Lime Mud
Crops

Identification of Petitioned Substance

Chemical Names:
Lime mud

CAS Numbers:
None known

Other Name:
Lime mud, calcium carbonate, precoat mud, Somerset lime mud, dewatered lime mud

Other Codes:
None known

Trade Names:
None known

Characterization of Petitioned Substance

Composition of the Substance:
Several sources were used to evaluate the composition of lime mud. The portion of lime mud that is calcium carbonate can vary from 15% to 95%. For example:

- Lime mud is composed of greater than 95% calcium carbonate ($CaCO3$), according to the petition.
- A laboratory analysis (Maine Environmental Laboratory, 06-26-02) indicated a composition of 98.7% calcium carbonate equivalence.
- The MSDS from National Institutes of Environmental Health Studies indicates a composition of 15 to 85% calcium carbonate (CAS no. 1317-65-3), 0.1 to 0.5% sodium hydroxide (CAS no. 1310-73-2), and 84.9 to 19.5% non-hazardous.

It is likely that the composition of lime mud varies depending on specific, and possibly idiosyncratic, process-related factors. In any case, at least 2.3% and possibly up to 85% of the composition of lime mud may be something other than calcium carbonate. According to the petition, this is extremely high quality lime and typically has 96-99% available calcium carbonate equivalents. Lime mud never comes in contact with the pulp bleaching portion of the mill.

The petition indicates that small quantities of calcium hydroxide may be present.

Calcium carbonate is a natural component of soils. Indeed, about 4% (by weight) of the earth's crust is calcium carbonate, making it one of the most common minerals on the planet (www.mineral.galleries.com). Calcium carbonate is the most common nonsiliceous mineral (www.encyclopedia.com).

The petition includes analytical data for inorganic components as well as a range of organic chemicals. The majority of results are listed as ND (not detected). However, in general it is not possible from the information provided to determine the detection limits. It is possible that the chemicals are present at some concentration less than the detection limit. If the detection limit is less than a level of interest or concern, then it can be concluded that the material does not present a risk. However, in the absence of information about detection limits, it is not possible to reach a conclusion about whether concentrations are below levels that could present a risk. Also, in some cases the analytical results are given in units of liquid and in others in units of solid phase materials. The analytical data provided with the petition is of limited usefulness.

Analytical data for lime mud from several sources is compiled in Table 1 of this TAP. The table is limited to metals and other inorganics. The first column lists the analytes included; the second column provides data on lime mud from the petition; the third column provides data on lime mud from the University of Georgia (2004); the forth column presents data on agricultural lime from the University of Georgia (2004); the fifth column provides commonly used ecological screening levels (where available); and the sixth column provides commonly used human health screening levels. Both the human health screening levels and the ecological screening levels are generally considered protective, and may include a margin of uncertainty (safety) of up to several orders of magnitude. Where concentrations are less than the screening level, it is reasonable to assume that the material does not present a toxic risk to that receptor. However, where concentrations exceed screening levels it is not reasonable to assume that the material does present a risk. Using the petitioner's data, only one analyte exceeds the human health criterion: arsenic. However, the arsenic concentration provided by the petitioner is lower than background arsenic levels in soil in much of the U.S. Seven analytes exceed the ecological screening levels, generally by a factor of less than 3. Only manganese and boron exceed the ecological screening level by a greater margin. For 3 analytes, it is not known whether concentrations in the petitioned lime mud exceed ecological screening levels, because the analytes were not detected, but the detection limit was higher than the screening level: antimony, silver, and vanadium. For comparison, baseline or background concentrations of some of these analytes, as described in Shacklette and Boerngen (1984; also known as USGS 1984) range as high in the U.S. as:

- Arsenic 25.9
- Chromium 208
- Manganese 2,532
- Molybdenum 4.37
- Lead 55.4
- Zinc 183

(all units in mg/kg, equivalent to parts per million). Even the highest levels listed on Table 1 for lime mud are less than the upper end of the natural range in the U.S. for all of these analytes except zinc. In summary, in general, inorganic analyte concentrations in lime mud are either below screening levels for protection of human health or ecological receptors, or are within the range of natural background surface soil concentrations in the U.S. This conclusion applies only to inorganic analytes.

Properties of the Substance:
According to www.physics.helsinki.fi lime mud is a powder consisting of small particles with a diameter of about 0.1 to 100 um. Calcium oxide is the main component.

According to the MSDS from the National Institute of Environmental Health Studies (date unknown), lime mud is a solid material with greenish to light gray color. It may have a slight hydrogen sulfide odor, and has a specific gravity of about 3.0. Lime mud is slightly soluble in water, and has a pH of <12.5.

