Calcium Chloride

crops

Executive Summary

The petition is for the use of calcium chloride to include low concentrations in solution to be applied as a foliar nutrient spray to crops and plants other than apples. NOSB originally voted to allow this material for use to control bitter pit in apples, and as an emergency defoliant for cotton. This material was considered nonsynthetic, and was not included in the list of allowed synthetic materials at 7CFR 205.601 or as a prohibited nonsynthetic at 205.602.

Calcium chloride can be produced from a number of sources by various methods. Some of these are naturally occurring, some require extraction and beneficiation that is not considered by most reviewers to be a chemical reaction, and some are entirely synthetic. Those extracted from brine are generally considered nonsynthetic, although certain steps to purify the brine may be considered synthetic. Productions by the Solvay process and by reaction of a calcium source with hydrochloric acid are both clearly synthetic.

All the reviewers concluded that the material is inappropriate for soil application given the high chloride content and high solubility. Two of the three reviewers would prohibit all production uses except for foliar applications to correct nutritional deficiencies. All three reviewers agree that natural sources of food-grade calcium chloride should be allowed as a postharvest dip. One would support adding synthetic food-grade sources to the National List for postharvest treatment.

Summary of TAP Reviewer Analysis[1]

Synthetic or Nonsynthetic	Can be obtained from either Synthetic or Nonsynthetic sources (3)

Allowed or Prohibited

Possible National List Section	***Synthetic or Nonsyntheti c***	***Add to National List?***	***Suggested*** *Annotation*
205.601(j) as plant or soil amendments	List as synthetic	No (3)	None: Two reviewers supported a requirement for nonsynthetic sources when used for fertility amendment. One reviewer did not support any use as fertility amendment.
205.601(*l*) floating agents, postharvest	List as synthetic	Yes (1)	One reviewer considers synthetic forms acceptable for postharvest treatment, could be listed in crops section under floating aids.
205.602 prohibited nonsynthetics for use in crop production	List as nonsynthetic	Yes (3). List as prohibited nonsynthetic, with restrictions that allow use.	(2) Prohibited—unless nonsynthetic brine sources are used for foliar application at minimum concentrations required or food-grade source are used for postharvest handling (1) Prohibited unless nonsynthetic brine food-grade sources are used postharvest only.

[1] *This Technical Advisory Panel (TAP) review is based on the information available as of the date of this review. This review addresses the requirements of the Organic Foods Production Act to the best of the investigator's ability, and has been reviewed by experts on the TAP. The substance is evaluated against the criteria found in section 2119(m) of the OFPA [7 USC 6517(m)]. The information and advice presented to the NOSB is based on the technical evaluation against that criteria, and does not incorporate commercial availability, socio-economic impact, or other factors that the NOSB and the USDA may want to consider in making decisions.*

Identification

Chemical Names:
calcium chloride anhydrous, calcium chloride dihydrate

Other Name:
anhydrous: calcium dichloride

Trade Names:
anhydrous: Briners Choice™
dihydrate: DowFlake™, Tetra 80™

CAS Numbers:
anhydrous: 10043-52-4
dihydrate: 10035-04-8

Other Codes:
dihydrate: EINECS 233-140-8
INS #: 509 (doesn't specify type)

Characterization

Composition:
Anhydrous: $CaCl_2$

Calcium chloride also forms mono-, di-, tetra-, and hexa-hydrates (Budavari, 1996). The dihydrate is sold as DowFlake™ or Tetra 80™, and the anhydrous material is available in pellet form as Briners Choice™. Freshly prepared solutions are alkaline due to the presence of a small amount of lime (0.2%). The purified product isolated from brine contains up to 4% magnesium and alkali salts, mostly sodium chloride (Kemp and Keegan, 1985; Dow, 2001).

Properties: It is a white, odorless, salt that reacts with water forming hydrates. It is cubic crystals, granules, or fused masses (Budavari, 1996) found in both anhydrous and dihydrate forms. Anhydrous forms readily hydrate. Both the anhydrous salt and the hydrates release heat as they pick up water. The heat released is useful in melting ice and snow, and the material is used commercially as a de-icer. Calcium chloride is extremely soluble in water, and very concentrated solutions are possible. Calcium chloride is also used as a dust suppressant on dirt and gravel roads (Kemp and Keegan, 1985).

How Made: Calcium chloride can be obtained by extraction of nonsynthetic brines. When calcium chloride is extracted from a nonsynthetic source, its molecular structure is not changed during extraction and thus should be classified nonsynthetic. However, Dow (the major supplier) and other producers use synthetic chemicals during the purification of the brine, as discussed below.

Hydrochloric acid method
Calcium chloride is produced industrially by at least three methods. In one process, hydrochloric acid is added to calcium carbonate, producing calcium chloride and carbonic acid:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + H_2CO_3$$

This is a synthetic process (Krohn et al., 1987). Potentially, this method can produce material of highest purity, and this is the process used by Tetra Chemicals for most of their production (Mishra, 2001).

