín-Diana et al., 2007). The excess washing solution is removed.

Flavor enhancer

Calcium chloride is an increasingly important flavor enhancer as the demand for low salt and reduced fat options persists. Flavor difference between cucumber pickles prepared with NaCl and calcium chloride is negligible (Pérez-Díaz et al., 2015; USDA-ARS, 2014). Scientists also found that calcium chloride contributed the most favorable flavor in reduced fat mortadella when compared to other salt substitutes (Horita et al., 2011).

Nutritional supplement

Calcium chloride is a common nutrient supplement. Calcium fortification of foods is common worldwide (Palacios et al., 2021). Wheat flour fortified with calcium salts is commonly used in bakery products (Sarion et al., 2021). Calcium chloride is one of the common sources of calcium fortification in tofu in the U.S. (Palacios et al., 2021). In dairy products, calcium fortification often involves blends of calcium forms (Acosta et al., 2020; Barone et al., 2022). Processors develop these blends specific to individual food products based on several factors, including the nutritional aim and the impact on the physical interactions with the milk proteins (Barone et al., 2022).

pH control agent and brewing water additive

Brewers use calcium chloride as a source of calcium and chloride for beer production (Krottenthaler & Glas, 2009). Calcium reduces mash pH via phosphate precipitation and is essential to yeast activity

(Kordialik-Bogacka et al., 2019). Chloride is an important component in beer flavor profiles and may require supplementation depending on content available in the malted barley (Howe, 2020; Ropp, 2013). Calcium chloride added to the brewing liquor can also facilitate the precipitation of calcium oxalate that can cause overflow and unwanted foaming in bottled beer (Gresser, 2009).

Processing aid in baking

Calcium chloride is effective at reducing acrylamide contamination in bakery products (Sarion et al., 2021. Acrylamide is a by-product found in heat-processed carbohydrate rich foods. Calcium chloride can also strengthen wheat dough (Sarion et al., 2021).

Stabilizer and thickener

Calcium chloride can stabilize the medium of fruit jams and jellies (Ruiz, 1958; Suutarinen et al., 2002). The inclusion of calcium chloride in these products reduces the pectin, acid, and sugar necessary for adequate gelling (Halliday & Bailey, 1924; Ruiz, 1958).

Processors use calcium chloride as a synergist in combination with sodium alginate to produce calcium alginate (Hefft & Adeutnji, 2024). Calcium alginate is a thickening agent and stabilizer for emulsions found in dressings, sauces, and soups (see *Combinations of the Substance* for further information).

Tenderizer/texturizer

Calcium chloride is an effective tenderizing agent (Gerelt et al., 2002). Marinating, injection, and infusion are all methods by which calcium chloride can improve texture and increase tenderness of meat. The effective concentration of calcium chloride varies by application method.

Approved Legal Uses of the Substance:

When producers use calcium chloride as a food additive or ingredient, it falls under the jurisdiction of the U.S. Food and Drug Administration (FDA) regulations, as well as the United States Department of Agriculture (USDA). Also falling under FDA oversight, food processors may use calcium chloride in a sanitizing solution formulation for food contact articles. As an ingredient in post-harvest pest control products, calcium chloride could fall under EPA jurisdiction.

FDA

In 2016, the FDA published an updated Final Rule on GRAS substances, which amended the rule so that the GRAS notification program was voluntary (81 FR 54960-55055). Therefore, identifying whether a substance is or is not considered GRAS by some experts (such as within food manufacturing businesses) may not always be possible for all (or any) uses. The following information is based on what is published by the FDA.

The FDA considers calcium chloride to be Generally Recognized as Safe (GRAS) when used as a direct food substance for human consumption (21 CFR 184.1193). Two additional GRAS notices have been published, for which the FDA had no questions:

- GRN No. 634; for use in the manufacturing of potato snacks to reduce the formation of acrylamide at use levels of 1 percent or less.
- GRN No. 785; for use as an anti-browning agent in processed fruits and vegetables.

The FDA specifications for calcium chloride in § 184.1193 are very detailed, and are broken down into four main sections:

- chemical identity [§ 184.1193(a)]
- specifications [§ 184.1193(b)]
- types of use [§ 184.1193(c)]
- use in specific foods [§§ 184.1193(d), 172.560(b)(5)]

Additionally, the FDA also includes calcium chloride in the formulation of an iodine sanitizing solution, allowed on food processing equipment, utensils, and other food contact articles [§ 178.1010(b)(40)]. This formulation contains several other ingredients.

Identity under FDA

The FDA identifies calcium chloride as [§ 184.1193(a)]:

- calcium chloride ($CaCl_2 \cdot 2H_2O$, CAS Reg. No. 10035–04–8)
- anhydrous calcium chloride ($CaCl_2$, CAS Reg. No. 10043–52–4)

The FDA states that calcium chloride "may be commercially obtained as a byproduct in the ammonia-soda (Solvay) process and as a joint product from natural salt brines, or it may be prepared by substitution reactions with other calcium and chloride salts" [§ 184.1193(a)].

Specifications under FDA

It must also meet the specifications of the third edition of the Food Chemicals Codex [§ 184.1193(b)], which we have included below (National Research Council, 1981b).

Description

White, hard, odorless fragments or granules. It is deliquescent. One g dissolves in 1.2 ml of water at 25°, in 0.7 ml of boiling water, in 10 ml of alcohol at 25°, and in 2 ml of boiling alcohol. The pH of a 1 in 20 solution is between 4. 5 and 8.5.

Identification

A 1 in 10 solution gives positive tests for Calcium, page 516, and for Chloride, page 516.
Assay: Not less than 99.0% and not more than the equivalent of 107.0% of $CaC1_2.2H_20$.
Arsenic: (as As) Not more than 3 ppm.
Fluoride: Not more than 0.004%.
Heavy Metals (as Pb): Not more than 0.002%.
Lead: Not more than 10 ppm.
Magnesium and Alkali Salts: Not more than 4%.

Types of uses, under FDA

The FDA notes a wide variety of specific uses for calcium chloride [§ 184.1193(c); see Table 4, below].

Table 4: Uses and applicable FDA regulations for calcium chloride, as referenced by 21 CFR 184.1193(c).

Use	21 CFR reference	FDA definition at included reference
Anticaking agent	§ 170.3(o)(1)	Substances added to finely powdered or crystalline food products to prevent caking, lumping, or agglomeration.
Antimicrobial agent	§ 170.3(o)(2)	Substances used to preserve food by preventing growth of microorganisms and subsequent spoilage, including fungistats, mold and rope inhibitors, and the effects listed by the National Academy of Sciences/National Research Council under "preservatives."
Curing or pickling agent	§ 170.3(o)(5)	Substances imparting a unique flavor and/or color to a food, usually producing an increase in shelf-life stability.
Firming agent	§ 170.3(o)(10)	Substances added to precipitate residual pectin, thus strengthening the supporting tissue and preventing its collapse during processing.
Flavor enhancer	§ 170.3(o)(11)	Substances added to supplement, enhance, or modify the original taste and/or aroma of a food, without imparting a characteristic taste or aroma of its own.
Humectant	§ 170.3(o)(16)	Hygroscopic substances incorporated in food to promote retention of moisture, including moisture-retention agents and antidusting agents.
Nutrient supplement	§ 170.3(o)(20)	Substances which are necessary for the body's nutritional and metabolic processes.
pH control agent	§ 170.3(o)(23)	Substances added to change or maintain active acidity or basicity, including buffers, acids, alkalis, and neutralizing agents.
Processing aid	§ 170.3(o)(24)	Substances used as manufacturing aids to enhance the appeal or utility of a food or food component, including clarifying agents, clouding agents, catalysts, flocculants, filter aids, and crystallization inhibitors, etc.

Use	21 CFR reference	FDA definition at included reference
Stabilizer and thickener	§ 170.3(o)(28)	Substances used to produce viscous solutions or dispersions, to impart body, improve consistency, or stabilize emulsions, including suspending and bodying agents, setting agents, jellying agents, and bulking agents, etc.
Surface active agent	§ 170.3(o)(29)	Substances used to modify surface properties of liquid food components for a variety of effects, other than emulsifiers, but including solubilizing agents, dispersants, detergents, wetting agents, rehydration enhancers, whipping agents, foaming agents, and defoaming agents, etc.
Synergist	§ 170.3(o)(31)	Substances used to act or react with another food ingredient to produce a total effect different or greater than the sum of the effects produced by the individual ingredients.
Texturizer	§ 170.3(o)(32)	Substances which affect the appearance or feel of the food.

Use in specific foods, under FDA

The FDA describes numerous foods in which calcium chloride may be used [§ 184.1193(d); see *Table 5*, below]. It can be used in foods at levels not to exceed current good manufacturing practices [GMP; § 184.1(b)(1)].

Table 5: Limits on the use of calcium chloride in food products, as referenced by 21 CFR 184.1193(d).

Food product	21 CFR reference describing food	Maximum amount allowed, in accordance with GMP (as % of food)
Baked goods	§ 170.3(n)(1)	0.3
Nonalcoholic beverages and beverage bases	§ 170.3(n)(3)	0.22
Cheese	§ 170.3(n)(5)	0.2
Coffee and tea	§ 170.3(n)(7)	0.32
Condiments and relishes	§ 170.3(n)(8)	0.4
Dairy product analogs	§ 170.3(n)(10)	0.3
Gravies and sauces	§ 170.3(n)(24)	0.2
Jams and jellies	§ 170.3(n)(28)	0.1
Meat products	§ 170.3(n)(29)	0.25
Plant protein products	§ 170.3(n)(33)	2.0
Processed vegetables and vegetable juices	§ 170.3(n)(36)	0.4
All other food categories		0.05

In dairy products, under the USDA

The USDA has oversight of calcium chloride when it is used in dairy plants approved for their inspection and grading service (7 CFR part 58). Under the USDA, calcium chloride (used in cheese making) must meet the requirements of the Food Chemicals Codex (7 CFR 58.434). They do not state which edition of the FCC should be used. The current edition (12th ed.) of the FCC is only available through subscription. Specifications described by the third edition (required by the FDA) are shown in the section *Specifications under FDA* (above).

The USDA regulations require that, when used as an ingredient in the manufacturing of cottage cheese, calcium chloride shall be of food-grade quality and free from extraneous material [§ 58.520(a)].

In meat products, under the USDA

The USDA's Animal and Plant Health Inspection Service (APHIS) includes calcium chloride as a substance allowed to treat meat products (see *Table 6*, below). It is allowed for use as a tenderizing agent and film-forming agent (9 CFR 424.21).

Table 6: USDA -APHIS allowed uses for calcium chloride, taken from 9 CFR 424.21.

Class of substance	Substance	Purpose	Products	Amount
Film forming agents	A mixture consisting of water, sodium alginate, calcium chloride, sodium carboxymethyl-cellulose, and corn syrup solids	To reduce cooler shrinkage and help protect surface	Freshly dressed meat carcasses. Such carcasses must bear a statement "Protected with a film of water, corn syrup solids, sodium alginate, calcium chloride and sodium carboxymethyl-cellulose."	Formulation may not exceed 1.5 percent of hot carcass weight when applied. Chilled weight may not exceed hot weight.
Tenderizing agents	Calcium chloride	To soften tissue	Raw poultry muscle tissue of hen, cock, mature turkey, mature duck, mature goose, and mature guinea, and raw meat cuts	Solutions consisting of water and approved proteolytic enzyme applied or injected into raw meat or poultry tissue shall not result in a gain of more than 3 percent above the weight of the untreated product.
Tenderizing agents	Potassium, magnesium, or calcium chloride	To soften tissue	Raw poultry muscle tissue of hen, cock, mature turkey, mature duck, mature goose, and mature guinea, and raw meat cuts	A solution of approved inorganic chlorides injected into or applied to raw meats or poultry cuts shall not result in a gain of more than 3 percent above the weight of the untreated product.

