Calcium Hydroxide

Handling/Processing

Identification of Petitioned Substance

Chemical Names:
Calcium hydroxide

Other Names:
Cal, Caustic Lime, Hydrated Lime, Limewater, Milk of Lime, Pickling Lime, Slaked Lime, Loeschkalk, Calcerea caustica, Calcium dihydroxide

Trade Names:
Nixtacal, VitaCal

CAS Numbers:
1305-62-0

Other Codes:
INS: 526
CHEBI: 31341
EPA PC Code: 075601
PubChem Compound ID: 14777

Summary of Petitioned Use

Calcium hydroxide appears on the National List of nonagricultural (nonorganic) synthetic substances allowed as ingredients in or on processed products labeled as "organic" or "made with organic (specified ingredients or food groups)" at 7 CFR 205.605(b). The National Organic Standards Board (NOSB) is reviewing this listing of calcium hydroxide as part of the sunset process.

Characterization of Petitioned Substance

Composition of the Substance:

Calcium hydroxide dissociates in water as Ca^{++} and 2 OH^{-} (Johnston & Grove, 1931). Food grade calcium hydroxide contains a minimum of 95% $Ca(OH)_2$ (FCC, 2022). Inorganic impurities of concern are arsenic, with a limit of 3 mg/kg (0.0003%) to meet food grade, lead, with a limit of 2 mg/kg (0.0002%), fluoride, with a limit of 0.0005%, magnesium and other alkali salts, with a limit of 4.8%, and carbonate, with no more than slight effervescence[1] to hydrochloric acid (FCC, 2022). Another noted impurity is iron (Lewis, 2016).

Source or Origin of the Substance:

Calcium hydroxide is made from mined limestone, which is mostly calcium carbonate, in what is roughly a two-step process (Oates, 2010). The limestone, sometimes simply referred to as mined or raw lime, is heated to make calcium oxide, or quick lime. The quick lime is then hydrated with water to form slaked lime, or calcium hydroxide. Slaked lime may be purchased already prepared in liquid or powder form, or it may be made *in situ* from quick lime. The process is described in detail in Evaluation Question #2.

Unless otherwise specified, the term "lime" in this report refers to food-grade calcium hydroxide, either pre-hydrated or prepared at the location of food processing by hydrating food-grade calcium oxide. Limestone quarrying, lime kilning, and slaking are all ancient industries that span different civilizations and cultures, and the products engender a wide range of applications. Thus the terminology that has evolved is often confusing (Kenny & Oates, 2007). A further explanation on the specific terminology in this technical report may be useful, especially for those who are most familiar with the common uses of the words "lime" and "liming" in organic agriculture and soil management.

[1] The carbonate content of a mineral can be quantified by the amount of weight lost or CO_2 generated resulting from the addition of hydrochloric acid to the material (Kennedy & Woods, 2013). Effervescence refers to the bubbling that occurs when the CO_2 gas is released.

Those in the lime and limestone manufacturing industry use the generic term “lime” to refer to both calcium oxide (quick lime) and calcium hydroxide (slaked lime) (Oates, 2008). Many agricultural and soil science sources regard “lime” in the strictest sense to refer only to calcium oxide (Brady, 1984; Herren & Donahue, 1991). However, within the organic agriculture community, “lime” has long been used to refer to “stone lime” or calcium carbonate (Parnes, 1990; Rodale, 1961). The generic term “lime” is also used in agriculture to refer to any substance used to raise soil pH (Dalal-Clayton, 1981). This may include mined limestone, chalk, dolomite, or other substances that contain calcium carbonate, magnesium carbonate, or other alkali substances.

As a practical matter, various lime industry, soil science, and fertilizer technology sources concede that farmers frequently refer to mined calcium carbonate as “lime” and its application to soil as “liming.” However, those same terms have long been used as generic terms for any number of soil amendments employed to raise soil pH (Bear, 1942; Brady, 1984; Collings, 1950; Oates, 2008). The agricultural references to “lime” when referring to mined limestone are regarded as incorrect by the limestone and lime industry (Oates, 2008). However, in some applications such as sugar refining, “lime” and the “liming process” may refer to the vertically integrated and circular production of “milk of lime” (calcium hydroxide) from limestone (calcium carbonate) and quick lime (calcium oxide), with carbonation resulting in the production of calcium carbonate as a by-product available for use as a soil amendment (Asadi, 2006; Baikow, 1982).

Additionally, “lime” is also the common name for the tree, *Citrus aurantifolia,* and its fruit (Herren & Donahue, 1991). This technical report uses the term “lime” only to refer to the nonagricultural mineral sourced food ingredient, calcium hydroxide. The citrus fruit and its agricultural product derivatives, along with mined calcium carbonate and other agricultural soil amendments, are not within the scope of this review.

Properties of the Substance:

Table 1. Physical and chemical properties of calcium hydroxide.

Property	Characteristic / Value	Source
Molecular Formula	$Ca(OH)_2$	(Merck, 2015)
Molecular Weight	74.09	(Merck, 2015)
Percent Composition	Ca: 54.09%, O: 43.19%, H: 2.72%	(Merck, 2015)
Color	White	(FCC, 2022)
Physical state	Soft crystalline powder	(Lewis, 2016)
Melting point	580°C	(Royal Society of Chemistry, 2022)
Boiling point	2,850°C	(Royal Society of Chemistry, 2022)
Solubility in water	1 g / 630 mL at 25°C	(FCC, 2022)
Solubility in ethanol	Insoluble	(FCC, 2022)
Heat of solution	10.3 kcal	(Newman, 1957)
Density	2.25 g/cm^3	(Oates, 2010)
Electrical conductivity	8.888 mhos x 10^3	(Miller & Witt, 1929)
pH of Water Solution	12.4 at 25°C	(Lewis, 2016)

Calcium hydroxide is poorly soluble in water, and insoluble in ethanol, but it is soluble in glycerin and saturated sucrose solutions (FCC, 2022). Hydrated lime does not “melt” or “boil” in the typical sense. It loses water at 580°C (Lewis, 2016). Above 1,000°C, it begins to decompose, and it completely dissociates at 2,850°C (Royal Society of Chemistry, 2022). While some industrial sources report the color of calcium hydroxide as gray, food grade calcium hydroxide is described as white (FCC, 2022).

Specific Uses of the Substance:

Calcium hydroxide is used in food processing as a buffer, neutralizing agent, and firming agent (FCC, 2022). By volume, the largest single use in food processing is in the refining of sugar. Sugar beet (*Beta vulgaris*) processing into refined sugar uses approximately 250kg of calcium hydroxide per ton of sugar yielded (Oates, 2010). Sugar cane (*Saccarhum* spp.), as a purer source, uses about 5kg per ton of sugar yielded (Oates, 2010).

Another major food use is in the treatment of corn or maize[2] to make masa or tortilla flour. The process is known as nixtamalization, from the Nahuatl words *nixtli* or ashes and *tamalli* or dough (Serna-Saldivar, 2015). The nixtamalization process, and how it changes the chemical and physical properties of maize, has been the subject of much study. These modes of action of calcium hydroxide are described in greater detail under the Actions of the Substance section, as well as Evaluation Questions #6 and #7.

The traditional method for nixtamalization involves boiling then steeping the maize in an aqueous solution of lime (calcium hydroxide) overnight. The steeped and soaked kernels can be dried to make hominy. When the hominy is coarsely ground, the resulting meal is called hominy grits. The kernels can also be stoneground while still moist to make a wet dough. The dough is then washed to remove the pericarp and lime residue (Gasca-Mancera & Casas-Alencáster, 2007) and ground on stones (Serna-Saldivar, 2015). The product is fresh masa dough, used to make fresh corn tortillas and tamales. Masa flour—also called masa harina—is made in a similar manner by cooking maize in a lime solution after which it is steeped, washed, ground, and then also dried, pulverized and size separated. It may also be produced in a continuous process in which the maize is sprayed with lime and subjected to cooking steam, after which it is washed, ground and dried (Gasca-Mancera & Casas-Alencáster, 2007).

Other ancient grains that have been nixtamalized are amaranth (*Amaranthus hypochondriacus*) (Luque & Luque, 2014; Vargas-Lopez et al., 1991) and quinoa (*Chenopodium quinoa*) (Luque & Luque, 2014). Sorghum (*Sorghum bicolor*) may also be effectively nixtamalized (Gomez et al., 1989). Calcium hydroxide can also be used to treat other gluten-free grains, such as buckwheat, to modify the texture in foods ordinarily made from wheat (Han et al., 2012).