Tetra has one production plant in Amboy, California that produces calcium chloride contaminated with large amounts of magnesium chloride and sodium chloride. This is a crude material that is obtained merely by evaporating natural brine, but relatively small amounts are available, and in California only. Purer versions of this are available only by processing with lime in a process similar to Dow's (Funke, 2001). According to Surin Mishra of Tetra Chemicals, it is impossible to obtain high purity calcium chloride from a nonsynthetic source without processing with lime to remove the magnesium (Mishra, 2001).

Solvay Process
The Solvay process involves five reaction steps that use ammonia, sodium chloride, calcium carbonate, and water as initial reactants (Oxtoby, Nachtreb, and Freeman, 1990).

Sodium bicarbonate is decomposed thermally to produce sodium carbonate, water, and carbon dioxide:

(1) $NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

Calcium carbonate is heated to form lime and liberate carbon dioxide:

(2) $CaCO_3 \rightarrow CaO + CO_2$

The lime is then slaked to form hydrated lime:

(3) $CaO + H_2O \rightarrow Ca(OH)_2$

Ammonia is reacted with salt and carbon dioxide in an aqueous solution to form sodium bicarbonate and ammonium chloride:

(4) $NH_3 + 2NaCl + 2\ CO_2 + 2H_2O \rightarrow 2NHCO_3 + 2\ NH_4Cl$ *(aq)*

In the final step, ammonium chloride and calcium hydroxide are reacted to form sodium carbonate and calcium chloride:

(5) $2NH_4Cl + Ca(OH)_2 \rightarrow Na_2CO_3 + CaCl_2$

The net reaction yielding calcium chloride is represented as:

$NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2$

<u>Dow Process</u>

The third process is the Dow process, which accounts for 75% of the calcium chloride production in the U.S. (Kemp and Keegan, 1985). The starting material is a natural brine solution that is pumped out from underground salt beds. The liquid brine contains about 8-16% CaCl2, 3-4% MgCl2, 8-16% NaCl, 1-2% KCl, and 0.1-0.3% bromide (Mavity, 1978).

If the crude brine containing calcium chloride were used directly along with its impurities, it would be nonsynthetic. Whether or not the material is synthetic or nonsynthetic then relates entirely to the nature of purification.

In the Dow Process, the brine contains calcium, magnesium, sodium, chloride, and bromide ions. In an older process, electrolyis was used to get rid of bromide. Now, the salt solution is first treated with chlorine gas to oxidize bromide to bromine. The bromine is then blown out of the solution with air and collected as free bromine or as bromide (Smith, 1939; Hooker, 1939). A synthetic material, chlorine gas, is used in the purification process, but this is removed by heating of the brine before calcium chloride is isolated (Althouse, 2001).

At this point, calcium chloride from the natural brine is unchanged chemically, so it could still be considered a nonsynthetic material. However, it has been purified by using a synthetic chemical.

The solution is then treated with calcium oxide, making the briny solution alkaline (Collins, 1932). The added calcium oxide is obtained from the nonsynthetic material limestone ($CaCO_3$) by heating. Although the source of the CaO is nonsynthetic, the molecular structure of the mined limestone is changed by heat, and is thus the lime has to be characterized as a synthetic by the OFPA definition. When lime is added to the solution of brine, insoluble synthetic magnesium hydroxide precipitates and is filtered off. Some of the added lime remains in the brine (0.2%), and is isolated with the final calcium chloride product (Althouse, 2001).

The brine solution is then concentrated further by evaporating water. Since sodium chloride is less soluble than calcium chloride, it precipitates, and then is filtered off. The nonsynthetic calcium chloride is unaffected by this step (Althouse, 2001).

The remaining solution is concentrated by boiling in open kettles, then by heating in a rotating heated drum flaker. Flakes containing calcium chloride dihydrate are produced, containing 77-80% calcium chloride (Smith, 1928). This is Dowflake™ (Althouse, 2001).

To get a more anhydrous product, the concentrated solution is dried in the presence of hot solid flakes (Bennett and Carmouche, 1953). "The solution thereby becomes distributed on and absorbed by particles that assume the form of pellets." Pellets contain 90-92% calcium chloride. These are then dried to minipellets containing 94-97% calcium chloride (Althouse, 2001).

ASTM standards of purity for calcium chloride are <8.0% NaCl, <0.5% $MgCl_2$, and <1% other impurities.

Food grade standards are for the anhydrous material: not less than 93% $CaCl_2$; arsenic <3 ppm; fluoride <0.004%; heavy metals <10 ppm; magnesium and alkali salts <5%; and acid insoluble matter <0.02% (Reid and Kust, 1992).

Dowflake™ calcium chloride dihydrate is at least 96% calcium chloride dihydrate. The major impurity is magnesium and alkali salts <4%. Most of this is sodium chloride. Other impurities are: arsenic <3 ppm; fluoride <.004%; heavy metals <.002%; calcium hydroxide <0.2%; and iron <0.003% (Dow, 2001).

Briners Choice™ (Dow) is 90% calcium chloride, 3 ppm arsenic, 0.004% fluoride, 0.002% heavy metals, 10 ppm lead, <5% magnesium and alkali salts, 50 ppm iron, 0.2% lime, and 0.5% water insoluble impurity (Dow, 2001).