As an ingredient in post-harvest pesticides, under EPA

Pesticides used on food and food contact surfaces (as can occur during post-harvest handling) can result in residues on or in food (U.S. EPA, 2014). All pesticide ingredients (active and inert) in such products must have a tolerance or tolerance exemption under the Federal Food, Drug, and Cosmetics Act. Tolerances are maximum levels of pesticide residues allowed in foods (U.S. EPA, 2014).

While potassium chloride and sodium chloride are exempt from a tolerance as active ingredients, calcium chloride is not [40 CFR 152.25(f)(1)]. The EPA does not explicitly mention calcium chloride as having an exemption as an inert ingredient either [§ 152.25(f)(2)]. However, it may still qualify as a "commonly consumed food commodity," as described at § 180.950(a), which are ingredients that are also exempt from the requirement of a tolerance. The EPA does not list calcium chloride within Part 180, where ingredients with specific tolerances are described.

Calcium chloride is included on the now defunct 2004 EPA List 4B (U.S. EPA, 2004).

Action of the Substance:

The action of calcium chloride in food processing is often a function of the dissolved calcium ion (Ca^{2+}) rather than the chloride component. The use of calcium chloride as an antimicrobial agent, pickling agent, and firming agent relies on the interaction of the calcium ion with the cells of the fruit/vegetable or the cells of the pathogen (Alahakoon et al., 2014; Conway et al., 1994; Irfan et al., 2013; Ngamchuachit et al., 2014; Serrano et al., 2004; Shoukry & Said, 2019). Calcium ions also activate enzymes in meat, leading to tenderization, and encourage the coagulation of proteins in cheese and tofu production (Alahakoon et al., 2014; deMan et al., 1986; Gerelt et al., 2002; Wolfschoon-Pombo, 1997). As a flavor enhancer, it imparts a salty taste without the addition of sodium salt (Verma, 2011). As a nutrient supplement, both calcium and chloride ions help regulate various cellular processes (Bailone et al., 2022).

Antimicrobial agent

A combination of calcium salt treatment and heating helps to prevent post-harvest bacterial or fungal decay of some fruits, including apples, strawberries, and figs (Irfan et al., 2013; Serrano et al., 2004). This resistance to decay is related to increased firmness of the fruit; the strengthening of the cell wall makes the fruit less accessible to softening enzymes secreted by pathogens (Conway et al., 1994; Irfan et al., 2013; Serrano et al., 2004). However, calcium absorption in other fruits including tangerines, grapes, and papaya may cause surface damage such as discoloration (Serrano et al., 2004).

Calcium chloride reduces pathogen contamination in meat products, particularly in treatments combined with organic acids (Alahakoon et al., 2014; Eilers et al., 1994; Shoukry & Said, 2019). The antibacterial action of calcium chloride (and other salt preservatives) in meat is a result of the alteration of osmoregulation (the balance of water and dissolved salts) in bacterial cells, leading to an increase in the energy required to maintain metabolism (Alahakoon et al., 2014; Shoukry & Said, 2019). Antibacterial action also results from a pH reduction effect, which is more pronounced when using mixtures with acid (Yoon et al., 2013).

Coagulant

In cheese production, the addition of calcium chloride serves to increase overall calcium levels in milk, leading to an increase in calcium bound to casein (Wolfschoon-Pombo, 1997). Casein micelles carry a negative surface charge that prevents coagulation into curds by repulsive forces. Calcium neutralizes this negative surface charge by electrostatically attracting phosphate groups in casein, or by directly bonding to the carboxyl groups of amino acid residues in casein. This promotes the coagulation and firmness of the gel. Calcium also reduces the pH, resulting in an increased rate of aggregation (the coagulation of curds) and overall yield of cheese. Cheese processors generally use calcium chloride in combination with other coagulants like rennet rather than alone (Wolfschoon-Pombo, 1997).

The action of coagulants in tofu production is similar to that in cheese-making (deMan et al., 1986). Calcium or magnesium promotes crosslinking of proteins in soymilk, bonding to carboxyl groups, phytic acid, or imidazole groups.

Curing or pickling agent

Brine pickling involves the submersion of fruits or vegetables in a salt solution. These commodities contain pectin in their cell walls. The brining process increases the rate at which the pectin dissolves through demethylation (Howard & Buescher, 1990). To slow the dissolution of pectin, manufacturers add calcium chloride. Calcium binds to pectin in the cell wall and increases pectin's resistance to solubilization, leading to crispier pickles, a desirable texture in the commercial market (Buescher et al., 2011; Howard & Buescher, 1990). Alum (potassium aluminum sulfate) is commonly used in pickling to reduce softening by the same mode of action, but consumer preferences are shifting away from this material (Buescher et al., 2011). Distributors and consumers view calcium chloride as a superior alternative (Buescher et al., 2011).

Firming agent

Calcium chloride and other calcium salts reinforce fruit cell wall integrity by promoting the crosslinking of pectin through the formation of calcium pectate, resulting in firmer fruit (Irfan et al., 2013; Serrano et al., 2004). Calcium ions diffuse easily into cell walls where they are attracted to negatively charged carboxyl groups in pectin, leading to an initial firming effect (Ngamchuachit et al., 2014; Quintanilla et al., 2018). Further firming subsequently occurs during storage, as calcium is attracted to the negatively charged phospholipid head groups in plasma membranes and proteins (Ngamchuachit et al., 2014). Calcium ions strengthen the cell wall while also stabilizing the plasma membrane (Ngamchuachit et al., 2014).

Flavor enhancer

Calcium chloride is sometimes used as a sodium chloride replacement flavoring to impart saltiness in reduced sodium foods, but tends to produce undesirable metallic or bitter flavors (Barros et al., 2019).

Chloride salts can provide sweetness, fullness, and increased maltiness in beer (Montanari et al., 2009).

Nutrient supplement

As the consumption of dairy products declines, larger percentages of people consume less than the recommended daily value of calcium (Eledah, 2005). Calcium is an essential nutrient for bone and teeth mineralization and deficiencies can lead to osteoporosis, increased fracture rate, and bone loss (Eledah, 2005). Calcium is the most abundant metallic element in the human body and acts as an intracellular messenger in several cellular processes (Bailone et al., 2022; Bauer, 2013). Chloride maintains osmotic and acid-base balance in cells (Bailone et al., 2022). Most calcium supplement products are calcium carbonate, calcium citrate, calcium lactate, or calcium gluconate, however (Bauer, 2013).

pH control agent and brewing water additive

In beer brewing, calcium in the brewing water (Eumann & Schildbach, 2012; Montanari et al., 2009):

- contributes to reduced pH in the mash[2]
- acts as an alpha-amylase enzyme cofactor (a supporter in a biochemical reaction) in the conversion of starch to fermentable sugar
- promotes the precipitation of undesirable proteins
- precipitates dissolved oxalates (as calcium oxalate) which can lead to explosive "gushing" of beer if left dissolved following sealing and storage

In beer, dissolved calcium reacts with alkaline dipotassium hydrogen phosphate, yielding insoluble calcium phosphate and acidic potassium dihydrogen phosphate (Montanari et al., 2009). This reduces the pH to levels optimal for amylase enzymes to convert starch to fermentable sugar.

Tenderizer/texturizer

The fibers (myofibrils) in muscle begin to enzymatically fragment post-mortem (Gerelt et al., 2002). Calcium activates the enzymes that break down muscle fibers, tenderizing the meat (Alahakoon et al., 2014; Gerelt et al., 2002). This effect is heightened when processors mix calcium with organic acid treatments (Eilers et al., 1994). Marination, infusion, or injection of alkaline salt solutions also increases the water-holding capacity of meats, affecting the texture (Alahakoon et al., 2014; Gerelt et al., 2002).

Combinations of the Substance:

The Food Chemicals Codex recognizes the anhydrous and dihydrate forms of calcium chloride (National Research Council, 1981a). There is also a calcium chloride solution that contains 35-45% calcium chloride diluted in water. Calcium chloride derived from natural brines contains impurities (see *Composition of the Substance*).

Tomato processors use tablets containing either calcium chloride or a combination of calcium chloride and sodium chloride (Barrett et al., 1998). It is common practice to add these tablets to the tomato juice fraction of individual cans or to a calcium chloride dip for the solid tomato fraction prior to canning, for products packed into bulk drums.

Processors use calcium chloride in combination with sodium alginate to produce calcium alginate. Calcium alginate is a thickening agent and stabilizer for emulsions. Some of the foods that use calcium alginate for this purpose include sauces, dressings, and soups (Hefft & Adeutnji, 2024). Calcium alginate is also used in spherification, a technique for producing food spheres within a thin gelled membrane or gelled throughout. Processors use this method to make pimento stuffed olives (Lee & Rogers, 2012). Maleki et al. (2020) also demonstrated lab production of a spherical snack food containing barberry syrup using this combination of materials.

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[2] Mash is the term used to describe malted grain suspended in hot water, thereby activating the enzymes which convert starches to fermentable sugars.

Status

Historic Use:

Calcium chloride appears in the historic record as early as the 15th century but was not commercially available until after the mid-19th century. Initially, it was simply a waste product of the Solvay ammonia soda-ash process (Kemp & Keegan, 2003). Around 1860, Isaac Solomon began adding calcium chloride to canning water to increase the boiling temperature of the water and reduce the time required for canning (Tucker & Featherstone, 2021). By 1913, food scientists were investigating the effects of adding calcium chloride to milk for cheese production (Price, 1927). By 1919, calcium chloride had several industrial applications including as a refrigerant for food preservation (Stone, 1919).

A bulletin by the United States Geological Survey (USGS) published in 1919 mentions calcium chloride as a drying aid for vegetables, fruits, and organic liquids (Stone, 1919). In 1940, researchers at the New York State Agricultural Experiment Station started publishing research on the effects of calcium salt addition on the firmness of canned, peeled whole tomatoes (Barrett et al., 1998). These experiments formed the foundation for the current calcification practices used for processed tomatoes.

In 1952, the Boston Laboratory of the U.S. Fish and Wildlife Service published a technical note outlining a method of immersion-freezing of cod, haddock, and ocean perch at sea using a solution of calcium chloride and glucose (Holston, 1952).

Organic Foods Production Act, USDA Final Rule:

OFPA does not include any reference to calcium chloride (Organic Foods Production Act of 1990, 1990).

For processing and handling purposes, USDA organic regulations include nonsynthetic calcium chloride on the National List without annotation [7 CFR 205.605(a)(7)]. It was included in the first iteration of the Final Rule, published on December 21, 2000 (65 FR 80548). Synthetic forms of calcium chloride may also be used as a nutrient [§ 205.605(b)(20)], but not for other uses.

USDA organic regulations also include a restriction on the use of calcium chloride in crop production [7 CFR 205.602(c)]. Under these regulations, calcium chloride is prohibited for use, "except as a foliar spray to treat a physiological disorder associated with calcium uptake." However, calcium chloride is also present on the 2004 EPA List 4, and therefore allowed for use (under USDA organic regulations) as an inert ingredient in pesticides [7 CFR 205.601(m)(1)], despite the limitation noted at § 205.602(c).

International:

Calcium chloride is allowed under several other international organic standards (see *Table 7*, below). All of these standards allow calcium chloride as a handling ingredient. While not included in the table below (*Table 7*), all of these standards also allow calcium chloride to be used as a crop amendment and or plant fertilizer.