Specific Uses of the Substance:
The intended petitioned use of lime mud "as a plant or soil amendment micronutrient." "It is to be used for crops at a maximum rate of 2 tons per acre as a top dressing, or 3 tons per acre incorporated. The method of application is by agricultural lime spreader."

According to the University of Maine (2004), 0ther common uses of lime mud include:

- Agricultural liming material in conventional agriculture
- Stabilizing/solidifying agent for hazardous waste treatment
- Cementitious material in construction

Research conducted in Thailand suggests that lime mud is effect at precipitating (removing) certain metals from wastewaters (Wirojanagud 2004).

Approved Legal Uses of the Substance:
The petitioner has been approved and licensed by Maine Department of Environmental Protection (DEP) to sell residual lime mud for agricultural utilization. License numbers S-022170-SD-A-N, S-021958-SG-C-M, S-021513-SG-B-M. The Maine Department of Environmental Protection is charged with considering the following criteria as it regulates agricultural utilization of solid wastes (Wright 2001):

- Land application will benefit crops or soil
- Protect public health
- Protect the environment

Beneficial re-use generally implies that the material will not pollute the air or water. Maine prohibits use of these materials within a protected natural resource.

Also, when it is used beneficially and applied at recommended rates, the Georgia Department of Environmental Resources (Environmental Protection Division) does not consider lime mud an industrial waste, and it can be used without the user obtaining a specific permit. However, the distributor must be licensed by the state. (University of Georgia 2004)

Calcium carbonate is affirmed by the U.S. Food and Drug Administration (FDA) as GRAS (generally accepted as safe) for use in food with no limitation other than current good manufacturing practice (FDA 2000). As a result, for example, it is exempt from certification as a color additive to drugs (assuming that the calcium carbonate meets the specification in the U.S. Pharmacopeia) (CFR Title 21, Volume 1, rev April 1, 2002, Chapter I, Part 73, Section 73.1070 Calcium Carbonate).

Action of the Substance:
Lime mud has an alkaline pH. When added to acidic soils, it acts to neutralize the pH. Because of the small size of lime mud particles and the presence of hydroxides in lime mud, lime mud raises soil pH more quickly than does limestone (the more commonly used raw material) (University of Maine, 2004). Lime mud also increases soil levels of calcium (more quickly than does limestone) and sodium (not enough to be a problem) (University of Maine, 2004).

Status

International
Lime mud is not specifically listed for the petitioned use or other uses in the following international organic standards:

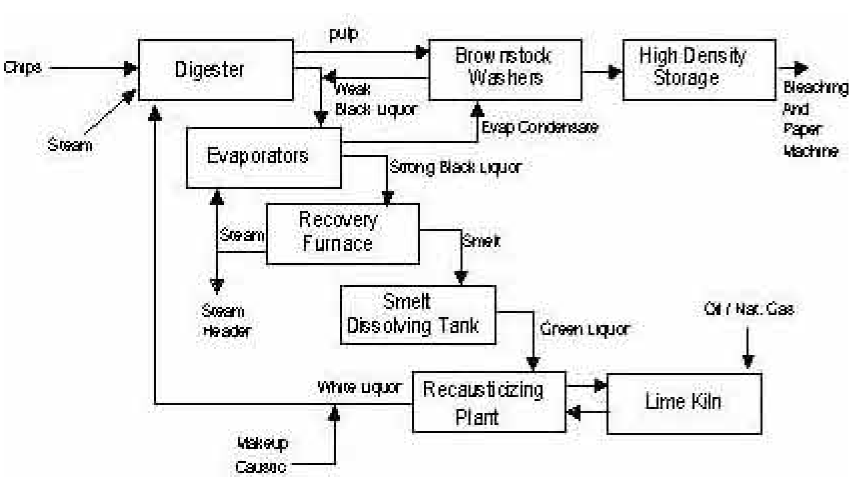
- Canadian General Standards Board
- CODEX Alimentarius Commission
- European Economic Community (EEC) Council Regulation 2092/91
- International Federation of Organic Agriculture Movements
- Japan Agricultural Standard for Organic Production

Evaluation Questions for Substances to be used in Organic Crop or Livestock Production

Evaluation Question #1: **Is the petitioned substance formulated or manufactured by a chemical process? (From 7 U.S.C. § 6502 (21))**

The overall process that yields the petitioned lime mud is depicted in the following figure.