<u>Specific Uses</u>: Calcium chloride has been manufactured and sold for over 100 years. Uses other than agriculture are mainly de-icing, drying agent, dust control, as an accelerant in concrete, in oil well drilling, in animal feed, for food processing, and as a process chemical for chemical production. U.S. consumption is about 600,000 to 700,000 tons a year (Reid and Kust, 1992).

Control of Physiological Disorders: In agriculture, calcium chloride has been used to manage about 35 different physiological disorders of plants. Annual sprays of $CaCl_2$ increased yields of Anjou pears and decreased incidence of alfalfa greening and cork spot (Raese and Drake, 1996). Late season sprays of $CaCl_2$ reduced cork spot and increased yields of pears (Raese et al., 1994). Four sprays in a season on Bartlett pears increased yields and reduced incidence of black end by 25-68% (Raese and Sugar, 1994).

Bitter pit of apples was slightly reduced by sprays, but considerably reduced by a 30-40 second dip of 1-4% $CaCl_2$ (Kokkalos, 1996). Foliar calcium and magnesium chloride sprays helped control grape stem dieback, although magnesium sulfate turned out to be more effective (Boselli and Fregoni, 1986).

Sprays of developing fruit on fig trees reduced the susceptibility to fruit cracking (Aksoy et al., 1994). Sprays of 0.5% $CaCl_2$ solutions have been used to reduce rain cracking in sweet cherries. Three applications at weekly intervals before harvest were suggested (Rupert et al., 1997; Alexander, 1986). However, Looney (1985) found calcium sprays did not meet expectations for prevention of cherry fruit cracking in British Columbia. Also, calcium chloride did not provide protection from botrytis or result in any quality differences—positive or negative—in strawberries in a series of trials conducted in Ohio (Erincik, Madden, Scheerens, and Ellis, 1998).

Calcium chloride reduced physiological disorders of lettuce when sprayed once or twice a week before head formation (Alexander, 1986). Aqueous sprays containing $CaCl_2$ reduced blossom end rot of tomatoes and increased marketable yields (Wada et al., 1996). Sprays were timed for bud formation of first cluster, beginning of flowering of first cluster, and weekly spraying at the fruitlet stage (Alexander, 1986). Foliar applications of calcium reduced tipburn on Chinese cabbage (Marota et al., 1986).

Postharvest Treatments: A 5-minute dip of LeConte pears in 2% $CaCl_2$ increased shelf life and reduced decay (Akl et al., 1995). Calcium chloride has been used as a postharvest spray in pears to control brown core, cork spot and superficial scald (Raese and Drake, 2000).

Highbush blueberry firmness has been improved by postharvest applications of calcium chloride (Hanson et al., 1993). Calcium chloride treatment of grapes reduced postharvest rot (Babalar et al. 1999). Calcium chloride extended storage life of mango (Sanjay et al., 1998). Preharvest sprays reduced postharvest decay of grapefruit (Salem et al., 1991).

Postharvest treatment of apples reduced decay and storage breakdown of apples (Scott and Wills, 1975). Dipping apples in $CaCl_2$ solutions reduced the incidence of bitter pit in stored apples (Scott et al., 1980). Smaller apples were more resistant to postharvest decay and breakdown than larger apples after postharvest dips in calcium chloride (Lidster et al., 1978).

Foliar Sprays to Increase Yields: Yields of pears are increased by foliar sprays of $CaCl_2$ (Raese and Drake, 1996; Raese et al., 1994; Raese and Sugar, 1994). The petition states that foliar sprays of calcium chloride applied to corn, soybeans, and a number of other crops can increase yields (BioGard, 2001). The reviewers did not find any studies to support this.

A number of studies show crop responses to foliar calcium, but these are not necessarily based on experiments with the chloride form. For example, a spray that contained calcium oxide increased yields and average fruit size of tomatoes (Gezerel, 1986).

Action: Application of foliar calcium sprays relieves calcium physiological disorders because these are local deficiencies due to calcium transport problems. Local availability of calcium in new shoots and fruits can help solve the problem (Kirkby and Pilbeam, 1984; Hanson, 1984).

Combinations: The petitioner listed this as confidential business information.

Status

Historic Use: Calcium chloride was discovered as early as the 15th century, but received little attention until the late 18th century. Commercial quantities were not available until the discovery of the Solvay process in the mid-1800s. It has been used for ice and dust control, in oil well drilling, in food processing and as accelerant for hardening in concrete (Kemp and Keegan, 1985). Uses in agriculture are reviewed above under "Specific Uses."

OFPA, USDA Final Rule:
Not listed in the Final Rule under the crops sections of "synthetic substances allowed" or "nonsynthetic substances prohibited." [The NOSB recommendation at Indianapolis meeting in 1996 was "nonsynthetic—extracted from brine.

Allowed for use to correct bitter pit problems in apples; allowed for use to comply with emergency spray programs (cotton desiccant) or to prevent immediate crop loss."]

Listed in the processing section at 205.605(a)(4): nonsynthetics allowed.

Section 205.203(d) states: "A producer may manage crop nutrients and soil fertility to maintain or improve soil organic matter content in a manner that does not contribute to contamination of crops, soil, or water by plant nutrients, pathogenic organisms, heavy metals, or residues of prohibited substances by applying: . . . (3) A mined substance of high solubility, *Provided*, That, the substance is used in compliance with the conditions established on the National List of nonsynthetic materials prohibited for crop production…."