Table 7: Allowance of calcium chloride in processing and handling applications under a selection of international organic standards

Standard	Applicable regulations	Allowed?	Source and use restrictions (if applicable)
Canada Organic Standards (CAN/CGSB 32.311-2020)	PSL Table 6.3, Ingredients classified as food additives.	Yes	Permitted for: a) milk products; b) fat products; c) soybean products; and d) fruits and vegetables.

Standard	Applicable regulations	Allowed?	Source and use restrictions (if applicable)
European Union Organic Standards (EU No. 2021/1165)	Annex V, Part A: Authorised food additives and processing aids referred to in point (a) of Article 24(2) of Regulation (EU) 2018/848: Section A1 – Food additives, including Carriers. Section A2 – Processing aids and other products, which may be used for processing of ingredients of agricultural origin from organic production.	Yes	E 509. Permitted as a coagulation agent for milk-based products, products of plant origin, and meat-based sausages.
Japanese Agricultural Standard for Organic Processed Foods	Appended Table 1-1 Additives (Organic processed foods other than organic alcohol beverages). Appended Table 1-2 Additives (Organic alcohol beverages).	Yes	INS 509. Limited to the use as a coagulant in processed products of plant origin and as a coagulant in cheesemaking, or the use in edible oils or fats, processed vegetable products, processed fruit products, products containing legumes, dairy products, or processed meat products. Also allowed as an additive in organic alcohol beverages.
Codex Alimentarius Commission—Guidelines for the Production, Processing, Labelling and Marketing of Organically Produced Foods (GL 32-1999)	Annex 2, Table 3: Ingredients of non-agricultural origin referred to in Section 3 of these guidelines. Annex 2, Table 4: Processing aids which may be used for the preparation of products of agricultural origin referred to in Section 3 of these guidelines.	Yes	INS 509. Allowed for use as an ingredient in a variety of food of plant or animal origins (see below). Also allowed for use as a coagulation agent for plant products. Additionally, it may be used as a firming or coagulation agent in cheese making. 04.0 Fruits and vegetables (including mushrooms and fungi, roots and tubers, pulses and legumes, and aloe vera), seaweeds, and nuts and seeds.[3] 06.8 Soybean products (excluding soybean products of food category 12.9 and fermented soybean products of food category 12.10). 12.9.1 Soybean protein products. 12.10 Fermented soybean products. 01.0 Dairy products and analogues, excluding products of food category 02.0. 08.2 Processed meat, poultry, and game products in whole pieces or cuts. 08.3 Processed comminuted meat, poultry, and game products. 08.4 Edible casings (e.g., sausage casings).
IFOAM-Organics International	Appendix 4 – Table 1: List of approved additives and processing / post-harvest handling aids. Appendix 4 – Table 2: Indicative list of equipment cleansers and equipment disinfectants.	Yes	INS 509. Allowed for use as an additive, processing aid, and post-harvest handling aid. Also allowed for use as an equipment cleanser/disinfectant.

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[3] These numbers reflect the food category system used by the Codex Alimentarius, and are found within CODEX STAN 192-1995.

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)].

According to several sources (Kemp & Keegan, 2003; Lewis & Harrison, LLC, 2018; Patnaik, 2003), calcium chloride is produced from three different sources/processes:

- from natural brines
- reaction of calcium hydroxide with ammonium chloride (Solvay ammonia-soda process)
- reaction of hydrochloric acid with calcium carbonate

TETRA Technologies, Inc. (2023) claims a fourth method:

- as a byproduct of the manufacturing of magnesium oxide

However, we were unable to find details on this manufacturing process method, and it was not mentioned elsewhere.

As of 2003, manufacturers relied on natural brines and the Solvay process for over 90% of the calcium chloride produced (Kemp & Keegan, 2003).

From natural brines:

Much of the information in this section relies on the *Handbook of Lithium and Natural Calcium Chloride* (Garrett, 2004). This resource provides a deep and broad summary of literature on calcium chloride brine production, and is based on hundreds of sources, including patents, academic papers, and government reports.

As discussed above in *Source or Origin of the Substance*, natural calcium chloride brines form when bodies of water containing minerals evaporate and subsequently react with calcium containing minerals, such as calcium carbonate (Garrett, 2004). In places where magnesium chloride brines are formed adjacent to calcite (such as limestone rock formations), it reacts to form calcium chloride and dolomite ($CaCO_3 \cdot MgCO_3$). These natural brine deposits often occur near natural potash or halite (NaCl) geologic deposits, and often contain other dissolved minerals/elements as well, including sodium or magnesium salts, bromine, and iodine. While this is one of the primary geologic mechanisms that forms calcium chloride brines, there are others. For example, calcium chloride brines can also occur in petroleum deposits, deep sea vents, inland geothermal springs, and in lakes. In some cases, the mechanisms that form a specific brine source is not clear (Garrett, 2004).

There have been (and still are) many variations on brine processing. As manufacturers switch to different brine sources, they also shift brine processing steps. Instead of purely innovation-driven changes, many changes in brine processing have to do with the unique chemical makeup of each brine source. It is reasonable to expect that some processing steps that are retired when one brine source is exhausted may reappear again later on, after brine sources with those specific minerals are discovered. We include a description of several different processes that have been used over time and in different locations, below.

Marshall formation brine (Michigan):

Manufacturers such as Dow have changed their processing steps to extract calcium chloride from different brine sources in Michigan over the years (Garrett, 2004). For example, beginning in 1914, Dow's first operation used a shallow and dilute brine pool that was part of the Marshall formation in Michigan. When processing this brine (Garrett, 2004):

1) Dow first converted bromide to bromine using electrolysis, and then blew it out of the brine using air. They then collected the bromine for the manufacture of other chemicals.

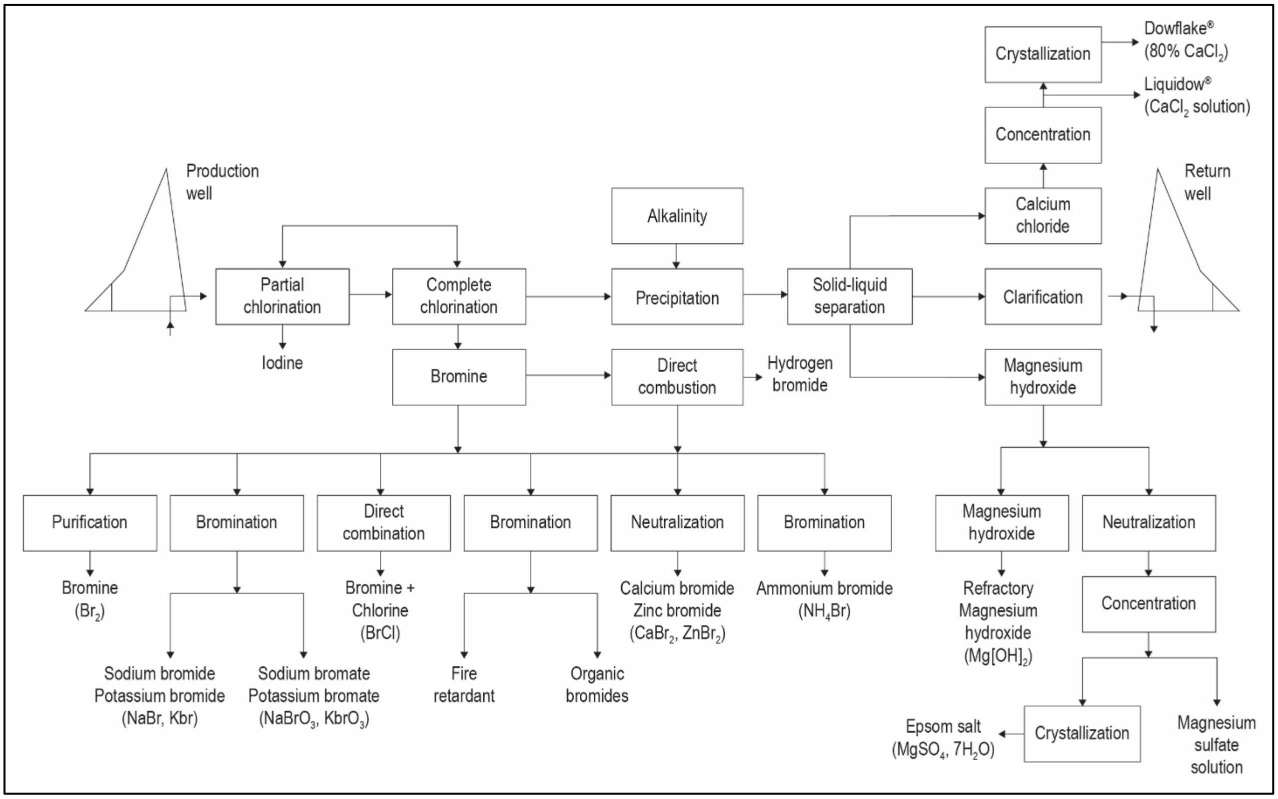
2) Then, they evaporated the remaining brine, where sodium chloride crystallized. They separated sodium chloride and then converted it into chlorine, caustic soda, and hydrogen- again, using electrolytic cells.
3) Next, they evaporated the brine again, crystallizing magnesium chloride. They separated the magnesium chloride, and then converted it into magnesium oxychloride.
4) They then reacted the brine with slaked lime ($Ca[OH]_2$), which precipitated the rest of the magnesium as magnesium hydroxide. This also likely added calcium to the brine in the process.
5) Finally, they evaporated the remaining brine again, producing a 38% calcium chloride solution.

Sylvania formation brine (Michigan):

Later on, Dow began using brine from deep within the Sylvania formation, also in Michigan (Garrett, 2004). This deposit also contained iodine (Garrett, 2004).

1) To process it, they acidified the brine and treated it with a small amount of chlorine to free elemental iodine (see *Figure 2*, below).
2) They then blew the iodine out of the brine using air, much like the process for bromine. This was performed in specialized towers.
3) They heated the brine and passed it through another tower. Within the tower, they blew steam and more chlorine through the brine, which converted bromide to bromine. This was carried away in the steam. After they isolated the bromine, it was treated with sulfuric acid (to dry it), and redistilled.
4) Magnesium chloride and calcium chloride were then recovered, ostensibly in a manner similar to their previous operation.

Figure 2: Flow chart showing the products of Sylvania Formation brine, produced by Dow Chemical Co. Adapted from Garrett, 2004.