When used as a firming agent, the primary application of lime is in pickling. Vegetables can be pre-treated with lime to improve firmness before being preserved through acid fermentation or pickling (Nummer, 2006). Jellies and jams that require pectin are firmer when a calcium source is used to strengthen the saccharide bonds.

Calcium hydroxide may be used to fortify the calcium in various foods, but its bitter taste limits its use (Palacios et al., 2021). Its advantage over other calcium sources is that it is one of the most soluble and available sources of dietary calcium (Rafferty et al., 2007).

Calcium hydroxide, commonly referred to as slacked lime in agricultural applications, is used in crop production as a fungicide and soil conditioner. Hydrated lime is permitted without annotation in USDA organic crop production as a crop disease control at §205.601(i)(4). Otherwise, soil application of slaked lime as a soil amendment, liming agent, calcium fertilizer, and pH adjuster is prohibited for USDA Organic production [§ 205.105(a)]. Livestock producers use calcium hydroxide as an external parasiticide, including in organic livestock production as permitted at §205.603(b)(6) (USDA, 2015). The annotation for calcium hydroxide use in organic livestock production does not permit its use to cauterize physical alterations or deodorize animal wastes. Some poultry rations will use it as an ingredient in feed to promote shell formation (Lewis, 2016).

Most calcium hydroxide produced is not used in food but is rather used to make construction materials, primarily concrete and cement (Oates, 2010). It is used in petrochemical manufacturing, including fuels, plastics, lubricants, and adhesives; ammonia recovery, sulfur dioxide removal, and other air pollution control; in dentistry and pharmaceutical manufacturing; and in paper manufacturing (Lewis, 2016; Merck, 2015; U.S. NLM, 2022).

[2] The word "maize" is used through most of the text to refer to the grain of *Zea mays*, but some references are made to "corn," and it is considered synonymous unless otherwise stated.

Approved Legal Uses of the Substance:

Food grade calcium hydroxide is Generally Recognized As Safe (GRAS) for food use by the U.S. Food and Drug Administration (FDA) with no limitation other than current good manufacturing practice [21 CFR 184.1205]. More details about the GRAS status are explained in Evaluation Question #4.

FDA also approves calcium hydroxide for dental use as a cavity liner [21 CFR 872.3250]. It is permitted by FDA for use as an ingredient in anti-diarrheal, over-the-counter products with annual sales of less than $25,000 [21 CFR 310.545(a)].

Calcium hydroxide is used as both an active and a non-active (inert) ingredient in U.S. EPA-registered pesticides. In its review as an active ingredient, calcium hydroxide and calcium oxide were considered together as calcium oxides (Harrigan-Ferrelly, 2011). Lime is exempt from the requirement of tolerance for pesticide chemical residues in food when used as an active ingredient [40 CFR 180.1231]. Calcium hydroxide is exempt from the requirement of a tolerance as an inert ingredient used pre- and post-harvest in growing crops [40 CFR 180.910]. U.S. EPA classified calcium hydroxide as a List 4B inert ingredient (U.S. EPA, 2004), making it acceptable for use in organic production in pesticide formulations with allowed active ingredients [7 CFR 205.601(m)(1) and 7 CFR 205.603(e)(1)].

Action of the Substance:

Calcium hydroxide forms alkaline solutions in water with a pH of approximately 12.4 at 25°C (Lewis, 2016). As a divalent cation, calcium (Ca^{++}) disassociates two hydroxyl anions (OH^-) giving it a lower activity co-efficient than sodium hydroxide (NaOH) and potassium hydroxide (KOH), which have univalent cations. However, calcium hydroxide still shows the properties of a strong base despite this lower activity coefficient. It also has the unusual property of increasing solubility with decreasing temperatures, in contrast to other basic salts (Johnston & Grove, 1931). The mode of action of calcium hydroxide in food processing is best explained with reference to specific applications.

Sugar

To understand the action of calcium hydroxide in sugar processing, the steps that precede liming should be explained. Refined sugar is composed almost entirely of sucrose. The goal of refining is to clarify the raw sugar to have the purest sucrose in a crystalized or granular form. Sugar purity is measured by industry-set methods (ICUMSA, 2022). Standards for sugar quality depend on the target market and specific application. While sugar is present in every plant, almost all commercial sugar is extracted and refined from either cane or beets (Schiweck et al., 2007).

Cane or beets are harvested, cleaned, and mechanically chopped into smaller pieces to increase surface area, and a juice is extracted (Cheesman, 2004; Schiweck et al., 2007). Sugar cane is approximately 50% water, and sugar beets are approximately 75% water (Asadi, 2006). The cane or beet juice is cooked in a diffuser to concentrate the sugar levels in the juice (Cheremisinoff et al., 2008). Once the juice has been extracted and the solid residual mass—known as “bagasse” in the case of cane and commonly called pulp in the case of beets— has been removed, the resulting juice will be approximately 14-17% sugar (Baikow, 1982; Cheesman, 2004). The remaining impurities will vary by source, process, and local conditions. In the case of unclarified cane juice, these include gums, waxes and albumin (Baikow, 1982). Unclarified juice from sugar beets will have dissolved minerals, amino acids such as betaine, colloids, and suspended solids not removed in the pulp (Asadi, 2006).

The liming process is used to clarify (i.e., remove impurities from) the unrefined cane or beet juice. The specific details of the liming process will vary, depending on the sugar source and mill equipment, among various other factors. The classical method of lime and carbonation has been the predominant practice of the sugar industry for the past century (Schiweck et al., 2007). The processing of sugarcane will use between 2 and 5 kg lime per metric ton of sugar produced, while sugar beet processing uses about 200 kg per metric ton (Oates, 2008). Various equipment has been developed to increase the efficiency of the liming and carbonation process (Asadi, 2006; Baikow, 1982; Cheesman, 2004; Schiweck et al., 2007).

Once juice is extracted from either beets or cane it is evaporated. As the juice evaporates, the refractometric brix of the juice is measured, where 1 gram of dissolved solids in 100 grams of a sugar-containing solution equals 1° brix (ICUMSA, 2022). When the sugar juice is evaporated to about 65° brix, a saturated solution of calcium hydroxide in the form of milk of lime is added to remove the remaining impurities, where it goes into solution as Ca^{++} and $2(OH)^{-}$. Carbon dioxide is then passed through the solution—a process known as "carbonation"—where the lime reacts with it to form calcium carbonate and water as represented in the following equation:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Lime and carbon dioxide have several modes of action in sugar juice (Asadi, 2006; Baikow, 1982; Cheesman, 2004; Kenny & Oates, 2007; Oates, 2008; Schiweck et al., 2007).

1. Lime neutralizes the acidity of the solution.
2. The lime flocculates pectins, celluloses, proteins, and high-mass non-sugar substances.
3. The Ca^{++} in solution reacts with and precipitates polar anionic substances such as phosphates, sulfates, and various Krebs cycle acids.
4. Lime destroys invertase and other enzymes.
5. Lime also degrades invert sugars and polysaccharides.
6. The alkali solution hydrolyzes proteins and complex amino acids.
7. Carbonation precipitates the cations in solution, including the calcium but also magnesium and other minerals.
8. Calcium hydroxide has anti-microbial activity that prevents the biodegradation of sucrose.

In the process of precipitating the calcium carbonate, other solids will bind to what is called the "lime mud" which can be removed from the juice centrifugally, by gravity, or by filtration. The juice is then further clarified by ion exchange, such as through activated carbon, diatomaceous earth, or various synthetic resins. After lime clarification and carbonation, the juice is boiled down to a thick syrup. The syrup is seeded with sugar crystals to initiate crystallization. The crystals are separated from the remaining water and molasses by centrifugal force, and the refined sugar is ready for use. It is also possible to make sugar from a thin syrup. There are several other methods or additional steps that may be involved, but liming and carbonation are standard industry practice (Asadi, 2006; Baikow, 1982; Schiweck et al., 2007).