Section 205.206(d) states: "Disease problems may be controlled by . . . (2) Application of non-synthetic biological, botanical, or mineral inputs."

Regulatory: EPA/NIEHS/Other Sources

EPA – Not regulated.

NIEHS – It is not listed by the NIEHS as a problem chemical. There are no occupational exposure limits established by OSHA or NIOSH.

Other Sources –
Not Listed on Extoxnet. Not listed as a carcinogen by EPA, IARC, NTP, OSHA or ACGIH. NFPA Rating: Health = U; Fire = 0; Reactivity = 1.

Status Among U.S. Certifiers

California Certified Organic Farmers (CCOF) –CCOF Certification Handbook (rev. January 2000): §8.3: Natural sources only. Prohibited for soil application because of very high chloride content. May be used as a foliar spray to correct bitter pit in apples. May be used as a cotton desiccant only in cases of weather emergencies and to meet government mandated plowdown dates. May be used as a dust suppressant in non-crop areas, and is cross-referenced with other dust suppressants.

Maine Organic Farmers and Gardeners Association (MOFGA) –2000 materials list has no specific mention of calcium chloride. List does say "not permitted - Highly soluble nitrate, phosphorus, and chloride whether natural or synthetic."

Midwest Organic Services Association (MOSA) – 1999 materials list states allowed for use to correct bitter pit in apples, and as emergency spray desiccant for cotton.

Northeast Organic Farming Association of New Jersey (NOFA-NJ) – 2001 lists as regulated - calcium chloride based foliar materials.

Northeast Organic Farming Association of New York (NOFA-NY) –2000 edition—mineral amendments: For calcium sources, regulated: calcium chloride based foliar materials.

Northeast Organic Farming Association of Vermont (NOFA-VT) – 1999 lists calcium chloride based foliar materials as regulated.

Oregon Tilth Certified Organic (OTCO) – OTCO Generic Materials List (April 30, 1999), Fertilizers and Soil Amendments: May be used to correct bitter pit problems in apples. May be used as a cotton desiccant for compliance with emergency spray or to prevent immediate crop loss in cotton. Natural sources only. Discouraged for soil application because of very high chloride content. Document need. As Crop Production Aids, Dust Suppressants, Regulated: Calcium chloride, magnesium chloride, emulsified plant resins, and tall oils. Long term use is discouraged. Not allowed for the suppression of roadside vegetation.

Organic Crop Improvement Association International (OCIA) – OCIA International Certification Standards, Section 9.3, Crop Production Materials List: Natural sources only. For foliar use to correct bitter pit in apples. Prohibited for soil application because of very high chloride content. May be used as a cotton desiccant only in cases of government declared weather emergencies to meet mandated plow down rates. May be used as dust suppressant in non-crop areas.

Texas Department of Agriculture (TDA) Organic Certification Program – TDA Organic Certification Program Materials List; Crops: Natural sources only. For foliar use to correct bitter pit in apples only. Prohibited for soil application because of very high chloride content. May be used as a cotton desiccant only in cases of government declared weather emergencies to meet mandated plow down dates. May be used as dust suppressant in non-crop areas.

Washington State Department of Agriculture Organic Food Program – Chapter 16-154 WAC Organic Crop Production Standards, WAC 16-154-070. Listed in the section titled "Fertilizers, growth promoters, crop production aids and soil amendments" at points k (calcium chloride) and rr (under mined minerals) as an approved material with no annotations.

International

CODEX – Listed in Annex 2, Table 3 with specific conditions: milk products/fat products/fruits and vegetables/soybean products.

EU 2092/91 – Listed in Annex II, Part A, Products and by-products of plant origin for fertilizers, Calcium chloride solution. Foliar treatment of apple trees, after identification of deficit of calcium. Need recognized by the inspection body or inspection authority.

IFOAM – Listed in Section C, Appendix 1: "Products for Use in Fertilisation and Soil Conditioning" under minerals, with no restriction on use.

Canada – Listed for use in A3.1.2 Pest Management as calcium chloride, naturally derived.

Japan – Listed in the Notification No. 60 of the Ministry of Agriculture, Forestry and Fisheries, Table 1 concerning processed foods: Limited to be used for coagulating agent or used for edible fat and oil, vegetable processed products, fruit processed products, or processed products of beans. Not listed in the crops tables.

Section 2119 OFPA U.S.C. 6518(m)(1-7) Criteria

1. *The potential of the substance for detrimental chemical interactions with other materials used in organic farming systems.*
   Calcium chloride, when used as a foliar spray or a postharvest dip, probably has low potential for interaction or interference with other materials used in organic farming.

2. *The toxicity and mode of action of the substance and of its breakdown products or any contaminants, and their persistence and areas of concentration in the environment.*
   Calcium chloride has low toxicity to mammals. The acute oral LD50 in rats is 1,000 mg/kg. However, contact with skin can cause irritation. The dust can irritate eyes, and breathing the dust can irritate the nose, throat, and lungs (Kemp and Keegan, 1985; Pestline, 1991).