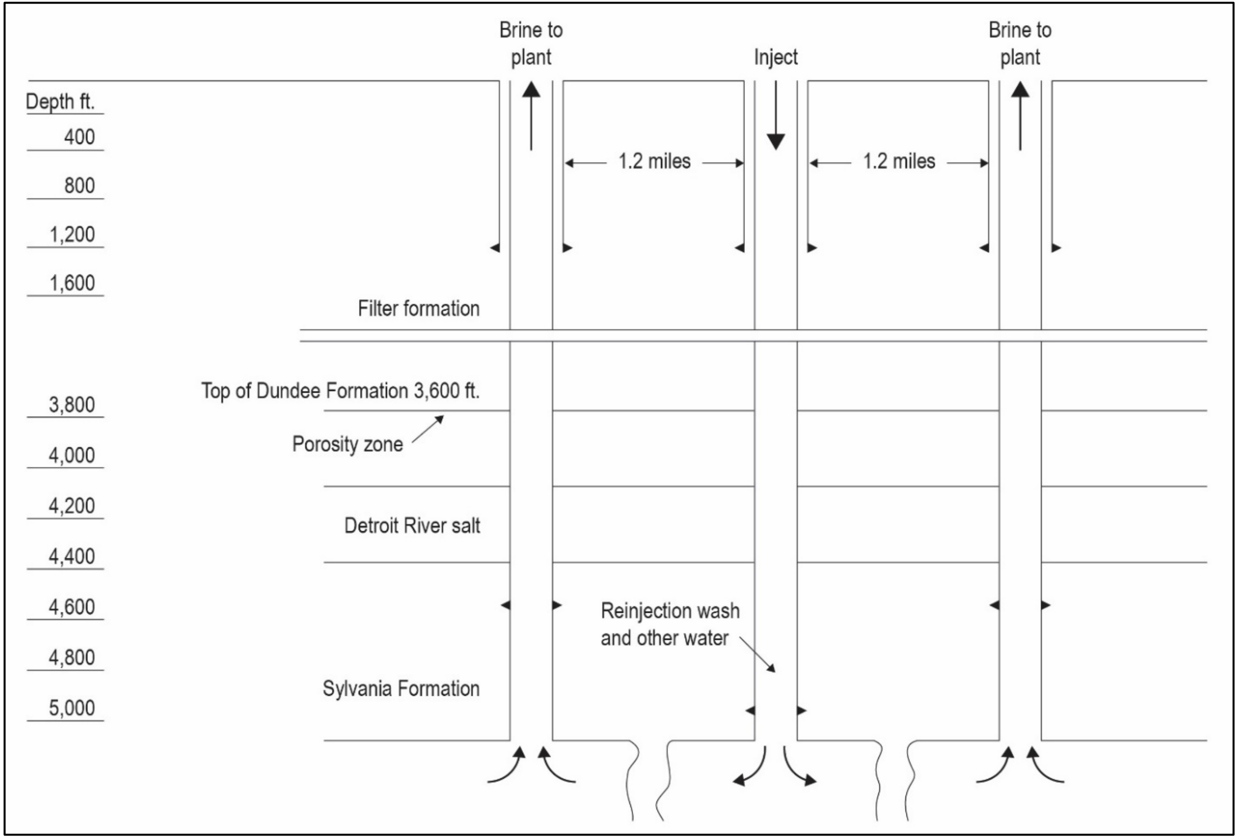


Filer formation brine (Michigan):

As of 2002, Dow was collecting brine from the Filer formation, again, located in Michigan (Garrett, 2004).[4] This brine contained around 17% calcium chloride, along with magnesium chloride, sodium chloride, potassium chloride, and bromine, but not iodine. To recover it, Dow used 17 wells. In order to maintain a large flow rate, they re-injected other water and salts at the periphery of the formation (see Figure 3, below) (Garrett, 2004).

1) They removed bromine from the brine by releasing it with steam, similar to the processing used with the Sylvania formation (see Figure 4, below).
2) Next, they added slaked dolime ($CaMg[OH]_2$), which caused magnesium hydroxide to precipitate.
3) They sent the remaining brine to evaporators, where it was concentrated to 32-45% calcium chloride (from 24-25%).
4) During this evaporation process, some salt crystallized, which was then removed by centrifuges. They then dissolved this salt in water and injected it on the periphery of the Filer formation.
5) Some of the liquid calcium chloride was sold at 32-45% concentration (also containing about 2.5% sodium chloride/potassium chloride and 1% other salts).
6) They further concentrated other portions of the liquid to form 77-78% calcium chloride flakes. In order to concentrate the liquid, they used high pressure steam in a single stage forced circulation evaporator. They then dipped cooled drums into the hot solution, causing calcium chloride flakes to “freeze” on the drum’s outer surface, which were scraped off, collected, and further dried by flue gas.
7) With another portion of the liquid, they concentrated it to make 90-94% calcium chloride pellets. They sprayed concentrated liquid directly into a dryer and heated with flue gas. They then collected the solids from the dryer, screened, and bagged them.
8) To make food grade calcium chloride, they simply filtered 45% calcium chloride solutions.

Figure 3: Schematic of the brine recovery and reinjection wells in the Sylvania and Filer Formations. Adapted from Garrett, 2004.



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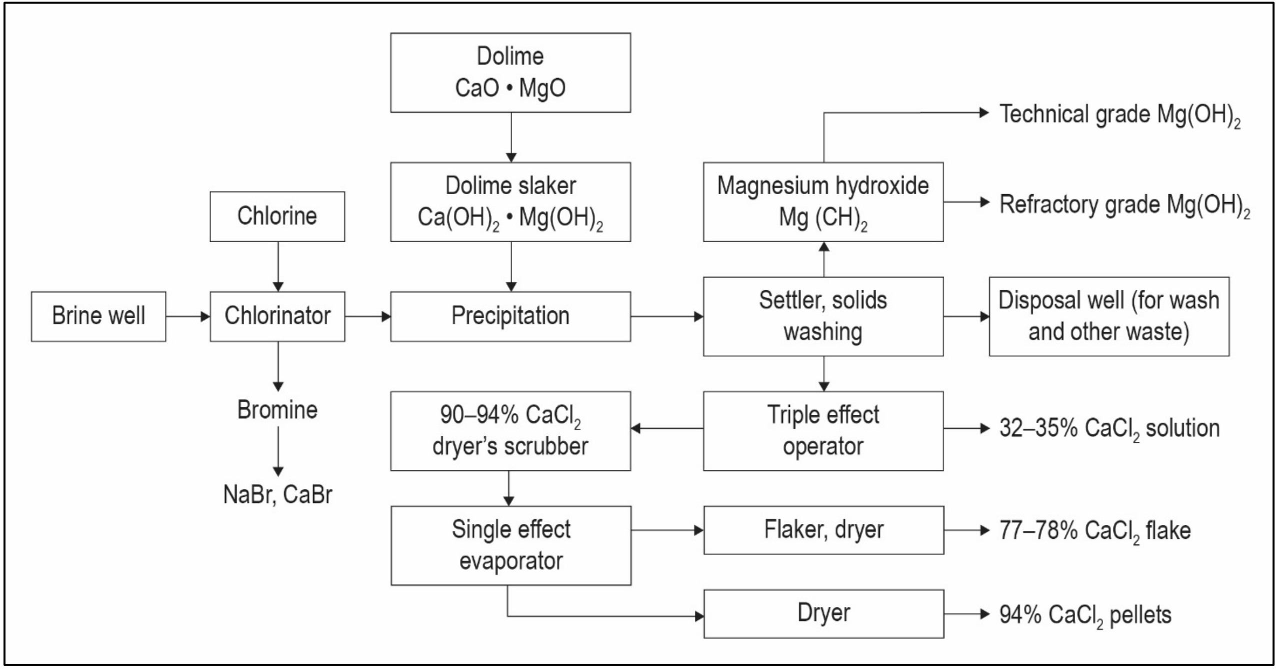
[4] Dow closed their wells in the Filer formation in 2003. OxyChem later purchased Dow’s Michigan brine plant (Luddington), which currently uses brine from the Filer formation.

Figure 4: Flow chart showing Dow Chemicals process for recovering calcium chloride from the Filer Formation (Michigan) in 2002. Adapted from Garrett, 2004.



<u>OxyChem pre-processed brines (Michigan)</u>

By 2003, Dow announced that it would close their wells in the Filer formation, and instead purchase brine to further process from Martin Marietta Magnesia Specialties Co. (also using the Filer formation) (Garrett, 2004). This brine was depleted of magnesium before being sent to Dow. OxyChem purchased Dow's Luddington, Michigan plant in 2009 (Michigan Chemistry Council, 2022). OxyChem appears to still use the Filer formation to produce calcium chloride.

<u>Bristol and Cadiz Lake brines (California)</u>

In California, companies such as the National Chloride Company of America and Tetra Technologies extract calcium chloride from Bristol Lake, a brine formation near the surface (Garrett, 2004). Producers have commercially recovered brine products from this lake since around 1910. This lake has been the home for several companies over its long history. Nearby Cadiz Lake is also used for similar brine production. The process that producers use can be generalized as follows (Garrett, 2004):

1) As the brine source is a dry lakebed, producers gather brine in trenches and pits, instead of wells. Portable diesel pumps and canals are used to transport brines between areas of a brine operation.
2) Producers use solar evaporation ponds to concentrate the brine to 32-36% calcium chloride.
3) As the ions in the brine become more concentrated, sodium chloride begins to precipitate as it is less soluble than calcium chloride. When the brine reaches a concentration of 35% calcium chloride, so much sodium chloride has precipitated that only 1% is left dissolved in the brine.
4) This process of evaporation lasts between 2 months to as little as 2 weeks, depending on the weather.
5) Calcium chloride from Bristol Lake is often sold as an impure liquid.
6) Producers make solid products by further concentrating the brine and using chilled rollers to solidify the calcium chloride.
7) In some cases, solid products may be treated with sodium hydroxide in order to increase the pH and decrease its corrosiveness. Corrosion inhibitors may also be added, such as sodium chromate or dichromate.

Additional processing to make solid calcium chloride products from purified liquid brines

While the processes manufacturers use to obtain calcium chloride brines vary, solid calcium chloride products are typically made as follows (Garrett, 2004):

1) Once it is obtained, producers concentrate the brine in triple effect evaporators to a concentration of 40-50% calcium chloride. At this point, the brine has a high boiling point and is very viscous.
2) In order to increase the concentration to 55-65%, producers switch to using single-effect evaporators.
3) Producers then cool and solidify calcium chloride on drums or rolls. At this point, the solids are near the dihydrate form, which contain 75.5% calcium chloride. The calcium chloride is scraped off the rolls as flakes.
    a. In some processes, low-value fines from later steps are added into the calcium chloride brine before it is solidified on rolls.
    b. In another process, producers added sodium silicate, a combination of sodium silicate and calcium hydroxide, or a combination of calcium hydroxide ($Ca[OH]_2$) and gypsum ($CaSO_4 \cdot 2H_2O$) to the brine before rolling.
4) The solids are dried in a drier or kiln to 76-78%, or up to 94%. At 85.5%, calcium chloride is a monohydrate.

To make granular products, producers spray a 55-60% solution of neutralized calcium chloride into a gas-fired, fluidized bed dryer-granulator (Garrett, 2004). Alternatively, prilling towers, drum or disc granulators, and other equipment may be used (Garrett, 2004).

From the reaction of calcium hydroxide with ammonium chloride (Solvay ammonia-soda process):
Calcium chloride is also a byproduct of soda ash (sodium carbonate) manufacturing via the Solvay ammonia-soda process, hereafter referred to as the "Solvay process" (European Commission, 2007; Kemp & Keegan, 2003; Kent et al., 2017). Soda ash is an important raw material for the production of glass, detergents, and other chemicals (European Commission, 2007).

Soda ash can also be produced in other ways, such as through the chlor-alkali process, or by utilizing an ore called "trona" (Kent et al., 2017). These other processes do not produce calcium chloride as a byproduct. Trona ore (sodium sesquicarbonate dihydrate) is rare in the European Union, and so soda ash is produced almost entirely from the Solvay process there (European Commission, 2007). Therefore, calcium chloride is produced in Europe as a byproduct of this process.

However, in the United States, trona is plentiful, with roughly 95% of all worldwide deposits (Kent et al., 2017). Because production of soda ash from trona ore is cheaper, very little soda ash is produced from the Solvay process in the United States (Kent et al., 2017). Therefore, calcium chloride is not generally produced from the Solvay process in the United States.