Nixtamalization

Lime used to treat maize and other grains has a different mode of action. The traditional method is to take whole maize and add water at a ratio of 1:1 or slightly greater and then add lime to between 0.17 and 0.58% of maize weight, and boil for an hour (Bressani, 1990). The lime may be food-grade calcium oxide that is hydrated on-site, or pre-hydrated calcium hydroxide (Serna-Saldivar, 2021). The maize is steeped in the alkali solution for 12-14 hours and washed. The washed maize, or nixtamal is then milled into dough (masa) (Bressani, 1990). The dough can then be made into food products such as tamales, tortillas, tacos, enchiladas, and many others. It can also be dried into a flour and stored for later use.

Nixtamalization weakens the cell walls, facilitating removal of the outer protective coating of the kernel known as the pericarp (Gomez et al., 1989). The longer the steeping, the more alkali solution is absorbed and the grains swell, until the waxy cutin below the pericarp disappears when viewed through x-ray diffraction (Caballero-Briones et al., 2000). Once the pericarp and waxy layer are removed in the wastewater, the germ and endosperm are exposed. Those removed constituents are disposed of, along with most but not all of the "nejayote," which is the by-product consisting of the water and lime not absorbed by the masa, along with the fiber and other constituents removed from the kernel. The starches in the endosperm then gelatinize and become more digestible (Santiago-Ramos et al., 2018). The endosperm makes up approximately 83% of the kernel, the germ makes up 11%, the pericarp 5%, and the tip cap 1%(Gwirtz & Garcia-Casal, 2014). Nixtamalization removes the fiber, vitamins and minerals from the pericarp and tip cap, but concentrates the protein, vitamins, and minerals stored in the endosperm and germ. The remaining nutrients are more digestible and nutritionally available (Bressani, 1990; Gwirtz &

Garcia-Casal, 2014; Sefa-Dedeh et al., 2004; Serna-Saldivar, 2021). The nutritional implications of nixtamalization are discussed in greater detail in Evaluation Question #7.

Firming Agent

Calcium hydroxide reacts with natural pectin in fruit to preserve the integrity of fruit particles (Saltmarsh, 2000). Fruit cell walls are strengthened by the free calcium in solution, binding with soluble pectin (Odake et al., 1999). Pickles treated with calcium hydroxide are crisper (Nummer, 2006). Fermented plums (Umeboshi) treated with calcium hydroxide had skins that were less prone to damage and disintegration, and had significantly firmer texture when judged by a sensory panel (Odake et al., 1999).

Combinations of the Substance:

Calcium hydroxide is a precursor commonly combined with many different substances during food processing. It is used with various carboxylic acids, such as citric, lactic, and acetic acids to make the calcium salts—calcium citrate, calcium lactate, and calcium acetate respectively. In beverage manufacturing, calcium hydroxide is used to fortify various juices, but may be combined with lactic acid, citric acid, or malic acid to make it more palatable (Assmann et al., 2003; Haro et al., 2006; Palacios et al., 2021).

As a disinfectant, calcium hydroxide has a synergistic effect with the bleaching agent sodium hypochlorite (Toyofuku et al., 2017). Buckwheat noodles made with the polysaccharide konjac glucomannan (KGM) will be synergized by the addition of calcium hydroxide to improve the texture and tensile strength of the noodles, making them less brittle and more like a noodle made with a gluten-bearing grain (Han et al., 2014).

Status

Historic Use:

Use of lime in food preparation is believed to be pre-historic, with evidence of its preparation in some of the oldest civilizations. Limestone quarrying has been dated to the Stone Age (Kenny & Oates, 2007). The kilning of limestone into quick lime and the hydration of quick lime into slaked lime, along with their various uses have been dated as far back as 1,000 B.C.E. (Kenny & Oates, 2007). The use of lime to treat maize (corn) flour—a process known as nixtamalization—is essential to the making of masa. As such, it is pre-Columbian in the Americas, and archeological evidence suggests limewater was used by the Mayans, Aztecs, and possibly other people indigenous to the center of origin for maize. Archeological evidence suggests that lime was being used to treat maize as early as 100 B.C.E. in Mayan civilization (Katz et al., 1974). Although the use of wood ash appears to predate the use of lime, and continued after it was developed as an alternative, lime resulted in a preferable masa for many Meso-American cultures (Serna-Saldivar, 2015). Nixtamalization was spread throughout the pre-Columbian New World along with maize and possibly other ancient grains (Katz et al., 1974; Serna-Saldivar, 2015).

Calcium hydroxide has historical use in Asia for the treatment of the nuts and leaves of the betel palm (*Areca catechu*) to make a paste that is chewed as a digestive aid. The earliest English-language documentation of this food processing application of lime was dated 1642 (Norton, 1998).

European food processing uses of calcium hydroxide are more recent than those found in traditional foods from the Americas and Asia. The earliest applications of lime in water solution, forming calcium hydroxide, was as a firming agent with pickled vegetables. Calcium hydroxide made the development of sugar from sugar beets possible in the late-18th and early-19th centuries (C.E.) through its removal of non-sucrose impurities from beet juice.

Other uses of calcium hydroxide in food involve the manufacture of food additives such as calcium citrate, calcium lactate, and calcium tartrate from citric, lactic, and tartaric acids respectively (Oates, 2010). Calcium hydroxide can also be used to make calcium phosphate from phosphoric acid. Dietary supplements may use calcium hydroxide as an ingredient.

The National List citations for both sodium hydroxide and potassium hydroxide have limitations on their use in peeling fruits and vegetables sold as organic [7 CFR 205.605(b)]. Calcium hydroxide has no such limitation. In experiments that compared calcium hydroxide use in fruit and vegetable peeling to the same use of sodium hydroxide and potassium hydroxide, calcium hydroxide was significantly less effective (Das & Barringer, 2006). There were no studies found in the literature or other evidence found that shows calcium hydroxide to be used to peel fruit or vegetables, including no reference to calcium hydroxide being an effective peeling agent in a recently published comprehensive review of peeling techniques (Zhou et al., 2022).

Along with copper sulfate, calcium hydroxide has a long history of use in organic production for plant disease control as a component of Bordeaux mixture[3]. Sulfur is combined with calcium hydroxide to make lime-sulfur or calcium polysulfide. It is also used as a non-active ingredient in pesticide formulations. Hydrated lime's historical use as an external parasiticide in organic livestock production was described in a 2015 Technical Review (USDA, 2015).

<u>Organic Foods Production Act, USDA Final Rule:</u>

Calcium hydroxide is currently allowed for use in all scopes of organic production and handling: crops, livestock, and food processing. This report focuses on its use in organic food processing, per its listing on the National List of nonagricultural (nonorganic) synthetic substances allowed as ingredients in or on processed products labeled as "organic" or "made with organic (specified ingredients or food groups)" at 7 CFR 205.605(b). Calcium hydroxide was one of the substances reviewed and recommended by the NOSB in 1995 and 1996 for inclusion on a future National List based on its long-standing use in organic handling and food processing.

Hydrated lime also appears on the National List as a synthetic substance allowed for use in organic crop production for disease management at 7 CFR 205.601(i)(5). It is also a synthetic substance allowed for use in organic livestock production at §205.603(b)(6), with the limitation to use as an external pest control, and not permitted to cauterize physical alterations or deodorize animal wastes.

<u>International</u>

Canada, Canadian General Standards Board—CAN/CGSB-32.311-2020, Organic Production Systems Permitted Substances List

Calcium hydroxide appears on Table 6.5 of the Canadian General Standards Board Organic Production Systems Permitted Substances List, CAN/CGSB-32.311, for use as a Processing Aid without any annotation (CAN/CGSB, 2021). Table 7.4 includes calcium hydroxide as a cleaner that is permitted on organic product contact surfaces for which a removal event is mandatory. Hydrated lime also appears on Table 4.2 (column 2) for plant disease control, and on Table 5.3 for livestock health care with the annotation that it shall not be used to deodorize animal wastes.

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

The Codex Alimentarius Commission's Guidelines for the Production, Processing, Labeling, and Marketing of Organically Produced Foods includes calcium hydroxide on Table 4, Processing aids which may be used for the preparation of products of agricultural origin (FAO/WHO Joint Standards Programme, 2013).

European Union Regulation—(EU) 2021/1165

The current legislation governing organic food standards in the European Union (EU) permits calcium hydroxide to be used as a processing aid for the processing of ingredients of agricultural origin in Annex V Part A2 (Processing aids and other products, which may be used for processing of ingredients of agricultural origin from organic production) of (EU) 2021/1165. The EU standards also permit calcium hydroxide to be used as a fungicide only in fruit trees, including nurseries, to control the pathogen *Nectria*

[3] Bordeaux mixture is one of the oldest fixed-copper fungicides in which calcium hydroxide enhances the efficacy of the copper sulfate.

galligena. The EU organic aquaculture standards permit calcium hydroxide to be used in the cleaning and disinfecting of equipment and facilities in the absence of aquatic animals.