   As a foliar spray, it has minimal effects on insect populations (Abdel et al., 1998). It should not affect beneficial insects. It should not persist on foliage. Any not absorbed by the plant should be washed off with rain. Calcium chloride is extremely soluble in water, and low concentrations from foliar use should not build up in soil, unless it is used in low rainfall areas with minimal irrigation. Any water-soluble calcium or chloride not absorbed by plant roots would drain into surface waters or be leached into groundwater.

3. *The probability of environmental contamination during manufacture, use, misuse, or disposal of the substance.*
   During manufacture from brines, the liquid brines are pumped out from underground, and do not present the kind of problem usually seen with strip mining. The only toxic chemicals involved are chlorine and bromine, and they are handled so that environmental contamination is low. The chlorine is recycled, and bromine is isolated as bromide or bromine and is sold as a chemical product.

   Excess lime added in processing is isolated as part of the final calcium chloride. The magnesium hydroxide produced is used to prepare other magnesium salts and magnesium metal by electrolysis. It is not dumped into the environment. The sodium chloride isolated in the process is sold as table salt or for chemical production. Spent solutions are recycled and pumped back underground to isolate a new concentrated brine (Althouse, 2001).

   Disposal of spent solutions after postharvest dips could be a problem. These are initial dilute 1-4% solutions, within the capacity of wastewater treatment plants. When the treated water is released into surface waters, there could be a transient spike of chloride and calcium ions. Large spills in water could be hazardous to fish, if concentrations reach 10,000-20,000 ppm (Kemp and Keegan, 1985). Effluent from a packing house would need to be diluted to concentrations of acceptable levels before it could be discharged into surface waters. Both calcium and chloride are considered dissolved solid pollutants reportable under 40 CFR 403.12(g)(2) (US EPA, 1995).

   The greatest environmental contamination comes from its use on roads for snow and ice control or as a dust suppressant. However, "high chloride concentrations are seldom found in U.S. water supplies, even in areas of high salt usage for dust and ice control" (Kemp and Keegan, 1985). Calcium chloride is not classified as hazardous by DOT and is not subject to specific handling requirements. It is transported by truck and railcar in solid form, and also is transported as a liquid solution (Kemp and Keegan, 1985).

4. *The effects of the substance on human health.*
Calcium chloride is not generally considered toxic. The acute oral LD50 in rats is 1,000 mg/kg. However, contact with skin can cause irritation. The dust can irritate eyes, and breathing the dust can irritate the nose, throat, and lungs. Chronic contact with dust in an occupational setting can lead to dermatitis (Kemp and Keegan, 1985; Pestline, 1991).

Calcium is an essential element for life, and the human dietary need is about 1g per day. It accumulates in bones and is needed to establish action potentials for nerve conduction. In medicine, 2-5% intravenous solutions of calcium chloride are used as an antispasmodic and to combat tetany. Injections into muscle can cause damage and tissue necrosis, and solutions given orally can irritate the gastrointestinal tract (Kemp and Keegan, 1985).

It could be a problem in drinking water, as levels of 150 ppm can be tasted, and 50 ppm can cause hardness in water. Seawater has about 400 ppm calcium.

5. *The effects of the substance on biological and chemical interactions in the agroecosystem, including the physiological effects of the substance on soil organisms (including the salt index and solubility of the soil), crops and livestock.*
Plants need shoot concentrations of about 0.5% calcium for adequate growth. The figure for chloride is about 100 mg/kg. The ability of plants to take up calcium chloride and its toxicity to plants varies widely. Low levels of chloride can inhibit plant growth, and problems with plants are mostly due to the chloride ion (Reid and Kust, 1992; Greenway and Munns, 1980). Concentrations in excess of 1,000 ppm can retard plant growth (Kemp and Keegan, 1985).

Calcium chloride obtained from natural salt brines has a significant amount of sodium chloride, usually about 3-4%. Sodium chloride has a high salt index and should not be applied to soil (Rader, et al., 1943). Calcium chloride may have a high salt index, but there is no published salt index for it. Application to soil could lead to chloride phytotoxicity (Greenway and Munns, 1980).

6. *The alternatives to using the substance in terms of practices or other available materials.*
If apples are quickly chilled before storage, the incidence of bitter pit is less, but is not as low as with calcium treatments (Scott et al., 1980).

Since bitter pit of apples is a calcium deficit disorder, an alternate form of calcium, such as limestone, gypsum, or rock phosphate, could be used.

7. *Its compatibility with a system of sustainable agriculture.*
Use of calcium chloride to stop physiological diseases of apples, pears, tomatoes and other crops is compatible with a system of sustainable agriculture. Well-focused foliar sprays to correct calcium deficiencies would be compatible with a system of sustainable agriculture.

TAP Reviewer Discussion[2]

Reviewer 1 [Organic farmer, organic inspector, works with organic certifier; West Coast]

Response to the Criteria Points

*[Calcium chloride d]*oes not create waste products or contaminate the environment. It is unusually clean for a mining operation. . . *[It is]* not harmful to human health. . . It is highly soluble and does increase the salt index. Alternatives exist but are not as effective. . . It is compatable with sustainable agriculture. . . It should be allowed with annotation limiting its use to foliar or low quantity applications. . . . Annotation should be made limiting the quantity used. Foliar applications should be allowed, postharvest dips and cotton defoliation. The problems associated with the use of $CaCl_2$ are directly related to the quantity used.