The Solvay process contains multiple steps, but the global equation can represent more simply (See *Equation 1*).

$$CaCO_3 + 2NaCl \rightarrow Na_2CO_3 + CaCl_2$$

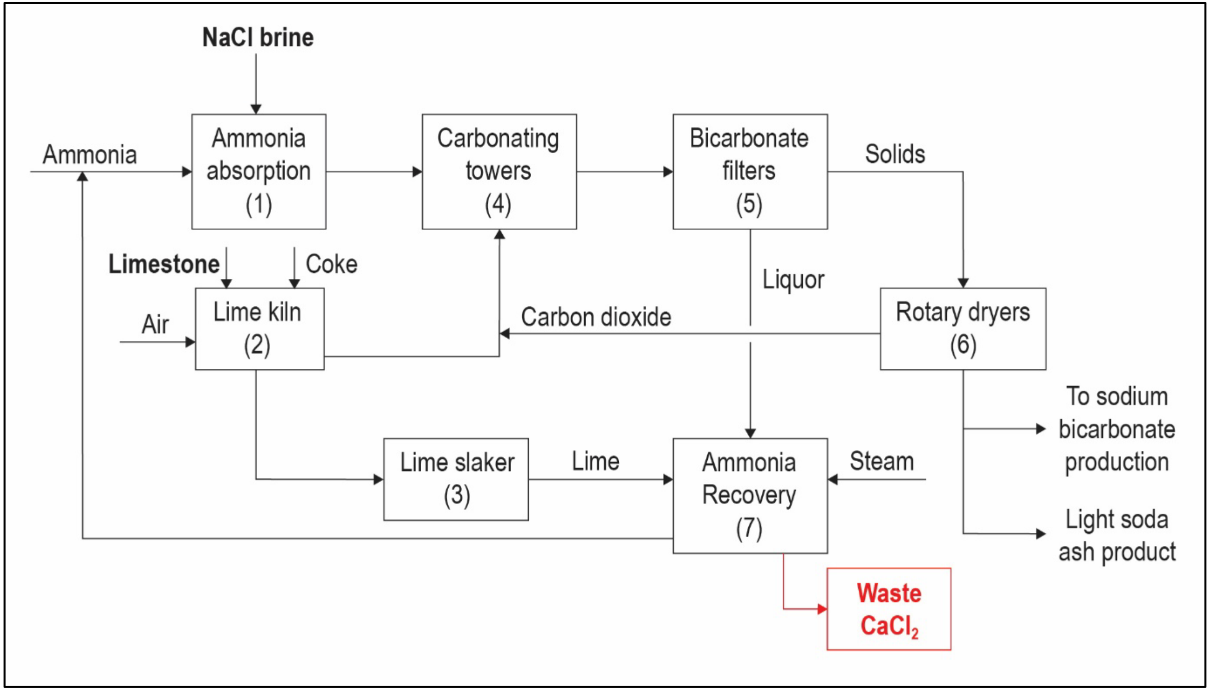
Equation 1

Generically, manufacturers create soda ash and calcium chloride via the Solvay process (see *Figure 5*, below) as follows (European Commission, 2007; Kent et al., 2017):

1) The manufacturer heats limestone until it decomposes into calcium oxide and carbon dioxide.
2) Carbon dioxide from this process is used to carbonate sodium bicarbonate from an ammoniated sodium chloride brine. Manufacturers use ammonia in the process as a catalyst and to create an alkaline solution.
3) The carbonation occurs in towers filled with alternating discs and rings which promote the contact of the ammoniated brine with the carbon dioxide gas. This process also creates carbonic acid.
4) A slurry of crystallized sodium bicarbonate and other materials leaves the bottom of the tower.

5) During the process, heat is generated as carbonic acid is neutralized. Manufacturers use water to cool the slurry.
6) The manufacturer then uses a filter (such as a rotary vacuum filter) to separate the sodium bicarbonate from the slurry.
7) They then heat the sodium bicarbonate in rotary dryers, where it decomposes to sodium carbonate (soda ash) and carbon dioxide (which is recycled).
8) They mix the remaining brine, containing ammonium ions, with hydrated calcium oxide (produced from the previously mentioned decomposition of limestone). This reaction regenerates ammonia.
9) They then recover the ammonia using steam distillation (steam stripping), leaving behind a solution containing calcium chloride.

Figure 5: Flow chart for Solvay ammonia-soda process. Adapted from (Garrett, 2004).



Recently, Solvay announced that it developed a new proprietary process for soda ash, called "e.Solvay," which is being tested in France (Solvay, 2023). Solvay purports that this process reduced CO_2 emissions, as well as lowering energy, water, salt, and limestone consumption. The process substitutes the lime kiln with an electrochemical process (Solvay, 2023).

From the reaction of hydrochloric acid with calcium carbonate:

Aqueous solutions of calcium chloride can also be produced by the neutralization of hydrochloric acid and calcium carbonate (see Equation 2) (Krohn et al., 1987).

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2O$$

Equation 2

In a patent, Krohn et al. (1987) describes the process, which we have simplified below:

1) The manufacturer charges a reaction vessel with calcium carbonate.
2) They then continuously feed aqueous hydrochloric acid to the reaction vessel.
3) The two substances react to form an aqueous solution of calcium chloride, carbon dioxide, and unreacted bits (*fines*) of calcium carbonate and related materials.
4) The carbon dioxide forms a foam at the top of the liquid, which traps some of the fines.
5) The trapped fines are continuously skimmed from the surface, producing a purified calcium chloride solution.

It is unclear how relevant this method is for current industrial production. However, according to TETRA Technologies, Inc. (2023), treating limestone with hydrochloric acid produces high purity calcium chloride. TETRA uses this method at their Kokkola Industrial Park facility in Finland (TETRA Technologies, Inc., 2023).

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.

Calcium chloride is listed at 7 CFR 205.605(a), and so with the exception of nutritional uses allowed under § 205.605(b)(20), only nonsynthetic forms are allowed in organic production. Calcium chloride can be either synthetic or nonsynthetic, depending on how it is made (see Evaluation Question #1, above). Calcium chloride derived from the Solvay ammonia-soda process is synthetic, as well as calcium chloride derived from the reaction of calcium carbonate and hydrochloric acid. Calcium chlorides derived from brines are nonsynthetic in many cases. However, some brine processes involve steps that make classifying calcium chloride more complicated. Below, we discuss the classification of different sources of calcium chloride in more detail, using NOP 5033-1, *Decision Tree for Classification of Materials as Synthetic or Nonsynthetic* as a guide.

Classification: from natural brines

1. *Is the substance manufactured, produced, or extracted from a natural source?*

Yes. Brines are a natural source. They are comparable to an extracted product, except that calcium chloride is typically what is left when other materials are extracted from the brine. For the purposes of classification using the decision tree, we will consider calcium chloride from brines to be an extracted material.

2b. *At the end of the extraction process, does the substance meet all of the criteria described at 4.6 of NOP 5033?*

- *At the end of the extraction process, the material has not been transformed into a different substance via chemical change;*
- *The material has not been altered into a form that does not occur in nature; and*
- *Any synthetic materials used to separate, isolate, or extract the substance have been removed from the final substance (e.g., via evaporation, distillation, precipitation, or other means) such that they have no technical or functional effect in the final product.*

It depends. Calcium chloride produced with minimal processing meets all of the above criteria (such as those using processes similar to Bristol and Cadiz Lake brines). The authors of the *Calcium Chloride* (Crops) report written in 2021 relied on the NOSB's previous classification under the handling scope (NOP, 2021). That is to say, that calcium chloride from brines were nonsynthetic. However, the NOP's current guidance on classification (NOP 5033-1) is based around evaluation criteria that is specific to each manufacturing process. Considering that manufacturing processes for calcium chloride produced from brines must vary according to the composition of the natural source, it is not possible to definitively state that calcium chloride produced from brines is categorically nonsynthetic.

For more heavily processed brines (such as those using processes similar to Dow/OxyChem brines from Michigan), processing aids added to remove other substances such as magnesium and bromine may be present. The use of these chemicals may leave residues of calcium and chloride, which could become incorporated into the final calcium chloride product. These residues would likely be indistinguishable from their natural counterparts.

Whether or not these products meet all of the criteria described in NOP 5033-1 question 2b falls into a gray area. The materials are not added with the *intent* of becoming a technical or functional part of the calcium chloride brine. However, as they become a part of the final calcium chloride product, they may exert a functional effect. The literature we reviewed that provided the most detailed manufacturing processes did not quantify the ions that remain from processing aids. However, the authors of the 2021 *Calcium Chloride* (Crops) report noted that for one brine process, less than 1 percent of a calcium oxide additive remains in the brine (NOP, 2021).

Complicating the issue is the annotation for calcium chloride at § 205.602(c) [emphasis added]: "Calcium chloride, brine process is natural…" Ostensibly, the NOP was aware of the 2001 TAP report Calcium Chloride, Crops (NOSB, 2001), where the authors refer to the "Dow Process," and describe the use of processing aids such as chlorine gas and calcium oxide to purify brines to obtain calcium chloride. [5]

The guidance leaves unclear precisely how material review organizations and certification agencies *should* consider these additives when classifying calcium chloride. Therefore, they must develop and apply their own material review policies to individual-cases.

For example, OMRI has reviewed and listed dozens of products containing calcium chloride, mostly in foliar sprays (for crop use) under § 205.602(c). Processing aids used to obtain the calcium chloride in these products include lime, slaked lime, chlorine, hydrochloric acid, magnesium oxide, sodium bisulfate and sulfur dioxide. OMRI has followed a historical interpretation that while ambiguous, the use of processing aids in brine-extracted calcium chloride is allowed, based on the annotation for calcium chloride at § 205.602(c).

For examples of steps involving processing aids that could become incorporated, see the following manufacturing processes in *Evaluation Question #1* (above):

- Marshall formation process, step 4 (use of slaked lime)
- Sylvania formation process, steps 1 & 3 (use of chlorine)
- Filer formation process, step 2 (use of slaked dolime)
- Additional processing to make solid calcium chloride products from purified liquid brines, step 3b (use of sodium silicate, calcium hydroxide, and gypsum)

2. *Has the substance undergone a chemical change so that it is chemically or structurally different than how it naturally occurs in the source material?*

It depends. Calcium chloride extracted with minimal processing is effectively unchanged (such as those using similar processes to Bristol and Cadiz Lake brines), except that it has been concentrated and other ions have been removed. When minimally processed, calcium chloride is the remaining material after other substances have been extracted, leaving a nonsynthetic material remaining. This type of processing is what is described above in *Evaluation Question #1* at Bristol and Cadiz lakes.

In some of the more heavily processed brines (such as those similar to Dow/OxyChem brines originating from Michigan), other chemicals may be added, such as calcium hydroxide or slaked dolime ($CaMg[OH]_2$). The calcium hydroxide or slaked dolime is used to precipitate magnesium hydroxide, leaving behind calcium ions, which may become incorporated into the calcium chloride product later on. Similarly, when chlorine is used to free bromine from brines, it may be transformed into hydrogen chloride, and could become part of the calcium chloride product.

In some of the solid calcium chloride products, additives may be used, including: sodium silicate, a combination of sodium silicate and calcium hydroxide, or a combination of calcium hydroxide ($Ca[OH]_2$) and gypsum ($CaSO_4 \cdot 2H_2O$). These additives are synthetic, and likely remain in the final product.

3. *Is the chemical change created by a naturally occurring biological process, such as composting, fermentation, or enzymatic digestion; or by heating or burning biological matter?*

For minimally processed brines (such as those similar to Bristol or Cadiz Lake brines), there is no chemical change to consider, and therefore these materials are nonsynthetic.

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[5] The "Dow Process" referred to in the 2001 TAP review (NOSB, 2001) is an informal term that those authors use to describe one process among several employed by Dow to make calcium chloride. Dow has since sold their calcium chloride plant to OxyChem. Furthermore, different processes are typically used to produce flake products from liquid calcium chloride. These can include the use of processing aids as well. The Dow Process should not be considered an official term.

For more heavily processed brines (such as those similar to Dow/OxyChem brines in Michigan), changes may occur that are not due to naturally occurring biological processes, and therefore could be considered synthetic. As mentioned above, the interpretation and application of this part of NOP 5033-1 with respect to calcium chloride is a gray area. These processes involve the addition of calcium or chloride to the brines from sources other than the brine (potentially synthetic), which become a part of the calcium chloride end-product.