Japan Agricultural Standard (JAS) for Organic Production

Calcium hydroxide (INS 526) is permitted, but limited to use in processed products of plant origin, in the JAS standard for organic production (Japanese Agricultural Standard for Organic Processed Foods, 2017).

IFOAM-Organics International

The IFOAM Standards permit calcium hydroxide (INS 526) to be used as a food additive for maize tortilla flour and as a processing aid for sugar (IFOAM, 2014). Slaked lime (calcium hydroxide) is also included in the indicative list of equipment cleansers and equipment disinfectants, and to clean and disinfect livestock housing and equipment. Hydrated lime (calcium hydroxide) appears on the list of crop protectants of mineral origin with the limitation that it is for application on aerial plant parts only.

Evaluation Questions for Substances to be used in Organic Handling

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

Calcium hydroxide is produced through four steps: 1) Mining or quarrying raw limestone; 2) preparation of the limestone for the kilns; 3) calcining the limestone to produce quick lime (calcium oxide); and 4) hydrating the quick lime. Lime is produced from either a mined mineral or a biological product that has undergone two chemical changes in the manufacturing process. While calcium carbonate and thus calcium hydroxide can be obtained from sea shells, coral reefs, aragonite and marble, almost all commercial production of food-grade lime—in both quick (calcium oxide) and slaked (calcium hydroxide) forms—used in the United States originates from mined, high-calcium limestone (Oates, 2008). Lime—both quick and slaked—is the product of the high-temperature calcination of limestone (U.S. EPA, 1998). Figure 1 is a flow chart of the industrial processes involved in quick lime and slaked lime manufacturing.

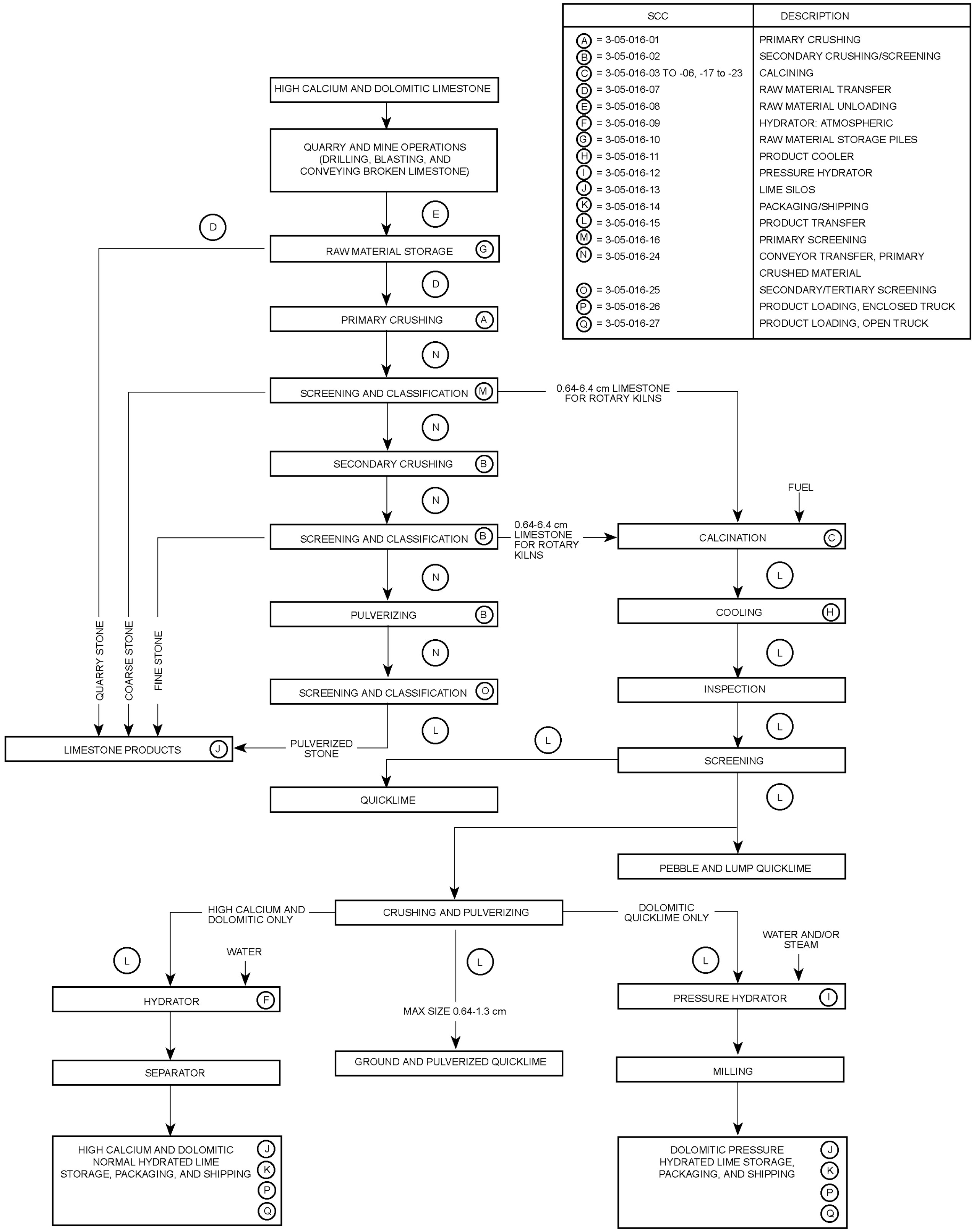

Figure 1: Lime manufacturing process flow diagram (U.S. EPA, 1998).

The limestone is crushed, pulverized, sized, and graded before it is further processed. Most of the limestone is sold as construction or fertilizer grade, and as such does not need to meet as high a level of purity as that for food, chemical, and pharmaceutical grade products. Higher-grade limestone will undergo beneficiation through scalping, screening, washing, scrubbing, and sorting. Impurities, such as lead and other heavy metals that tend to be in finer fractions than calcium carbonate, are removed through the settling in slurry ponds (Oates 2008). The chemical specifications of high-calcium limestone are provided in Evaluation Question #2.

Once the product has been sorted and beneficiated, it is graded to separate for further processing via calcination. The grading is based on a) particle size distribution, b) shape, c) contamination, d) cleanliness, and e) consistency (Oates, 2008). Calcination involves the heating of limestone to temperatures above 900°C. The process is ancient and originally relied on the combustion of wood. The prevailing fuel used for processing is coal, either in the form of anthracite or coke (U.S. EPA, 1998). A growing amount of quick lime is produced using natural gas as a fuel. Natural gas has the advantage of producing quick lime with fewer impurities, and is therefore more likely to meet food-grade specifications (Huege et al., 2008). Petroleum has also been used as a fuel (Oates, 2008). The chemical process of making quick lime is discussed further in Evaluation Question #2.

Historically, calcium hydroxide was made in small batches from quick lime and used shortly afterwards. Such a process was labor intensive, and the quality was poor and variable. Modern industrial production has enabled greater volumes to be made in purpose-built plants. Most plants operate on a four-stage process: quicklime handling and crushing; hydration; classification; and storage/shipping (Oates, 2008). Most hydrated lime fails to meet food-grade specifications (Huege et al., 2008).

Food-grade hydrated lime is made by a handful of basic processes. The techniques differ in the equipment used, the temperature and pressure of the water used for hydration, and the length of time of the reaction process. The oldest and simplest process uses water at ambient temperatures and standard pressure. The hydration process using this older process takes between 12 and 24 hours. Production plants can be made without special equipment, and energy expenditures are minimal. This low-technology process is labor-intensive, and quality is variable. Such simple processing is rarely used to manufacture food-grade calcium hydroxide in most of the industrial world (Oates, 2008). Simple techniques may be used in regions with lower labor costs, limited access to capital, and markets that do not exclusively require food-grade specifications.

An early modification of the low-technology process injects mechanically-prepared steam into quick lime (Kuntz, 1933, 1934). The resulting hydrated lime is dried and then sorted into heavier and lighter particles through centrifugal force in a conical separator. The result is faster and more complete hydration with better sorting into different grades. The patents claim that all grades can be made using this process.