Alternatives

1. There are alternative methods of providing calcium to crops and for postharvest handling. In some cases, calcium chloride is the most effective way to prevent disease. One example is its use on apples as a foliar spray and as a postharvest dip to protect against bitter pit. This has already been approved by the NOSB.

2. Although there are alternatives for providing calcium to crops, in some situations, calcium chloride is the only effective material that prevents certain diseases.

[2] *OMRI's information is enclosed is square brackets in italics. Where a reviewer corrected a technical point (e.g., the word should be "intravenous" rather than "subcutaneous"), these corrections were made in this document and are not listed here in the Reviewer Comments. The rest of the TAP Reviewer's comments are edited for any identifying comments, redundant statements, and typographical errors. Text removed is identified by ellipses […]. Statements expressed by reviewers are their own and do not reflect the opinions of any other individual or organizations.*

Compatibility
A. Reasons for compatibility
1. It can be considered at natural occurring mined material.
2. It is a safe material to use (see criteria ratings)

B. Reasons for incompatibility
1. It is highly soluble and could raise the salt index if applied in high concentrations.

[Reviewer 1] Summary/Conclusion
This material has had restrictions placed on it due to its high solubility and salt content, which is similar in some ways to synthetic fertilizers, and also because the concentration and purification process could be considered creating a synthetic material. The high solubility could be a problem if used in large quantities as a soil amendment. Therefore <u>maintaining restrictions on the amount used and the method of application is appropriate for organic agriculture</u> *[emphasis is the reviewer's]*. The method and applicability of measuring the salt index is uncertain and may best be left to the farmer to decide based on phytotoxic reactions on the crops. The definition of whether the material is synthetic or naturally occurring loses some relevance once the appropriate use of the material is considered. Calcium Chloride could *[be]* considered naturally occurring or synthetic and have the same restrictions applied to it in either category and still be appropriate for use in organic agriculture. Placing it under prohibited nonsynthetic with annotations insures that its use will be limited. My primary reason for reducing the former restrictions on the material is how well it fits the criteria for any material's compatibility in organic production. The material is safe and effective if used properly.

<u>Reviewer 2</u> [Ph.D. environmental toxicology, M.S. chemistry; East Coast]
Evaluation Criteria
. . . Unless the *[concentration]* of $CaCl_2$ is excessive enough to increase the salinity of the soil or soil solution, such as seen at 1000 ppm in a region where rainfall was infrequent or negligible, (Al-Saidi, *et al.*, 1988), this should not be a problem… I have misgivings about the use of $CaCl_2$ of low purity. We need to require a certain level of purity of $CaCl_2$, perhaps food grade.

. . . From some unpublished analyses that I have had performed on soils collected from alongside of roadways, I have found that there is a higher than background concentration of cadmium and arsenic in the soils. The frequency and application rates of the $CaCl_2$, if allowed for foliar applications, have potential for heavy metal contamination, although I do think that it would be minimal. A food grade level of $CaCl_2$ should be used, if any.

I don't see supporting evidence that this is entirely compatible. It appears that one of the reasons that Ca is deficient in the organs of certain fruits is that breeds of crops have been introduce to maximize fruit yield. If the deficiency is dependent on variety of fruit, would it behoove us to promote the use of varieties that do not exhibit the deficiencies? . . . Bhat et al. (1993) indicate that calcium deficiency disorders in pear are caused by unbalanced distribution of Ca in the plant and not due to poor uptake. If Ca deficiency is a universal problem that cannot be corrected using other organic practices, then I do think that foliar feeding should be reconsidered. . . Raese and Drake (1996) indicate that there is only minor, acceptable, [levels of] phytotoxicity associated with repeated spraying by $CaCl_2$, as well as improvement to the fruit. However, Looney (1985) saw cherries were not benefited by tree spraying using $CaCl_2$. I think that the use of this material, postharvest is still the best consideration.

[Reviewer 2] Conclusion:
This conclusion is based on the information and references that were provided. Unfortunately, I did not have the capability to do an extensive literature search of my own, which I would have preferred to do. I believe, based on the provided information, that the nonsynthetic form, that is, brine extracted calcium chloride, should be allowed to be used postharvest as a dipping agent to prevent spoilage in fruiting crops. I do not think there should be a stipulation on which crops should be permitted to use this agent. I do think that the purity of the material should be at least food grade, as indicated in the Characterization portion of this document.

There is evidence that calcium chloride as a foliar applicant improves calcium levels in plants, and thereby prevents fruit deterioration. However, there may be other sources of calcium that are less likely to induce a negative plant response. I recommend that it be not used as a foliar applicant, if an alternative source of calcium can be allowed, for that use, in the federal rule.

There are both synthetic and non-synthetic sources. I would allow the "brine extract" for postharvest fruit drip.

Reviewer 3 [technical services to organic and sustainable growers, M.S. agronomy; Midwest]

OFPA Criteria

1. The only possible interactions that might concern me in an agronomic setting might occur if calcium chloride were tank-mixed with another trace mineral salt—perhaps a sulphate. The concern here might be precipitation or some other negation of the purpose of the spray being mixed. I doubt that any harmful toxic or synergistic action might result in such a case, and it would be largely a matter of inconvenience to the grower.