Classification: from reaction of calcium hydroxide with ammonium chloride (Solvay ammonia-soda process)

1. *Is the substance manufactured, produced, or extracted from a natural source?*

No. Therefore, calcium chloride produced from the Solvay ammonia-soda process is synthetic.

Classification: reaction of hydrochloric acid with calcium carbonate

1. *Is the substance manufactured, produced, or extracted from a natural source?*

No. Therefore, calcium chloride produced from this reaction is also synthetic.

No forms of calcium chloride are agricultural. The first question in NOP 5033-2, *Decision Tree for Classification of Agricultural and Nonagricultural Materials for Organic Livestock Production or Handling* asks, *"is the substance a mineral or bacterial culture as included in the definition of nonagricultural substance at section 205.2 of the USDA organic regulations?"* Since calcium chloride is a mineral, it is classified as nonagricultural.

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)].
As discussed above, nonsynthetic forms of the substance exist and are commercially available.

Evaluation Question #4: 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.
Calcium chloride is considered GRAS for numerous uses by the FDA (see *Approved Legal Uses of the Substance*, above). The allowed uses for calcium chloride under USDA organic regulations are consistent with FDA allowances.

Evaluation Question #5: 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)].
Calcium chloride has numerous uses in food processing (see *Specific Uses of the Substance*). Various of these uses such as desiccant, curing agent, firming agent, and antimicrobial agent contribute to calcium chloride's role as a preservative in food processing (Garrett, 2004; Kemp & Keegan, 2003). Food processors employ calcium chloride to combat spoilage caused by physical conditions such as light, heat, pH, and oxygen exposure (Mishra et al., 2008). Calcium chloride also inhibits microbial (Barden et al., 1990) and enzymatic (Gao et al., 2020; Lewis & Harrison, LLC, 2018) activity that leads to spoilage and decay, thereby prolonging the shelf life of the treated food product.

Calcium chloride can delay the browning of processed fruits and vegetables, whether due to enzymatic (Lewis & Harrison, LLC, 2018; Manganaris et al., 2007) or bacterial action (Barden et al., 1990; Chikthimmah et al., 2005; Irfan et al., 2013). Two studies observed that calcium chloride applied via irrigation water during the cultivation of white mushrooms inhibited bacterial growth and associated post-harvest surface browning, thereby increasing the mushrooms' shelf-life:

- roughly 64% as reported by Barden et al. (1990)
- 87% when combined with hydrogen peroxide as reported by Chikthimmah et al. (2005)

Processors can also apply calcium chloride to post-harvest wash water for this purpose. Similarly, Irfan et al. (2013) applied calcium chloride to figs post-harvest and observed that it slowed the growth of bacteria, yeast, and molds during low temperature storage.

Gao et al. (2020) investigated the mechanisms by which calcium chloride treatment of papaya post-harvest delayed yellowing and other signs of decay. They found that the calcium chloride treatment inhibited the expression of enzymes involved in cell wall degradation, and the expression of genes that influence ethylene synthesis and signaling. The result of calcium chloride treatment in their study was preservation of the papaya fruit quality and postponing of disease development post-harvest. Manganaris et al. (2007) reported similar results and mechanisms for calcium chloride treatment of peaches post-harvest. They found inhibition of the same pectin-modifying enzymes, polygalacturonase and pectin-methyl-esterase, and also reported the efficacy of calcium chloride as a post-harvest preservation treatment (Manganaris et al., 2007).

<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)].
Calcium chloride has numerous uses in food processing, many of which affect the texture, color, flavor, and or nutrition of the final food product. Refer to *Specific Uses of the Substance*.

Firming agent
One of the uses of calcium chloride is as a firming agent, which processors use to maintain or improve the texture of canned foods such as cucumber pickles, black olives, tomatoes, and jalapeños (Buescher & Burgin, 1988; García-Serrano et al., 2020; Gu et al., 1999; Luna-Guzmán & Barrett, 2000). Calcium chloride can also maintain the firmness of fresh produce (Gao et al., 2020). It achieves this firming effect through various mechanisms. Calcium ions from the calcium chloride stabilize the cell membrane and increase the turgor pressure of cells. Calcium ions also complex with pectin in the cell wall and middle lamella – the space between cells, which is rich in pectin (Daher & Braybrook, 2015; Luna-Guzmán & Barrett, 2000). Gu et al. (1999) described how overheating foods during processing causes pectin-containing compounds in the food's cells and cell walls to solubilize, resulting in a sometimes undesirable softening of the final food product. In their study, Gu et al. (1999) observed that calcium chloride treatment of rotary-heated, canned jalapeños prevented pectin depolymerization and solubilization, thereby maintaining a more consistent texture throughout the product.

Tenderizer
Calcium chloride has a contrasting effect on texture in its application as a tenderizer of beef (Garrett, 2004) and other meats. With meat tenderizing, calcium chloride treatment softens and fragments some of the muscle tissue, thereby improving the meat's palatability (Gerelt et al., 2002). Researchers in one study dipped dehydrated meat samples in a 150-mM concentration solution of calcium chloride for three hours, and then stored them under refrigeration for 24, 48 or 168 hours. The results showed a decrease in the meat's firmness over the longer storage times, which correlated with higher tenderness scores for longer-stored meats once grilled (Gerelt et al., 2002). The calcium chloride treatment did not adversely affect other sensory measures, but improved reported scores for juiciness and taste as well (Gerelt et al., 2002).

Color retainer and flavor enhancer
Calcium chloride application to food can also affect color and flavor. Irfan et al. (2013) found that application of calcium chloride to figs post-harvest resulted in a notable retention of fruit color, along with texture and accumulated ascorbic acid. As to flavor, calcium chloride imparts a slightly salty flavor, though much weaker than sodium chloride (Briggs et al., 2004). Although processors sometimes use it as a replacement for sodium chloride in reduced sodium foods, it can produce undesirable metallic or bitter flavors (Barros et al., 2019). As an indirect effect on flavor, calcium chloride can prevent the deterioration of flavor that occurs with enzymatic browning in some fruits and vegetables (Lewis & Harrison, LLC, 2018).

<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)].
Calcium chloride is sometimes used to supplement food's calcium content for nutritional purposes (Acosta et al., 2020; Barone et al., 2022; Ziadeh et al., 2005). Calcium is an essential micronutrient at all stages of life, playing important roles in numerous physiological functions such as bone formation, blood clotting, muscle contraction, glycogen metabolism, and many others (Palacios et al., 2021). However, meeting the

daily recommended intake of calcium through diet alone may be difficult for some populations with limited dairy consumption (Barone et al., 2022; Ziadeh et al., 2005). The effects of calcium deficiency on human health can include preeclampsia, hypertension, rickets, osteomalacia, and osteoporosis (Barone et al., 2022; Palacios et al., 2021).[6] Conversely, sufficient calcium intake can help protect against hypertension, colorectal cancer, and lead toxicity (Ziadeh et al., 2005).

Products commonly fortified with calcium include bread, tofu, infant formula, energy drinks, and dietary supplement drinks for elderly adults (Barone et al., 2022; Ropp, 2013; L. Zheng et al., 2020; Ziadeh et al., 2005). In the UK, calcium fortification of wheat flour is mandatory (Palacios et al., 2021). Other products that manufacturers fortify with calcium include corn flour, rice, and even dairy products, which are already a good source of dietary calcium (Acosta et al., 2020; Barone et al., 2022; Palacios et al., 2021).

Food processors enrich the calcium content of foods using a number of different calcium compounds, including calcium chloride (Barone et al., 2022). The National List permits nonsynthetic calcium chloride in processed products labeled as "organic" at 7 CFR 205.605(a)(7) without annotation, and also permits synthetic calcium chloride as a nutrient in accordance with 21 CFR 104.20, under the nutrient vitamins and minerals listing at 7 CFR 205.605(b)(20). Thus, the NOP regulations permit both forms for nutritional supplementation of organic foods.

Different forms of calcium used for nutritional supplementation include inorganic forms such as calcium carbonate, hydroxide, chloride, and phosphate, and organic forms such as calcium gluconate, citrate, and lactate (Barone et al., 2022). These forms all differ in their solubility, calcium content/potency, counterions, and their effects on the physiological and sensory properties of the food to which they are added (Barone et al., 2022). For these reasons, formulators often use combinations of different calcium salts to maximize calcium content and bioavailability while minimizing adverse impacts on the sensorial properties of the food (Barone et al., 2022). Manipulating these combinations can also help food processors minimize detrimental interactions caused by calcium, such as unwanted coagulation of proteins and the settling of colloids out of solution (Acosta et al., 2020; Barone et al., 2022; Ziadeh et al., 2005). Processors supplementing the calcium content of food also use various combinations of calcium salts to meet additional nutritional requirements (i.e. chloride, phosphate) (Barone et al., 2022).

Calcium chloride's uses in food processing can overlap. A food manufacturer may use it for a primary purpose other than nutrition, while secondarily achieving positive effects on nutrition. Martín-Diana et al. (2007) point out that the use of natural calcium chloride as a preservative has the added benefit of providing calcium fortification to treated foods. Calcium chloride used to inhibit enzymatic browning of fruits and vegetables also helps maintain those foods' nutritional value that would otherwise be lost through the browning process (Lewis & Harrison, LLC, 2018). The use of calcium chloride in food processing, therefore, generally has a favorable effect on the nutritional quality of food.

Evaluation Question #8: 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)].
For calcium chloride, the FDA has not established "action levels" for poisonous or deleterious substances that are unavoidable in human food and animal feed (U.S. FDA, 2000). These action levels limit substances like aflatoxin, cadmium, lead, and polychlorinated biphenyls (PCBs) in various commodities, most of which are foods. A more limited number of non-food commodities such as ceramics and utensils also have FDA action levels for poison or deleterious substances.

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[6] Preeclampsia is a serious condition related to blood pressure that can develop during pregnancy; Hypertension is also known as high blood pressure; Rickets involves the softening of bones in children due to vitamin D deficiency; Osteomalacia and osteoporosis are both bone weakness diseases in adults (Cleveland Clinic, n.d.).

The of the Food Chemicals Codex (United States Pharmacopeial Convention, 2014) stipulates the following limits for impurities and contaminants in calcium chloride:

- arsenic, not more than 3 ppm (0.0003%)
- fluoride, not more than 0.004%
- heavy metals (as Pb), not more than 5mg/kg (0.0005%)
- magnesium and alkali salts, not more than 25 mg of anhydrous residue and not more than 20 mg of dihydrate residue

The European specifications for calcium chloride (E 509) according to Commission Regulation (EU) No 231/2012 are similar:

- fluoride: not more than 40 mg/kg (0.004%)
- lead: not more than 2 mg/kg (0.0002%)
- free alkali: not more than 0.15% as $CaOH_2$
- magnesium and alkali salts: not more than 5%

In 2019, the European Panel on Food Additives and Flavourings recommended lowering the limits for arsenic, lead, and mercury in a number of food additives, including calcium chloride, to ensure that these food additives would not be a source of exposure to heavy metals in food (EFSA Panel on Food Additives and Flavourings (FAF) et al., 2019).

<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)].

Calcium chloride in the environment

At the concentrations utilized for food commodities, calcium chloride is unlikely to negatively affect the environment when disposed. Calcium chloride dissociates into calcium and chloride ions in the environment, and, at low concentrations, could be easily metabolized by plants (White & Broadley, 2001, 2003) and microbes (Ksara et al., 2019; Seifan & Berenjian, 2019).