The second modification uses heated water at standard pressure to hydrate the quick lime in a hydrator in three stages: pre-hydrator, hydrator, and finishing stage (Oates, 2008). Most of these process details are proprietary, but some information is available in the patent literature. One patented process involves preparation of the quick lime in ultrafine particles. Water is preheated to between 50°C and 70°C in a mixing vessel. The solution is then moved to a mixing vessel where hydration takes place at temperatures between 70°C and 90°C. Because the reaction releases heat, temperatures will reach between 85°C and 110°C in the final mixing vessel. The solution is then cooled to a temperature of 30°C, degassed, and dried (Bestek et al., 1987). Once dried, it can then be further classified, sorted, graded, and packaged. The patent does not disclose the phase times, but indicates that they are "short" and the process can take place continuously rather than in batches (Bestek et al., 1987).

Another method used to make food grade calcium hydroxide simplifies it to a two-step classification process by dry screening the quick lime through coarse streams of -10 to -50 mesh, then a fine stream screen producing quick lime that passes through a -325 mesh screen. An air classifier removes impurities of different densities from a very fine stream (Huege & Chavez, 2005). The quick lime is then hydrated with steam and further wet screened through a hydrocyclone centrifuge (Huege et al., 2008). The patent holders claim that the technique consistently produces food-grade calcium hydroxide with levels of heavy metals significantly lower than what is obtained with -100 mesh screening (Huege & Chavez, 2005).

New techniques for the manufacture of calcium hydroxide continue to develop. Nanoparticles of calcium hydroxide were reported to be synthesized as early as 2001 (Salvadori & Dei, 2001). One article described calcium hydroxide as "one of the most magnificent materials in nanotechnology by virtue of its unique physical and chemical properties" (Harish et al., 2022). Most literature cited refers to medical or dental applications of calcium hydroxide nanoparticles. However, with growing interest in food applications of nanotechnology, food-grade calcium hydroxide nanoparticles may become commercially feasible.

<u>Evaluation Question #2:</u> 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.

Most food-grade calcium hydroxide originates from mined high-calcium or chemical-quality limestone, which is an ore that has over 94% calcium carbonate ($CaCO_3$) with a pH neutralizing value of greater than 97% (Oates, 2010). Limestone that has over 30% magnesium carbonate is known as dolomite or dolomitic lime (U.S. EPA, 1998). Mined limestone will also have various other minerals, including aluminum, iron, and silicon oxides, as well as sulfur, manganese, and other elements (Oates, 2010). Heavy metals may also be present in the ore, and the levels in the processed calcium hydroxide are discussed further in Evaluation Question #8. Dolomitic lime is not generally used to manufacture calcium hydroxide.

After the physical and mechanical processing steps of crushing and classification, the material undergoes a chemical processing step known as "calcination." In this process, limestone is heated in a kiln to temperatures above 900° C, which causes the limestone to dissociate into quicklime (calcium oxide) and carbon dioxide represented by the following chemical equation:

$$CaCO_3 + \text{Heat} \rightarrow CaO + CO_2$$

While there are many different kiln designs, using different fuels and unprocessed mined minerals, known as "feedstones" in the industry, two kiln types account for almost all commercial quick lime. In the United States, rotary kilns are the prevalent method used, accounting for about 90% of all lime production capacity in 1998, with shaft kilns making up most of the remainder, and only a few other specialized kilns that accounted for a small fraction of production.

Modern, high-volume calcination takes place in a two-phase process. The first phase or stage involves charging the pulverized limestone into the heated chamber, raising the temperature to the point of combustion, where carbon dioxide is released. The second phase involves quickly cooling the calcined quick lime to a temperature where it can be safely handled (Oates, 2008; U.S. EPA, 1998). Figure 2 provides a schematic diagram of the kilning process.

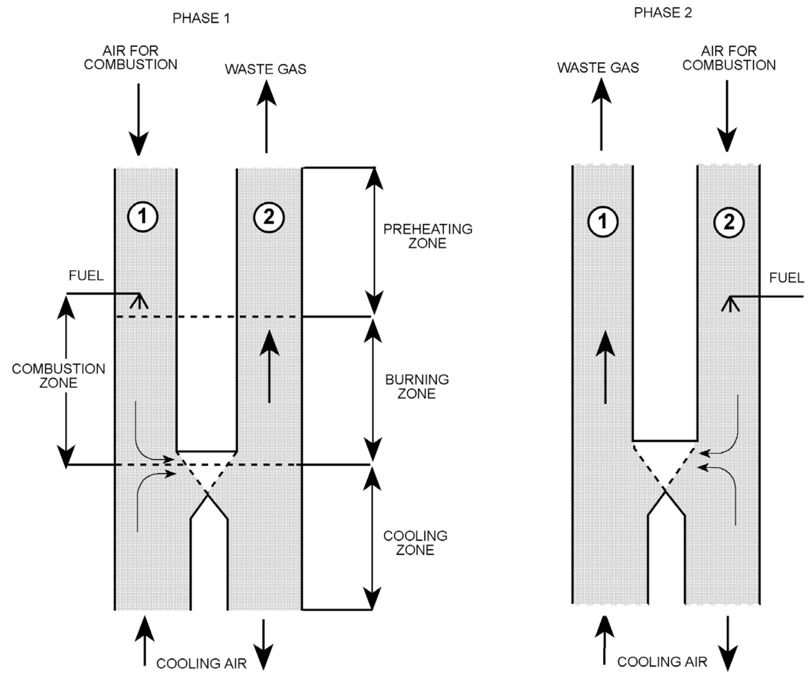

Figure 2: Lime calcination (U.S. EPA, 1998)**.**

The second step in the production of calcium hydroxide after calcination is called "slaking" and involves the hydration of quick lime with water. About 15% of all quick lime is hydrated to make slaked lime (U.S. EPA, 1998). The normal hydration process is carried out at atmospheric pressure and at the boiling point of water, 100°C. The reaction is exothermic, meaning that it produces heat. The reaction can be accelerated using high-pressure steam and is represented by the following equation:

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{Heat}$$

The hydrated lime is then sorted, graded, packaged and transported. Only a small percentage of hydrated lime meets the specifications for food-grade calcium hydroxide. Food-grade processes may involve greater sorting, preparation, and classification (Huege et al., 2008; Huege & Chavez, 2005). Some sugar manufacturers operate limekilns that are used to produce calcium hydroxide to meet sugar processing specifications (Cheesman, 2004; Oates, 2008; USGS, 2022). Ten such facilities were operating in the United States and Puerto Rico in 2021 (USGS, 2022).

<u>Evaluation Question #3:</u> **If the substance is a synthetic substance, provide a list of nonsynthetic or natural source(s) of the petitioned substance (7 CFR 205.600(b)(1)).**
The NOSB has determined on numerous previous occasions that calcium hydroxide is synthetic, and that no nonsynthetic source exists. The NOSB considered the substance for crop production in October 1995 and May 2002, for livestock production in 1995 with a sunset review in 2015 (USDA, 2015), and for processing in 1995. In every case, the NOSB determined that calcium hydroxide was synthetic and did not recognize the existence of any nonsynthetic or natural source. A search of the literature confirmed that there is no new information about a nonsynthetic source of food-grade calcium hydroxide.

<u>Evaluation Question #4:</u> **Specify whether the petitioned substance is categorized as generally recognized as safe (GRAS) when used according to FDA's good manufacturing practices (7 CFR 205.600(b)(5)). If not categorized as GRAS, describe the regulatory status.**
As noted above, calcium hydroxide is Generally Recognized As Safe (GRAS) for food use by the U.S. Food and Drug Administration, with no limitation other than current good manufacturing practice [21 CFR 184.1205]. The regulation refers to the Food Chemicals Codex third edition to describe food grade. Pharmaceutical (U.S.P.) grade calcium hydroxide is permitted as an ingredient in the food coloring caramel [21 CFR 73.85]. Soaps made from fatty triglycerides, marine oils, and the fatty acids of alcohols that are

saponified by calcium hydroxide may be used as a defoaming agent in the manufacture of food-grade paper and paperboard [21 CFR 176.210]. The FDA has established a specific labeling requirement for calcium hydroxide when it is used as an ingredient in ice cream and frozen custard [21 CFR 135.110(b) & 21 CFR 135.110(g)].