STEP 1: TRANSFORMING WOOD CHIPS TO PULP



http://www.paperloop.com/db_area/archive/extra/kraft.shtml

It is the recausticizing process, specifically, that can generate an excess of lime mud:

- Pulp digesting liquors are used to dissolve lignins from wood fiber. (McClung, date unknown)
- During the above process, sodium hydroxide is converted to sodium carbonate. (University of Georgia, 2004)
- Calcium oxide (quick lime) is added to convert the sodium carbonate back into sodium hydroxide so that it can be re-used. (University of Georgia 2004)
- Insoluble calcium carbonate, formed during the reactions, must be recovered from the liquor (commonly by filtration or clarifier) so that spent lime can be reactivated. (McClung, date unknown)
- Once separated, the calcium carbonate is converted to calcium oxide so that it can be re-used. One molecule of calcium carbonate yields one molecule of calcium oxide plus one molecule of carbon dioxide. This is a reversible reaction. (McClung, date unknown)
- *To re-causticize the pulp digesting liquors, large amounts of calcium oxide (CaO, quick lime) are used. The resulting chemical reaction generates lime mud (mostly CaCO3).* (Petition)

The lime mud is washed and added to the lime kiln, where it is converted to calcium oxide that is recycled into the recausticizing process (petition). However, when the process is not functioning properly or when it is down for repairs, excess lime mud is generated.

Therefore, the lime mud is the result of a chemical process that converts calcium oxide to calcium carbonate (as a by product of re-causticizing pulp digesting liquors). The particle size of the lime mud is affected by conditions in the slaking and causticizing processes (Tiljander 1997).

Evaluation Question #2: Is the petitioned substance formulated or manufactured by a process that chemically changes the substance extracted from naturally occurring plant, animal, or mineral sources? (From 7 U.S.C. § 6502 (21).)

CaO is the primary chemical compound that is added to the recausticizing cycle. Small quantities of drainage aids and coagulants are added to the process to assist in the dewatering and settling of lime mud. Salt cake (sodium sulfate) is added through the black liquor cycle. Periodically, sodium hydroxide and sodium hydrosulfide are added when the recausticizing process cannot maintain production requirements. In the process, calcium oxide is converted to calcium carbonate. Calcium carbonate is an abundant component of the earth's crust.

Evaluation Question #3: Is the petitioned substance created by naturally occurring biological processes? (From 7 U.S.C. § 6502 (21).)

Calcium carbonate is an abundant component of the earth's crust. However, the petitioned lime mud is not created by naturally occurring biological processes. It is created as a result of commercial processing of paper pulp, through a chemical process that allows pulp digesting liquors to be re-generated (re-causticized) and re-used. The petitioner emphasizes that lime mud never comes into contact with the bleaching aspects of the pulp and paper process.

Evaluation Question #4: Is there environmental contamination during the petitioned substance's manufacture, use, misuse, or disposal? (From 7 U.S.C. § 6518 (m) (3).)

Evaluation Question #1 provides information about the larger process of transforming wood chips to pulp. The larger process associated with kraft pulp mills is regulated by the U.S. Environmental Protection Agency (EPA) under the Clean Air Act (CAA), Clean Water Act (CWA), Resource Conservation and Recovery Act (RCRA), and EPCRA (EPA 1999). A wide variety of chemicals can be released to the environment through the various process areas of a plant. Both lime and lime mud are listed as example EPCRA Tier 2 chemicals in the chemical recovery/causticizing process area (EPA 1999). As obtained from EPA's website on July 4, 2005, lime mud, lime, calcium carbonate are not covered under the Toxics Release Inventory (TRI) (EPA undated). EPA 2002 provides a list of TRI releases for pulp and paper facilities.

No information was identified to indicate whether environmental contamination results from the process that generates lime mud. However, any contamination that is generated would be the result of the pulp and paper process itself; lime mud is not an intentional product, but rather a by-product. If not used productively (e.g., in agriculture), excess lime mud would be a waste product (although not necessarily considered "contamination").

Lime mud contains several inorganic chemicals. Calcium carbonate in nature can also be associated with other inorganic chemicals. Table 1 compares results of analysis provided in the petition with U.S. Environmental Protection Agency (USEPA) screening levels for soil.

The petition points out that:

> "The lime mud produced by the mills provides a local, low cost premium source of CaCO3 that has agronomic value to the local farms, and at the same time provides a means to recycle and conserve these resources, instead of placing them in a landfill where the value of the product is lost.
>
> This is a conservation minded source of crop and soil nutrient. It provides a high quality calcium lime by recycling nutrients while offering a significant savings to the farmer. Agricultural use of lime mud as a liming agent greatly reduces the amount of waste that is incorporated into a landfill, were (sic) it's (sic) agricultural values is wasted.
>
> Presently, non-organic farmers are using the lime mud product, and their agronomists have seen very beneficial results from it's (sic) use. "

Evaluation Question #5: Is the petitioned substance harmful to the environment? (From 7 U.S.C. § 6517 (c) (1) (A) (i) and 7 U.S.C. § 6517 (c) (2) (A) (i).)