Despite not being harmful to the environment at moderate concentrations, calcium chloride can become toxic to plants and animals when certain levels are exceeded (Vrana, 2001). In excess, calcium chloride can harm roadside vegetation and contaminate water supplies (Garrett, 2004). Calcium chloride is also corrosive to concrete, automobiles, and other structures (Garrett, 2004).

Road salt is a concern because of the high concentrations observed in the environment, lasting ecological effects, and contamination of drinking water (Hintz & Relyea, 2019). In the quantities utilized for road deicing and dust suppression, calcium chloride can become a problem due to the salinization effects of chloride (Findlay & Kelly, 2011). Salinization of water is a global issue, negatively affecting soil and water quality, microorganisms, plants, and aquatic organisms (Hintz & Relyea, 2019).

Calcium can increase soil stability, permeability, and aeration, likely through organic and inorganic particle agglomeration (Fay & Shi, 2012). However, the calcium cation can also exchange with heavy metals in soil, potentially releasing them into the environment (Public Sector Consultants, 1993). For this reason, Horner and Brener (1992) advise against applying calcium near metal-contaminated soils because the metals could be easily mobilized and released into water sources.
Water runoff that is contaminated with chloride can (Fay & Shi, 2012):

- change the density gradient of receiving water bodies
- alter its physical and ecological characteristics
- elevate chloride concentrations
- induce depletion of dissolved oxygen

In plants, excessive chloride exposure inhibits growth and causes browning, premature aging of leaves and needles, tree limb death, and plant death induced by osmotic stress (Fay & Shi, 2012). High and persistent chloride concentrations in streams adjacent to roadways can harm fish at concentrations from 400 to 12,000 mg/L, cause growth changes in plankton at concentrations greater than 1,000 mg/L, and affect amphibian skin through osmolality processes (Fay & Shi, 2012).

Environmental impact of calcium chloride's manufacturing process

In the United States, nonsynthetic calcium chloride is produced commercially through the evaporation and refining of natural brines (Althaus et al., 2007) in two locations: the Bristol drainage area (Bristol Dry Lake and Cadiz Lake) in California and the Ludington Plant in Michigan (Garrett, 2004), now owned by OxyChem (originally Dow). Reviewing the effects of brine mining in these two locations provides an overview of the environmental impact of calcium chloride manufacturing.

Ludington plant: groundwater and soil impact of brine extraction

In the early 2000s, Dow began purchasing leftover brine (rich in calcium chloride) that Martin Marietta Magnesia Specialties Inc. produces after the magnesium hydroxide recovery process (Martin Marietta Materials, Inc., 2003; Michigan Chemistry Council, 2022). In 2003, Martin Marietta Magnesia Specialties Inc. finished the construction of a pipeline that connected both facilities to allow the transportation of such brine (Martin Marietta Materials, Inc., 2003; Michigan Chemistry Council, 2022).

The extraction and recovery of underground brines typically resembles techniques used in the oil and gas industry (Shand, 2006). The secondary brine used to manufacture calcium chloride at the Ludington Plant is left over from the magnesium hydroxide recovery process. In order to obtain the initial brine, freshwater is pumped into drilled wells via a central tube, dissolving the salt from walls. The resultant brine is forced back to the surface through a tube system inserted in the well (Shand, 2006).

The underground brine mining process requires high pressure and high temperature water that not only dissolves minerals, but also causes fractures in the strata, which may result in hazards such as brine leakage or groundwater inrush (Zeng et al., 2018). Groundwater, sometimes used for public drinking water, is normally polluted following groundwater inrush, leading to contamination and threatening the health of local residents (Zeng et al., 2018).

In 2002, while owned by Dow Chemicals, the Ludington facility experienced a brine leak when an underground pipeline burst (French, 2020). Brine leaks impact groundwater and can kill vegetation (Braciszeski, 2002). The company worked to remove the brine-contaminated soil that exceeded 500 parts per million of calcium chloride. The spill also contaminated groundwater, elevating the calcium chloride levels to greater than residential standards (Braciszeski, 2002). The communications specialist for Dow pointed out that the removed material was deposited in a landfill and replaced with uncontaminated sand, and that the remaining 10-foot-deep clay layer was expected to prevent further infiltration (Braciszeski, 2002).

Ludington plant: Disposal of processed brine

Despite the agreement with the Ludington plant, Martin Marietta Magnesia Specialties Inc. still disposes the excess processed brines that are not sold to third parties by reinjecting them into its underground brine reserve network around the facility in Mainstee, Michigan (Michigan EGLE, 2021). Excess calcium chloride is also reinjected into a disposal well at the Ludington plant (EPA, 2017, 2020).

The spent brine, generated from Martin Marietta's process and used by the Ludington plant to produce their calcium chloride powder, is a mixture of wash water and filtered, high calcium liquids. It is considered non-hazardous waste (Michigan EGLE, 2021).

Processed brines are disposed in Class I, nonhazardous underground injection wells (EPA, 2020). Unlike the process to extract unprocessed brines, methods associated with the disposal of processed brines is less hazardous. This is because the disposal wells are designed and constructed with the objective of preventing the movement of injected fluids (Michigan EGLE, 2021). These wells are designed to isolate the disposal zone with over 2,300 feet of vertical separation from the freshwater zones, which prevents the migration of disposed fluids into the freshwater (Michigan EGLE, 2021). Both companies, Occidental Chemical Corp. and Martin Marietta Magnesia Specialties, utilize these wells (EPA, 2017, 2020; Michigan EGLE, 2021).

Rish et al. (2005) and EPA studies (Clark et al., 2005) claim that the risk of loss of waste containment and movement of the injected liquid in such wells is less than one in one million. After several decades of Class I well operations, only four significant cases of injected liquid migration have been documented, and none of these affected a drinking water source (Clark et al., 2005). However, if certain circumstances coexist (e.g. weakening a preexisting fault by elevating the fluid pressure with very large volumes of water), underground injection wells for disposal of brines seem to be linked with earthquake induction (Ellsworth, 2013, 2013; Finley, 2015; Folger & Tiemann, 2015).

Ludington brine plant: Impact on surface water

As mentioned above, once in the environment calcium chloride tends to dissociate into calcium and chloride ions. Excessive chloride is harmful to aquatic plants, animals and is corrosive to infrastructure (Garrett, 2004; Tapia Pitzzu et al., 2022), the environmental effects of the chloride ion are described in depth within the 2023 *Potassium Chloride* Technical Report (USDA, 2023). Martin Marietta Magnesium Specialties Inc. and Occidental Chemical Corporation (Ludington facility) are both NPDES-permitted facilities; meaning that they are allowed to discharge waste or wastewater into the surface waters of the state while following monitoring requirements for chloride (Tapia Pitzzu et al., 2022).[7]

From 2015 to 2020, Martin Marietta Magnesium Specialties Inc. had a 5- year average chloride discharge of 29,521.19 metric tons, while Occidental Chemical Corporation (Ludington facility) had a total discharge of 2,741.02 metric tons per year. This translates into 16.69% and 1.55% of the total contribution to the grand total of 176,858 metric tons of chloride that the NPDES-permitted facilities discharge in Michigan surface waters every year (Tapia Pitzzu et al., 2022). Martin Marietta Magnesium Specialties Inc. is one of the three main contributors for the total volume of disposed chloride (Tapia Pitzzu et al., 2022).

Bristol Dry Lake: Impact on groundwater and soil

Calcium chloride at Bristol Dry Lake is commercially mined by two companies: National Chloride Company of America and Tetra Technologies Inc. Underground brine reserves are pumped to the surface and stored in excavated brine trenches (collection ditches) and evaporative ponds. The construction of these trenches physically damages the structure of the lakebed. This damage is rarely repaired after mining has ceased (Williams, 2002). The limnological effects caused by physical disturbance to dry salt lake beds are not well known (Williams, 2002). Levees, causeways, and canals will clearly impede the free surface movement of water across the bed of the lake, but the consequences of this are not known and may not be significant (Williams, 2002). Williams (2002) and Ekrami et al. (2021) consider that tailing dumps, mining voids, vehicle tracks, and other physical impacts associated with both surface and deep mining destroy a core part of the aesthetic appearance of the lakes.

In terms of water usage, Tetra Technologies pumps groundwater directly from its 10,835 acre property (Pacific Institute Report, 2013). According to public records, the pumped water averages about 500 AFY (acre feet per year), which is about 163 million liquid gallons per year (The Cadiz Water Project, 2012). In comparison, a 3,500 acre agricultural operation close to the Bristol Dry Lake area requires almost four times this amount of water, approximately 1,867 AFY, to keep the operation running (The Cadiz Water Project, 2012).

National Chloride Company of America is authorized to mine 162 acres and it extracts a smaller, but proportionally similar, quantity of groundwater annually. As a smaller operation, it has not filed public records reporting its annual use (The Cadiz Water Project, 2012).

Calcium chloride mining has occurred in Bristol Dry Lake since 1910 (Garrett, 2004). Although monitoring data are scarce, groundwater levels appeared to be stable during 1983 through 1998 (DWR, 2004). However, historical data also indicates that the elevation of the dry lakes may has lowered as much as 4.6

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[7] NPDES stands for National Pollutant Discharge Elimination System (NPDES)

m over the past 100 years, raising the question of whether the long-term mining operations may have changed the hydrology of the region, and therefore influenced the flow of water between the Bristol and Cadiz Dry Lake (an adjacent lake) and their relative composition (Rosen et al., 2020).

Bristol Dry Lake: Impact on Air

Dry lakes are a source of abundant salt and dust (NASA, 2007). Mineral dust emitted from dry lake playas has a variety of potentially harmful effects to the environment and human health, including (Goodman et al., 2019):

- diseases (e.g., asthma, pneumonia, and valley fever)
- harmful algal blooms in lakes
- earlier snowmelt
- decreased runoff from mountain snowpack

However, the mineral dust emitted from Bristol Dry Lake surface is not entirely related to mining operations, but also to the dry nature of the place itself, and to the natural windstorms that occur in this location. We did not find studies that evaluated the direct effect of Bristol Dry Lake mining operations on the air quality of the region.

Bristol Dry Lake: Impact on Biodiversity

We only found literature describing one species that could be affected from the mining operations performed in Bristol Dry Lake region. *Saltonia incerta* is a threatened spider species that was previously believed to be extinct (Crews & Gillespie, 2014). Populations of this spider live under the salt flats of Bristol Lake close to the mining locations. The effects of mining on these populations is unknown (Crews & Gillespie, 2014). Long term population assessments are needed to determine how habitat disturbance affects the arthropod populations in these unique habitats (Crews & Gillespie, 2014).

Evaluation Question #10: 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)].

At the concentrations utilized in food products, calcium chloride is unlikely to negatively affect human health. Calcium chloride readily dissociates into calcium and chloride ions in water (National Industrial Chemicals Notification and Assessment Scheme, 2014). Once absorbed, the calcium and chloride ions are metabolized separately, and the health effects in animals are attributable to either ion (National Industrial Chemicals Notification and Assessment Scheme, 2014).

Calcium and chloride ions are essential body constituents in all animal species (Bailone et al., 2022; National Industrial Chemicals Notification and Assessment Scheme, 2014). Calcium is the most abundant metallic element in all animal species, primarily located in the skeleton. Chloride is the most abundant anion in animal species and is important for maintaining osmotic and acid–base balance (National Industrial Chemicals Notification and Assessment Scheme, 2014). See *Evaluation Question #7* (above) for a description of calcium chloride, used as a nutritional supplement.