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 hydroxide's primary technical function as a processing aid is as a moderately weak alkali that lowers acidity and aids in the removal of impurities (Saltmarsh, 2000). While it is not used primarily as a preservative in most food processing applications, calcium hydroxide demonstrates anti-bacterial and anti-viral properties, reducing populations of *Salmonella* infantis, *Escherichia coli,* and the virus responsible for avian influenza (Ruenphet et al., 2019). Alma et al. (2018) reported its use as a treatment of shell eggs for *Salmonella* reduction. Its disinfection properties have been more widely studied as a root canal treatment in dentistry and endodontics, where several literature reviews have been published on its efficacy and modes of action (Athanassiadis et al., 2007; Estrela & Holland, 2003; Farhad & Mohammadi, 2005; Siqueira Jr & Lopes, 1999). Specifically, the substance shows efficacy towards acid-tolerant and alkali-intolerant pathogens (Farhad & Mohammadi, 2005). It is broad-spectrum, with equal efficacy in reducing aerobic, anaerobic, gram-positive, and gram-negative bacteria (Estrela & Holland, 2003).

Calcium hydroxide used in combination with other anti-microbial food preservatives enhances the efficacy of those treatments; in other words, it is synergistic—that is, the effect of the combination of the two is greater than the sum of the efficacy of each of its parts. Calcium hydroxide enhances the efficacy of sodium hypochlorite as a treatment for *Salmonella* spp. and *E. coli* in poultry chill water (Toyofuku et al., 2017). While it may not result in a sufficient level of pathogen reduction and spoilage retardation by itself to be considered a preservative, the synergistic effect makes it an attractive co-formulant or adjunct with preservatives. One such application is the combination of glycerol, fumaric acid, propylene glycol, or sodium benzoate with lime water used for nixtamalization (Báez-Aguilar et al., 2022). Another is sodium benzoate or sodium bisulfite when making coconut toddy (Hariharan et al., 2014).

Evaluation Question #6: 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)).

Nothing found in the literature reviewed for this report suggests that calcium hydroxide is used to recreate or improve flavors or colors. Treatment of gluten-free grains, such as maize and buckwheat, with calcium hydroxide changes the texture of the flour to have greater tensile strength, and be less mealy or brittle (Han et al., 2012, 2014). Nixtamalization with calcium hydroxide imparts a distinct flavor profile that is associated with tortillas, but that is creating and not recreating a flavor. Mung beans can also be treated with calcium hydroxide to enhance and stabilize their flavor profile (Chanjarujit et al., 2018). Alkali treatment releases chemically-bound niacin (vitamin B_3) in maize and possibly other grains, improving their nutritional quality (FAO, 1992; Kodicek et al., 1959; Wall & Carpenter, 1988), but also reduces the total amount of niacin and other B-complex vitamins (Bressani, 1990).

Evaluation Question #7: 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)).

The processing of sugar beets and sugar cane into sugar removes almost all protein, vitamins, and minerals from the plants, leaving purified sucrose. The addition of calcium hydroxide is only one of several steps used to remove impurities, so not all removal of proteins, vitamins, and minerals in the process can be attributed to the addition of calcium hydroxide.

Sugar cane is a tropical grass and is not readily digestible by humans or monogastric livestock but can be eaten directly by ruminants, although it is not easily digested because of the hemicellulose and lignin content of the straw fiber (da Costa et al., 2015). The syrup extracted from the sugar cane before further refining has already had the protein removed. Before further processing, 100 grams of cane syrup has 13 mg calcium, 3.6 mg iron, 10 mg magnesium, 8 mg phosphorous, 63 mg potassium, 58 mg sodium, 0.19 mg zinc, 0.02 copper, 0.7 mg selenium, 0.13 mg thiamin, 0.06 mg riboflavin, and 3.3 mg niacin (USDA / ARS / NDL, 2016). These vitamins and minerals are for the most part removed during the refining process.

The USDA's National Nutrient Database does not have a separate entry for the juice obtained from sugar beets prior to treatment with calcium hydroxide. However, according to Mirmiran et al. (2020) and Vasconcellos et al. (2016), prior to further processing, 100 g of fresh beet juice will have 1.02 g protein, 93 mg sodium, 0.98 mg citric acid, 0.36 mg ascorbic acid, and 1.53 mg malic acid (Mirmiran et al., 2020; Vasconcellos et al., 2016). While most of the nutrients in the raw beets will be left in the pulp, some protein, minerals, vitamins, and accessory nutrients remain in the sugar juice after the pulp is removed. As noted above, most of these remaining nutrients will be removed by the treatment with calcium hydroxide and carbon dioxide. Calcium hydroxide would effectively remove most of the remaining minerals and acids in the beet juice.

Granulated white refined sugar from both sources almost always has a content of 99.7% sucrose (Schiweck et al., 2007). As such, that minimum sucrose content has been set as the internationally recognized standard for what can be sold as white sugar (FAO/WHO Joint Standards Programme, 1999). The remaining 0.3% includes water, complex and invert sugars, and some minerals. The USDA's National Nutrient Database lists granulated sugar at 99.98% carbohydrates and 0.02% water, effectively accounting for 100% of the mass. There are trace amounts of minerals listed in the standard reference: 1 mg of calcium, 0.05 mg of iron, 2 mg of potassium, 1 mg of sodium, 0.01 mg of zinc, 0.007 mg of copper, 0.004 mg of manganese, 1.2 µg of selenium per 100 g of granulated sugar. The only vitamin listed for trace amounts is riboflavin (vitamin B_2), with 0.019% per 100 g of granulated sugar. All other vitamins and minerals are listed as zero (USDA / ARS / NDL, 2016). Brown sugar is 98.09% carbohydrates and 1.34% water, accounting for 99.43% of the mass.

By contrast, lime is widely credited for improving the nutritional quality of maize (FAO, 1992). Diets that rely on maize as the primary source of grain nutrition have been linked to pellagra in the United States for about a century (Goldberger & Tanner, 1922). Pellagra is a nutritional disease believed to be caused by a deficiency of the vitamin niacin (B_3) and the essential amino acid tryptophan (Bressani, 1990; Goldberger & Tanner, 1922; Goldsmith et al., 1956; Rajakumar, 2000; Wall & Carpenter, 1988). Evidence from various experiments conducted on humans and laboratory animal models has yielded mixed results regarding the causal relationship between a maize-based diet and pellagra. Nixtamalization is considered by many to be responsible for low incidences of pellagra in pre-Columbian Meso-American cuisines (FAO, 1992; Rajakumar, 2000; Wall & Carpenter, 1988). Nixtamalization destroys the maize seed coat and releases chemically-bound niacin to make it digestible (Wall & Carpenter, 1988). Others question this link, given that lime treatment of maize reduces the total niacin in maize (Bressani, 1990). Experimental research found no difference in niacin uptake between human subjects fed lime-treated and untreated maize (Goldsmith et al., 1956). This latter study was conducted on a small sample size with human subjects that had been induced to have pellagra by manipulation of their diets (Kodicek et al., 1959).

A study that used pigs as the experimental animal found that 98.3% of the niacin in untreated maize was nutritionally unavailable, while 100% of the niacin in the calcium hydroxide treated maize was nutritionally available. Pigs fed untreated maize showed symptoms of a niacin deficiency, while those fed treated maize improved (Kodicek et al., 1959).

Diversity of the diet has long been known to be the best way to prevent pellagra (Goldberger & Tanner, 1922). It is not possible to know the contribution made by the alternative pre-Columbian grains amaranth and quinoa, as well as other foods rich in B-complex vitamins and amino acids, but that appears to some researchers to be a plausible explanation for the apparent lack of nutritional deficiency from a diet that relied on maize as the main staple grain.

While calcium hydroxide may make tryptophan and niacin more available in maize and possibly other grains, it reduces protein and vitamin levels in maize. Calcium hydroxide provides a nutritional benefit in treated maize products in the form of supplemental calcium. Treatment with lime increases calcium content in masa up to 400% of the content in untreated maize (Bressani, 1990; FAO, 1992). Lime treatment also has been observed to have a negative impact on certain accessory nutrients in some maize varieties.

Specifically, nixtamalization can cause anthocyanins in blue maize to leach (Zazueta-Morales et al., 2002). Most of maize's fiber content and some water-soluble vitamins, such as folic acid and choline, are also significantly lowered by nixtamalization (Gwirtz & Garcia-Casal, 2014; Santiago-Ramos et al., 2018).