2. I am in whole-hearted agreement that calcium chloride—when used as a foliar spray—presents almost no toxic or environmental hazards. It must be stressed that this is for foliar applications only, however. While it is doubtful that many producers would elect to use calcium chloride as a significant soil applied material, I question whether we would want that door left open.

3. Do our considerations here also include considerations of use in road dust and ice management? Whether they do or not, the information provided reinforces the notion that this substance presents little to no environmental hazard at the agronomic rates involved in foliar fertilization.

4. It is highly unlikely that anything but serious misuse of this product could have a negative impact on human health at the farm level. Agronomic rates for calcium chloride applied as a foliar spray would not have an impact on calcium levels in local water bodies.

[A condition for use should be:] disposal of spent water solutions from postharvest drips should be disposed of carefully so as not to cause excessive calcium levels in potable water reservoirs.

5. The information presented reinforces the need to stress that calcium chloride should not be permitted for use as a soil-applied material. Rates of use as a foliar feed should be low enough that no toxicity to beneficial organisms should occur. We should remember, that chlorine is, itself, a nutrient. The presence of chloride is not a problem; an imbalance of chlorine is. Most of those imbalances occur when excessive amounts of chloride salts are soil applied and/or climatic conditions lead to accumulation. The case of sodium is similar, while it is not recognized as an essential plant nutrient, a low percentage of sodium in soil solution and on clay colloids is considered beneficial to soil structure. Sodium is also required in animal nutrition.

6. Bitter pit and other physiological conditions that relate to calcium deficiencies can often be rectified through soil management that includes the applications of rock powders such as lime, gypsum & rock phosphate. This is the very correct implication of the statement as it is written. However, weather, native soil conditions, and other factors can conspire to cause deficiencies to occur even when soil levels of calcium are relatively high. Foliar fertilization is then the most efficacious means for rectifying the problem. It should be noted that sprayable forms of all three rock dusts—lime, gypsum, and rock phosphate—are commercially available (Peaceful Valley Farm Supply, 2000). However, while reference is made to their use as foliar fertilizers, I am unfamiliar with their efficacy under field conditions. These may be quite poorly absorbed for all I know. However, according to the *OMRI Generic Materials List* and National List at 205.601(j)(4), calcium lignosulfonate—a form of chelated calcium—is allowed as an allowed synthetic. Chelates have long been used in foliar fertilization and are quite effective, though their cost (in my experience) is often higher than non-chelated sources.

7. I think two points are worth making:
a) One of the basic tenets of organic (and sustainable) farming is that many insect and disease problems have their basis in poor crop nutrition. Physiological problems such as bitter pit and blossom end rot are merely more obvious examples. Applying a foliar fertilizer is an effective and highly efficient way of rectifying such problems using non-pesticidal substances that can have little to no negative environmental impact.
b) Another basic tenet of organics is that crop nutrition begins with feeding the soil; the well-nourished soil then feeds the plant. Foliar fertilization appears to be at odds with this philosophy. I think one can argue, however, that it is not. [The petitioner claims that] foliar fertilization …stimulate[s] beneficial biological activity in the rhizosphere of the plant. This is believed to contribute positively to the soil-building process.

[Reviewer 3] Conclusion

I feel that addition to the National List should be contingent on calcium chlorides use only as a foliar fertilizer to correct nutrient deficiencies and that it not be permitted as a soil additive. I believe it should be permitted as a postharvest dip. It should not be permitted as a cotton harvest aid or as a manure additive, though this might be subject to review in the future when guidelines for use are much clearer.

The TAP Reviewers were also asked the following questions:

Similar questions were posted to the OMRI web site. Where a Reviewer is not mentioned, the Reviewer did not have comments on the question.

1) *Are there any other generic names for calcium chloride?*
None of the Reviewers were aware of any.

2) *Are there other references that need to be considered?*
The Reviewers and some members of the public provided additional references.

3) *Do you agree that calcium chloride is a "mined substance of high solubility"? (The final rule does not define this.)*
All Reviewers agreed with this classification.

4) *a) Based on the descriptions, are all sources synthetic, are any of the sources nonsynthetic, or are they all nonsynthetic?*
All of the reviewers considered some sources to be synthetic and some sources to be non-synthetic. In particular, all sources derived from brine were considered to be non-synthetic by all reviewers. A number of their comments were incorporated in the 'How Made' section of the Review.

Reviewer 1: For this specific situation, the regulated nonsynthetic definition seems most appropriate and least confusing . . . .

b) Does removal of impurities from the natural brine constitute processing that makes the material a synthetic within the meaning of OFPA?
All three reviewers considered Calcium chloride derived from brine to be nonsynthetic.

Reviewer 1 adds: The primary purpose of the processing, including the use of chlorine, is purification of the mined material. If the primary purpose of processing were to create a new material, I would consider the material as synthetic. In this case, $CaCl_2$ is in the parent material and the final product. Even if some of the chlorine atoms in the final product come from added chlorine used in processing, it should still be considered nonsynthetic for regulatory purposes.

c) In particular, given the description of the Dow process, does the process of purification of brine extracts using chlorine gas as described constitute a synthetic reaction as defined by OFPA?
Two of the reviewers considered this to be synthetic, and one considered it to be nonsynthetic.
Reviewer 1: If an organic process is found for processing $CaCl_2$, it should still have restrictions on it.