Although rare, under certain circumstances, calcium chloride may cause soft tissue necrosis in humans (Nakagawa et al., 2020). Some of these cases are listed below:

- About 70 g of calcium chloride consumed by accident by an elderly woman caused gastric necrosis and hypercalcemia (Nakagawa et al., 2020).
- Concentrated calcium chloride solutions injected in smaller veins caused skin necrosis on 4 out of 371 patients, after thyroid surgeries (Lin et al., 2007).
- Calcium chloride caused soft tissue necrosis in one person when it dissolved on the skin and the site was not properly cleaned after such contact (M. P. Kim et al., 2007; Patel et al., 2010).
- Calcium chloride solutions that were injected improperly leaked into tissue surrounding the injection site, injuring eight patients (including six infants) (Yosowitz et al., 1975). In five of these cases, severe disfigurement or decreased limb function occurred (Yosowitz et al., 1975).

<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)].

There is evidence of a few physical methods for tenderizing meat that may eliminate the necessity of calcium chloride. We did not find evidence of a single method that is interchangeable for all the common uses of calcium chloride.

Tenderizer/texturizer

There are physical alternatives for the tenderization of meat. Aging meat is well established as a method of tenderization, but requires sufficient storage space and high energy consumption (Shi et al., 2021). Processing time and labor are additional costs associated with this method (Bhat et al., 2018).

Meat cuts and whole carcasses exposed to freeze-thaw cycles can also result in an improvement of tenderness of 13-34% reported as shear force reduction (Bekhit & Hopkins, 2023). For comparison, reduction of shear force with the addition of calcium chloride can range between 1.7-70.6%. Variables contributing to the effectiveness of calcium chloride include concentration, aging period, species, and specific muscle type (Bekhit et al., 2014). Aging is also a variable in the effectiveness of the freeze-thaw method.

High-pressure processing is a tenderizing method that typically involves applying 100-600 MPa at room temperature to a liquid confined to a vessel in order to apply uniform pressure to the meat in a sealed package (Bhat et al., 2018). Scientists applying high-pressure to beef produced more tender meat, reported as a 65% reduction of shear force.

Ultrasound is a relatively new meat tenderization technology with limited commercial application in the poultry industry (Al-Hilphy et al., 2020). Ultrasound utilizes soundwaves with frequencies above human hearing range (20-100 kHz). Scientists reported more tender meat with prolonged and high-intensity applications of ultrasound. Ultrasound applied in combination with aging can expedite the tenderizing process (Bhat et al., 2018). Ultrasound requires considerable initial investment but can reduce processing costs. It is also considered a nonpolluting method of tenderization (Al-Hilphy et al., 2020).

<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)].

Calcium chloride serves a variety of roles in processing. We found no evidence in the literature of a single allowed material offering the versatility that calcium chloride does. However, some materials may be acceptable calcium chloride alternatives for specific applications.

Carbon dioxide (§ 205.605(b)(10)) as an antimicrobial agent

Above normal atmospheric levels, carbon dioxide (CO_2) inhibits the growth of molds and aerobic bacteria (Ahn et al., 2021). However, storing fruit under elevated CO_2 levels (and consequentially, low oxygen levels) can create flavors that consumers dislike. In a low oxygen environment, anaerobic fermentation produces ethanol, which is the source of the unpleasant flavor (Ahn et al., 2021; Mditshwa et al., 2018).

CO_2 is readily available in domestic and global markets (EPA, 2022). Modified atmospheres require that personnel receive specialized training to monitor air quality and minimize the effects of exposure to low oxygen environments (Yahia et al., 2019). Exposure to low oxygen environments can impair judgment, physical coordination, and respiration. Sustained exposure to low oxygen environments can be lethal. The negative environmental impact related to the traditional extraction methods of CO_2 are under increasing scrutiny and challenge the sustainability of this option (Esposito et al., 2019). Environmental impacts of CO_2 are also discussed in the 2023 technical report, *Carbon Dioxide (Crops)* (NOP, 2023a).

Ozone (§ 205.605(b)(21)) as an antimicrobial and firming agent

Ozone is also an effective antimicrobial agent (Suslow, 2004). Processors use it commercially for a variety of crops including apples, cherries, onions, peaches, potatoes, and table grapes. Ozone is also effective for mushroom preservation (C. Zheng et al., 2023).

To a limited degree, ozone acts as a firming agent (Mayookha et al., 2023; Shezi et al., 2020). It does not strengthen the cell wall like calcium chloride, but rather inhibits the enzymatic activity responsible for ripening and softening. Further research is necessary to clarify the particular mode of action. There is some evidence that tomatoes do not appear to benefit from a firming effect from ozone (Venta et al., 2010).

Ozone generators require considerable initial investment. Ozone (triatomic oxygen) is produced on site, and it decomposes to molecular (diatomic) oxygen. On site equipment generates ozone and consequently using this material eliminates processor costs for maintaining physical storage space associated with other liquid disinfectants at volumes required for commercial production (Pandiselvam et al., 2019).

A worldwide survey of food professionals from industry, academia, and government, and analyzed by Jermann et al. (2015), indicated that ozone is available for food processing applications in North America and Europe. The survey analysts also recognized that survey participants from Australia and Asia were extremely limited compared to other continents. For this reason, the available technologies represented for those continents may not be comprehensive. Naito and Takahara (2006) also described the widespread commercial applications of ozone in food processing in Japan indicating that ozone is also available there.

For postharvest applications, producers use ozone concentration rates of 2-3 ppm in processing water. Modern injection systems can reach rates of 6 ppm or greater (Suslow, 2004). The OSHA permissible exposure limit for ozone is 0.1 ppm for an eight hour, five-day workweek (Rice, 2012). Even at this rate, workers sensitive to ozone may experience eye/nose/throat irritation, headaches, and shortness of breath. Scientists observed respiratory distress at ozone concentrations 0.5-1 ppm. Pneumonia and coma are possible side effects at ozone concentrations 1-10ppm. However, when workers have access to monitoring and good manufacturing processes, third-party hazard analysis testing suggests there is minimal health risk associated with postharvest ozone applications (Rice, 2012). Ozone treatment does not require high temperature and the energy required for ozone treatment is lower than radiation, microwave, and thermal methods (Pandiselvam et al., 2019).

Calcium phosphate [§ 205.605(b)(9)], calcium sulfate [§ 205.605(a)(8)], and magnesium sulfate [§ 205.605(a)(18)] as coagulants

Calcium phosphate demonstrates potential as an alternative coagulation aid for cheese. In Minas Frescal cheese, both full and partial replacement of the calcium chloride with calcium monophosphate produced cheeses with no significant difference in the physiochemical composition or yield compared to the control (da Silva et al., 2023).

Tofu alternative salts commonly used include magnesium sulfate and calcium sulfate (Zhang et al., 2018).

The concentration of coagulant processors use to make tofu depends on several variables, but a rate of 0.4% based on the volume of soymilk is not uncommon for calcium chloride, calcium sulfate, or magnesium sulfate (L. Zheng et al., 2020).

Other salts used as curing/pickling agents

A few allowed salts offer potential as alternative curing and pickling agents. Sodium chloride (allowed through exclusion at § 205.301) is the traditional preservative for many vegetable pickles (García-Serrano et al., 2020). However, recent trends towards increasingly strict conductivity waste regulations and human health guidance advocating for lower levels of dietary sodium chloride may limit some applications. Calcium hydroxide [§ 205.605(b)(8)] is an alternative pickling and firming agent for vegetable pickles (NOP, 2023b). Magnesium chloride [§ 205.605(a)(17)] and potassium chloride [§ 205.605(a)(23)] both perform similarly to calcium chloride in antimicrobial and sensory evaluations in curing brines for cod (Rodrigues et al., 2005).

Other sources of calcium used as firming agents

Calcium chloride is an ubiquitous firming agent for lightly processed and canned produce (Oms-Oliu et al., 2010). Processors alternatively use calcium sulfate [§ 205.605(a)(8)], calcium citrate [§ 205.605(b)(7)], or monocalcium phosphate [§ 205.605(b)(9)] in the preparation of canned tomatoes (Hui et al., 2003). Parsa et al. (2020) demonstrated that calcium sulfate was an effective firming agent for sweet cherries. Monocalcium phosphate, dicalcium phosphate [also § 205.605(b)(9)], and calcium carbonate [§ 205.605(a)(6)] are additional calcium salts classified as firming agents in the FAO codex (FAO and WHO, 2021). Calcium phosphate salts do not demonstrate the same toxicity concerns as those associated with the more soluble inorganic phosphates (EPA, 2021). Acute toxicity potential for these salts is relatively low.

Other sources of calcium as nutrient supplements

Calcium carbonate [§ 205.605(a)(6)], calcium citrate [§ 205.605(b)(7)], calcium hydroxide [§ 205.605(b)(8)], and calcium phosphate [§ 205.605(b)(9)] are other calcium salts that processors use regularly for calcium fortification (Crowley et al., 2014; Deeth & Lewis, 2015).

Calcium citrate and calcium phosphate can affect skim milk heat stability (Crowley et al., 2014). In contrast, calcium carbonate demonstrated no effect on skim milk heat stability. In prebiotic ice cream, scientists found that calcium citrate was a suitable alternative to calcium chloride as a source of calcium (Saremnezhad et al., 2020). Both materials offered consumers similar levels of dietary calcium fortification in combination with acceptable flavor and texture. Neither material negatively impacted the production process.

In fortified pita bread, consumers had similar sensory tolerance for calcium carbonate and calcium citrate (Ziadeh et al., 2005). These salts are available in domestic and global markets, as processors use these salts for dietary calcium fortification worldwide (Palacios et al., 2021).

The human health impact of dietary calcium fortification in the modern diet remains unclear. Generally, dietary calcium fortification aims to alleviate chronic conditions linked to hypocalcemia and the weakening of bones. It is unclear if hypercalcemia is a possible side effect of high levels of dietary calcium fortification observed in modern diets (Palacios et al., 2021).

Calcium sulfate [§ 205.605(a)(8)] as a pH control agent and brewing water additive

Calcium is important for controlling pH and oxalate formation in beer production (Eumann, 2006). Calcium sulfate is another form of calcium commonly added to brewing water. However, the choice between calcium chloride and calcium sulfate as a pH control agent is sometimes influenced by the choice of beer style (Maltman, 2021).

Other tenderizer/texturizer agents

Sodium chloride (allowed through exclusion at § 205.301) is a traditional tenderizing and texturizing agent for meat (T.-K. Kim et al., 2021). Nurmahmudi and Sams (1997) demonstrated that both calcium chloride and sodium chloride injected brines of similar conductivity levels yielded similarly tender chicken breast fillets, as reported by shear value. However, recent trends in human health guidance and subsequent consumer preference advocating for lower levels of dietary sodium chloride may limit some applications (T.-K. Kim et al., 2021).

Lactic acid [§ 205.605(a)(1)] can tenderize meat via marination or injection (Bhat et al., 2018). Lactic acid affects muscle pH (Shi et al., 2021). Sour flavor and grey color that can develop in meat with pH values below 5.0 may limit consumer acceptability of meat tenderized with lactic acid (Berge et al., 2001).

Lactic acid is available in domestic and global markets (Abedi & Hashemi, 2020). Lactic acid currently does not raise safety concerns for human health (Silano et al., 2018). The environmental impact of lactic acid in meat processing applications is also low, as long as wastewater is processed to counteract low pH.

<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)].

We found no evidence in the literature of an agricultural material that can fulfill any of the equivalent roles of calcium chloride.

Report Authorship

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

- Peter O. Bungum, Research and Education Manager, OMRI
- Colleen E. Al-Samarrie, Technical Research Analyst, OMRI
- Jarod T Rhoades, Standards Manager, OMRI
- Tina Jensen Augustine, Technical Department Operations Manager, OMRI
- Aura del Angel A Larson, Bilingual Technical Research Analyst, OMRI
- Doug Currier, Technical Director, OMRI
- Meghan Murphy, Graphic Designer, OMRI
- Ashley Shaw, Technical Assistant, OMRI

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

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