Soybeans can have their proteins concentrated and stabilized by calcium hydroxide hydrolysis (Peng et al., 2020). As with maize, calcium hydroxide also raises the calcium level in the soy protein concentrate.

<u>Evaluation Question #8:</u> List any reported residues of heavy metals or other contaminants in excess of FDA tolerances that are present or have been reported in the petitioned substance (7 CFR 205.600(b)(5)).
Limestone deposits contain impurities that include various heavy metals (Oates, 2008). The levels depend on the parent material mined and widely variable local conditions. While many of these heavy metals are removed by calcining, it is not possible to remove all. The FDA recognizes the tolerances for impurities in food-grade calcium hydroxide that are set forth in the Food Chemicals Codex. The limit for elemental arsenic is not more than 3 ppm (0.0003%), for lead not more than 10 ppm (0.001%), for total heavy metals (the test method for which uses lead ion as the control) not more than 0.004%, and fluoride not more than 0.005% (FCC, 2022). The sugar industry requires a lower level than the legal minimum of <2 ppm of arsenic (As) (Oates, 2010). Because sucrose is one of the most heavily consumed foods, it was seen as a major source of dietary lead by Food Chemicals Codex (Bigelow, 1992). Methods for separating arsenic and other heavy metals in quick lime before hydration, and sorting and classifying food-grade from non-food-grade have improved with new technologies (Huege et al., 2008; Huege & Chavez, 2005).

<u>Evaluation Question #9:</u> Discuss and summarize findings on whether the manufacture and use of the petitioned substance may be harmful to the environment or biodiversity (7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i)).
The literature on the environmental impacts of limestone quarrying and its processing into quick lime and hydrated lime is extensive. Limestone deposits occur in a wide range of geological formations that are connected to a variety of ecosystems. Almost all limestone is mined in open quarries or pit mines (Oates, 2008). Site preparation for open pit or quarry mining involves the clearing of trees, vegetation, and topsoil, resulting in the immediate loss of habitat (Ganapathi & Phukan, 2020). Some ecosystems are more sensitive to the intrusions of mining than others. The karst[4] topography associated with limestone deposits creates a wide range of potential environmental impacts, including habitat and biota loss; air, noise, and water pollution; and cascading environmental impacts to natural systems far from the mining location (Langer, 2001). Limestone mining creates dust and other air pollution (U.S. EPA, 1998). Karst forms caves that are ideal bat habitat. The dust and noise from limestone mining can result in loss of that habitat and cause remaining bats to suffer increased mortality and deafness (Langer, 2001). Discharges from limestone quarries can also result in surface water contamination with sediment, heavy metals, and asbestos. This in turn can result in adverse impacts on aquatic biota, including fish mortality (U.S. EPA, 1982).

Calcination of limestone to make quick lime is a source of greenhouse gas emissions (U.S. EPA, 1998). The most current estimates are that, on average, the calcination process releases 0.78 tons of carbon dioxide per ton of quick lime produced (Kenny & Oates, 2007). Older facilities and facilities in regions with less strict emission standards may release more. Newer facilities with better emission controls will release less.

A comprehensive global review of environmental impact analyses related to limestone mining, and its comparison to that of potential alternatives such as oyster shell lime deposits and coral reefs, is beyond the scope of this review.

Similarly, the ecological impacts of sugar production and processing and maize production and processing are also beyond the scope of this review. Strictly focusing on calcium hydroxide, the liming / carbonation process has been called the "Achilles' heel" of sugar technology from an environmental point of view (Vaccari et al., 2005). Calcium hydroxide used in sugar processing contributes to those impacts in two ways. One is that the effluent discharged from sugar operations is predictably alkaline, with a pH above 10

[4] Karst is a topography that is formed by the dissolution of soluble rocks such as limestone, among others. It is characterized by sinkholes and caves that form underground drainage systems.

in most cases (UNEP, 1982). The other is that dust from the use of calcium hydroxide contributes to sugar refining's air pollution in the form of total particulate matter released (Cheesman, 2004).

Maize processing into hominy and masa has a parallel environmental impact with the use of lime. Masa production is a major source of water pollution in Mexico, causing reduced biological oxygen demand (BOD), increased alkalinity, and concentration of calcium hydroxide (Ramírez-Araujo et al., 2019). Water quality regulations increasingly restrict releases and require treatment technologies before nejayote discharge (García-Zamora et al., 2015). These environmental constraints have driven research to find more ecologically sound nixtamalization methods (Campechano Carrera et al., 2012; Méndez et al., 2013; Santiago-Ramos et al., 2015).

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

Consumers have no direct exposure to calcium hydroxide used as a processing aid in organic food processing. Most human health exposure to calcium hydroxide is occupational, both in its manufacture, storage, and transportation, and by workers in organic food processing facilities. Data in the scientific literature for calcium hydroxide toxicity and other human health effects was often extrapolated from calcium oxide, which readily hydrolyzes into calcium hydroxide (Bartsch et al., 2016). Table 2 summarizes calcium hydroxide's toxicity data.

Table 2. Toxicity of calcium hydroxide.

Study	Results	Source
Acute oral toxicity	LD_{50} Rat: 7,340 mg / kg LD_{50} Mouse: 7,300 mg / kg	(Royal Society of Chemistry, 2022)
Dermal toxicity	LD_{50} Rabbit: >2,500 mg / kg	(Bartsch et al., 2016)
Carcinogenicity	Rat (two years): Negative	(Bartsch et al., 2016)
Genetic toxicity	OECD Test 471: Negative	(Bartsch et al., 2016)

Calcium hydroxide is a skin, eye, and upper respiratory tract irritant (Lewis, 2016). Because of its widespread use and many applications, calcium hydroxide is the most important cause of work-related alkaline burns in developed countries (Kivanc et al., 2016). Toxicity by ingestion is rated as Grade 1, or as a mild adverse event (Cheremisinoff, 1999). While it is caustic, it is less likely to result in permanent damage than sodium hydroxide or potassium hydroxide because of its low solubility and slow penetration into tissues (Gosselin et al., 1984). Application to rabbits at the highest dose of 2,500 mg / kg resulted in skin irritation but no mortalities (Bartsch et al., 2016). The greatest human health risk posed by calcium hydroxide is eye injuries (Klaassen, 2001). Powdered calcium hydroxide caused severe eye injuries to rabbits after one hour (Bartsch et al., 2016). Immediate first aid by irrigating the eye with water is generally an effective treatment (Kuckelkorn et al., 2002).

Calcium hydroxide does not appear on official lists of known or probable carcinogens (Cal-EPA, 2022; IARC, 2022; NIOSH, 2022). While there is no evidence that calcium hydroxide causes cancer, it is a suspected co-carcinogen for oral cancer with the consumption of betel quid and its closely related substitutes *gutkha* and *pan masala* (U. Nair et al., 2004; U. J. Nair et al., 1990, 1992).

Most guides suggest thoroughly rinsing fruit or vegetables that have been pre-treated with pickling lime to remove any excess that might lead to food poisoning (Willenberg & Mills-Gray, 2021).

<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)).

It is technically feasible to extract concentrated sucrose from sugarcane through physical and mechanical methods without the use of calcium hydroxide or other synthetic chemicals, a traditional method of production in India. The process takes longer, has lower yields and results in higher levels of non-sucrose impurities. These minimally refined specialty sugars have different technical and functional properties from refined sugar. In most cases, the resulting product would not meet the sugar industry's specifications (Rao, 2020). Research on non-chemical alternatives to make high-quality, high-yield sugar from cane has been the subject of research in the United States for over a century, and for even longer in Europe (Zerban, 1920). Researchers continue to search for commercially viable alternatives to the use of calcium hydroxide and carbon dioxide in the sugar juice purification process (Cheesman, 2004; Vaccari et al., 2005).

Jaggery—known also as gur (Bengali, Pashto, and Urdu), panela / piloncillo / tapa de dulce (Spanish), or rapadura (Portuguese) is a traditional product of sugar cane that predates refined sugar (Shrivastava & Singh, 2020). Concerns over the refined sugar's effects on human health and nutritional quality has generated interest in jaggery as a sweetener. The cane juice is slowly evaporated by cooking in open pans, leaving ungranulated blocks. Jaggery can be prepared without calcium hydroxide, but calcium hydroxide can be used—albeit at a lower rate—to prepare jaggery. Raising the pH to 6.2 with lime causes jaggery to granulate and increases the sucrose content to over 88% (J. Singh et al., 2013). It is a popular sweetener for candies made for traditional local cuisines in regions where sugar cane is grown in Asia, Africa, and Latin America.