Reviewer 3:
a) The process . . . which employs hydrochloric acid, is most definitely synthetic.
b) The crude material produced by Tetra . . . is definitely nonsynthetic.
c) The Solvay Process . . . is definitely synthetic.
d) The Dow Process . . . should be judged synthetic. As I read the OFPA 6502 (21), *synthetic* is defined by 'a process that chemically changes a substance extracted.' If the substance extracted is considered to be calcium chloride, the process does not alter it chemically, it only purifies by removing unwanted materials. This would argue for nonsynthetic status except that as part of the Dow process, some quicklime—calcium oxide—is left as residual. The circumstances might be comparable to kelp extracts, which are allowed synthetics because of the use and presence of extractant chemicals.

5) *The National List already has calcium chloride under 205.605(a)(4) as a nonsynthetic allowed in organic handling. In the crops section of synthetics, "flotation agents in postharvest handling" are listed under 205.601(l). Should the synthetic form be considered a 'flotation aid' that needs to be added at 205.601(l)?*

Reviewer 2: I think that this material should be used, in a highly purified form, as a dipping agent, postharvest, for fruit, to increase the storage life. There are several references to support this use. . . However, the synthetic production of this material (the Solvay process, and the Tetra Chemical reaction of calcium carbonate with hydrochloric acid) should not be allowed under organic practices.

Reviewer 3: a) Based on my belief that calcium chloride is a synthetic, it should be removed from 205.605(a)—*nonsynthetics allowed*—and moved to 205.605(b)—*synthetics allowed* for processing purposes.
b) 205.601(*l*) which lists "floating agents." …calcium chloride should be listed under this section as an allowed synthetic.

6) *Are there any uses that are not covered? In particular, the 1996 TAP review and NOSB recommendation considered its use as a cotton defoliant on an emergency basis. Do you have any information on calcium chloride as a cotton defoliant? Should this use as a production aid be considered? Is EPA registration a concern? Does it have a section 3 or is an emergency use or special local need permit required?*
Reviewer 3: Two points:
   a) Unless the NOSB's recommendation is specific and correct, I encourage you to use the term "harvest aid." There are technical differences between desiccants and defoliants. One is used to permit harvest with certain kinds of machinery and circumstances; the alternative favors another. . .
   b) . . . Calcium chloride is not listed either as a fertilizer of pesticide in Meister Publication's *Farm Chemical Handbook* in the 2001, 2000, or 1999 editions. I also scanned through the *Beltwide Cotton Production Research Proceedings*, which span 1956-1965 (also earlier meetings in 1949 and 1950), and find no mention of calcium chloride. I looked further into several general cotton production texts from the 1920s through the 1990s texts, our vertical file research collection, and the few publications we had shelved on organic cotton—again, no mention of calcium chloride. . . .Unless someone can come up with those usage guidelines and find them to involve low rates of application, I would discourage approval of calcium chloride as a harvest aid at this time. There appears to be considerable literature on thermal defoliation/desiccation suggesting that nonchemical harvest aid alternatives are available. Please note that I've included three enclosures—2 from organic cotton sources and one from a recent text on cotton production that reinforce the absence of mention of calcium chloride as a harvest aid.

7) *Please provide more information on interactions (OFPA question 5) with other materials used in organic farming. This was also another ingredient added to poultry litter to decrease ammonia volatilization. It sequesters ammonia in the form of ammonium chloride.*
Reviewer 3: . . .*[C]*alcium chloride *[is used]* as a manure additive to reduce volatilization (Heck, 1931). . . *[This reference]* cites work done mostly in Scandinavian countries in 1919 and the 1920s. More documentation comes from two publications from Sweden on chicken slurry (Witter, 1991), and from Netherlands, Denmark, and France on hogs (van der Peet-Schwering, et al., 1999) . . . The latter publication deals with feeding calcium chloride to hogs to control emissions and may not be relevant. However, the former deals with application of calcium chloride to both aerobic and anaerobic slurries and suggests *[that]* a chemical reaction that might well occur within an organic context. *[Witter, 1991 shows a]* chemical reaction . . . *[that explains]* how conservation of ammonia results. Calcium carbonate is among the precipitates, and free chloride ions result. There is nothing in this reaction that suggests a problem in an organic system where calcium chloride is applied at rates recommended for foliar fertilization. An issue might be raised in the future, however, regarding whether or not calcium chloride might be used to conserve ammonia in fresh manure in confinement of semi-confinement animal production. Since this would . . . *[increase the]* chlorine content *[of manure]*, it would raise the same question about management to avoid chlorine imbalances in the field.

8) *Please expand on OFPA question six. The petitioner describes many uses (see page 3 of the petition). What are alternatives? Why is calcium chloride beneficial over other alternatives?*
Reviewer 2: If chloride is such a problem, then delivering *[chloride]* in a ratio of 2 to 1 to the calcium ion, foliarly, will not be a good idea.

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