The literature did not contain any information about any viable alternatives to extract, refine, concentrate, or purify sugar from beets without calcium hydroxide.

Maize and other grains can be milled into meal and flour without nixtamalization. However, the products are technically and functionally different from masa and tortilla flour. Because of the wastewater impacts of calcium hydroxide and because of interest in reducing costs, a considerable amount of research has been done to find physical, mechanical, and other non-chemical alternatives to alkali nixtamalization. A comprehensive review is found in Ramírez-Araujo et al. (2019). Physical alternatives include ultrasound, microwaves, and ohmic (electroconductive) heating. (None of these techniques appear to be ionizing radiation and therefore excluded method for organic maize processing [7 CFR 205.105(f)].) However, most of the studies reduce rather than eliminate the amount of calcium hydroxide used to steep the maize and various other applications through improvements in the efficiency of calcium hydroxide and water use. Such efforts have been underway since early in the industrial mass-production of masa-based products (Anderson & Brown, 1963). Complete elimination of calcium hydroxide from the process would result in products that are distinct from masa or tortilla flour and have a different nutritional and flavor profile (Ramírez-Araujo et al., 2019).

Enzymes are another possible nonsynthetic alternative for grain nixtamalization that is already on the National List of Allowed Nonsynthetic Substances [7 CFR 205.605(a)]. One patent proposes the use of a protease enzyme. However, most of the examples given in the patent still use calcium hydroxide (Jackson & Sahai, 2002). The enzymes resulted in a more efficient use of calcium hydroxide, increasing yield and decreasing processing time, but was not presented as a substitute.

While there are many promising alternatives in the processing of maize-based products, none has replaced calcium hydroxide as the preferred method for preparation.

Some pickling guides discourage the use of calcium hydroxide because it is linked to botulism, caused by the anaerobic bacteria *Clostridium botulinum.* Some food preservation instructions even advise eliminating pickling lime altogether because of the increased botulism risk (Brochetti, 1996). Thus, not using pickling lime is seen as a lower food safety risk alternative, but texture and crispness are sacrificed.

<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 carbonate (mined limestone), calcium chloride obtained from brine, and calcium sulfate (mined gypsum) are all a nonsynthetic calcium salts currently on the National List of allowed nonorganic ingredients and processing aids [7 CFR 205.605(a)]. These all have the potential to be used as alternatives for various calcium hydroxide applications, including use as a pH buffer in pickling, brewing, and other fermentation processes, as well as in the malting process for grains. However, although it is inexpensive and easier to handle than calcium hydroxide, limestone may impart a chalky flavor that is considered undesirable by some consumers.

Diatomaceous earth—also referred to by the German word “kieselguhr” in the literature—can be used to remove impurities from sugar juice prior to evaporation and crystallization (Wiechmann, 1886; Zerban, 1920). Diatomaceous earth appears on the National List as an allowed nonsynthetic processing aid without limitations [7 CFR 205.601(a)]. It may be used to increase the yield and quality from liming and carbonation, rather than as a substitute practice.

Nonsynthetic calcium carbonate, calcium chloride, and calcium sulfate have all been used in experiments to prepare maize flour for various applications as part of an ecological nixtamalization process. One study compared tamales made from maize treated with calcium hydroxide to those treated with calcium carbonate, calcium chloride, and calcium sulfate by evaluating the textural and chemical properties of the tortillas. None of the other calcium salts remove the pericarp, which is almost completely removed in the nejayote with traditional lime water (Campechano Carrera et al., 2012). As a result, the tortilla flour will have higher fiber content with the alternative salts than with calcium hydroxide. In experiments with white, yellow, red, and black genotypes of maize, the alternative salts consistently resulted in smaller losses and higher levels of phenolics and anthocyanins in the finished tortillas that were cooked by an ohmic heating process (Ramírez-Jiménez et al., 2019).

Calcium chloride derived from brine [7 CFR 205.605(a)] may also be used as substitute for the rare use of calcium hydroxide in dietary supplements, but imparts a brackish flavor (Camire, 2000). Food-grade calcium chloride can also be used instead of calcium hydroxide in pickling brine, and does not lower the acidity as much as calcium hydroxide (Nummer, 2006). Nonsynthetic tricalcium phosphate ($Ca_3(PO_4)_2$) is a potential substitute for calcium hydroxide for some applications, but because of heavy metal and radioactivity contamination, meeting food grade is a challenge with mined sources.

<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)).

Traditional on-farm sugar cane processing in India sometimes relies on various plants to clarify and purify the cane juice. One of the plants used is *Abelmoschus esculentus,* familiar in the United States as okra, and known as bhendi in the Indian subcontinent. Bhendi powder was compared with various other clarifying agents—hydrogen peroxide, citric acid, a polyelectrolyte, and a proprietary chemical flocculent. The results showed that the plant-derived clarificant removed scum, increased non-reducible sugar content, and resulted in jaggery recovery rates that were comparable to the chemical agents (Patil et al., 2005). However, the resulting jaggery did not meet the specifications for refined sugar. The Organic Integrity Database listed 458 certified organic okra producers and 190 certified organic okra handlers in August 2022 (USDA / AMS / NOP, 2022).

There are many different sweeteners that are potential substitutes for sugar refined with calcium hydroxide. Among those commonly mentioned in the literature are honey, maple syrup, sorghum syrup, palm sugar, agave syrup, rice syrup, barley malt, and fruit sugars (P. Singh et al., 2020). These substitutes all have certified organic sources available (USDA / AMS / NOP, 2022). Honey production involves the use of pollinators. Its production has a beneficial effect on biodiversity when compared with sugar cane or sugar beet production. Honey includes vitamins and minerals that are not found in refined sugars (P. Singh et al., 2020).

Maple syrup production is extensive and relatively low impact. It relies on a perennial crop and can be grown in areas considered unsuitable for annual tillage and cultivation.

In addition, the Organic Integrity Database lists one handler of high-fructose corn syrup that is certified organic under the National Organic Program (USDA / AMS / NOP, 2022). Maize’s environmental impacts could be considered comparable to sugar beet production. The Organic Integrity Database also lists handlers that are certified organic for various sugar alcohols, such as certified organic erythritol and certified organic xylitol. Sugar alcohols are often derived from maize or other grains by fermentation (P. Singh et al., 2020).

Various plant-derived monosaccharides and oligosaccharides, as well as other non-sucrose sweeteners have been developed as alternatives to sucrose derived from the chemical industrial processing of sugarcane and sugar beets. Some of these alternatives are significantly sweeter than sucrose (Haq, 2000). Some have been developed and are commercially available from organic sources. One such sweetener is stevia, derived from *Stevia rebandiana,* a tropical plant native to Brazil and Paraguay. While stevia has been used in indigenous cuisines in South America for over 1,500 years, it was not Generally Recognized As Safe by the FDA until 2008. The Organic Integrity Database listed 165 certified organic producers and 364 certified organic handlers of certified organic stevia (USDA / AMS / NOP, 2022).

Some alkali treatment is essential for the preparation of masa and the various traditional Mexican foods made from it. Maize can be nixtamalized with wood ash, which was a traditional alternative for tribal cuisine in regions that lacked access to limestone quarries (Serna-Saldivar, 2015). Several societies—including the Aztecs—traditionally prepared maize with both lime and wood ashes (Katz et al., 1974). Wood ashes have also been used traditionally to treat maize to make hominy (Jones, 2017; Katz et al., 1974; Serna-Saldivar, 2015). The alkali in this case is potassium hydroxide and the process is referred to as lye treatment. The color, texture, and nutritional quality of lye hominy and masa made from lye differs from hominy and masa made from lime (Odukoya et al., 2022). Flavor is also commonly believed to differ, but few double-blind sensory panels have been conducted to confirm. One study showed slight but noticeable differences in flavor and aroma (Pappa et al., 2010). While maize nixtamalized with lye increased some trace nutrient mineral levels compared with lime treatment, it also resulted in a higher potential to contribute to aluminum toxicity (Odukoya et al., 2022). Hypothetically, a 100% organic hominy or masa can be made from burning wood from organic perennial fruit or nut trees and organic maize. However, there is no evidence in the available literature that such a practice is technically or commercially feasible, or any test data to support such an approach.

Report Authorship

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