Evaluation Question #4 provides additional information.

Calcium carbonate, the primary component of the petitioned lime mud material, is a natural component of the earth's crust. The MSDS says twice: "Do not allow material to enter waterways or wetlands." The MSDS also states that "contact with acidic materials may generate hydrogen sulfide gas." Hydrogen sulfide (H2S) has a characteristic rotten egg odor and can cause unconsciousness and death at sufficient acute exposure.

Evaluation Question #6: Is there potential for the petitioned substance to cause detrimental chemical interaction with other substances used in organic crop or livestock production? (From 7 U.S.C. § 6518 (m) (1).)

Based on the intended use of the substance (as well as its use in conventional agriculture), no information was uncovered to suggest that lime mud could cause detrimental chemical interaction with other substances used in organic crop production.

Evaluation Question #7: Are there adverse biological or chemical interactions in the agro-ecosystem by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)

No information distinct from that provided under Evaluation Qeustions #4, #5, and #6 was uncovered. Specifically, the MSDS provided with the petition states: "Do not allow material to enter waterways or wetlands." Calcium carbonate is a natural component of the earth's crust. Lime can control the environment in such a way as to reduce bacterial growth (National Lime Association, undated).

Evaluation Question #8: Are there detrimental physiological effects on soil organisms, crops, or livestock by using the petitioned substance? (From 7 U.S.C. § 6518 (m) (5).)

Based on the intended use (as well as its use in conventional agriculture), no information was uncovered to suggest that lime mud would have detrimental physiological effects on soil organisms, crops, or livestock.

Indeed, lime mud is commonly land applied in conventional agriculture. Studies comparing lime mud with agricultural limestone showed that lime mud produced yields of the following crops that were comparable to or higher than yields associated with agricultural lime mud: corn, wheat, soybeans, pearl millet (University of Georgia 2004).

The University of Georgia (2004) implies that over-application of lime mud can produce soil pH high enough to create crop growth problems.

<u>Evaluation Question #9:</u> Is there a toxic or other adverse action of the petitioned substance or its breakdown products? (From 7 U.S.C. § 6518 (m) (2).)

The primary component of lime mud is a natural component of the earth's crust, and is commonly used in conventional agriculture. No adverse effects are anticipated. However, according to the petition, contact with acids or oxidizers, lime mud may release hydrogen sulfide (H2S), which, at sufficient concentrations, can be acutely toxic on inhalation. The likelihood of such contact in agriculture practice may be low. According to the MSDS provided with the petition, the material: "Causes irritation and possible burns to the skin and eyes. Contact with extreme heat may generate carbon dioxide. Contact with acidic material may generate hydrogen sulfide gas. Prolonged skin contact may cause burns. Causes irritation and burns to the eyes and skin. This material is primarily calcium carbonate with a trace of sodium hydroxide." And later: "chemical goggles, impervious gloves and other protective equipment necessary to prevent skin contact. Particulate respirators if exposure limits may be exceeded. Barrier creams may also be used to supplement protective clothes."
Also according to the MSDS, storage of lime mud outdoors and uncovered can result in generation of dust.

The petition includes chemical analytical information for samples of lime mud. Table 1 of this TAP compares levels of inorganic analytes provided in the petition with (1) levels reported by the University of Georgia for lime mud, (2) levels reported by the University of Georgia for agricultural lime, (3) common ecological soil screening levels, and (4) common human health screening levels for residential soil. The petition provides analytical results for volatile organic compounds, semi-volatile compounds, pesticides, herbicides, and dioxins as well. Although the sample quantitation limits (detection limits) were not provided for the majority of organics analyses, none were detected except 1,2,3,4,6,7,8-HpCDD (detected in one of two samples at 0.167 picograms per gram), total HpCDD (in one of two sampes at 0.324 picograms per gram), and OCDD (in one of two samples at 1.42 picograms per gram). This level of dioxin congeners is not significant in light of a common ecological screening level of 38.6 mg/kg for total dioxins (USEPA Region 6, 2005) or a common human health screening level of 3.9E-6 mg/kg for the most toxic 2,3,7,8-TCDD form (USEPA Region 9, 2004).

<u>Evaluation Question #10:</u> Is there undesirable persistence or concentration of the petitioned substance or its breakdown products in the environment? (From 7 U.S.C. § 6518 (m) (2).)

No evidence was uncovered to suggest that use of lime mud would result in undesirable persistence of components or breakdown products. See also Table 1 and response to Evaluation Question #9.

<u>Evaluation Question #11:</u> Is there any harmful effect on human health by using the petitioned substance? (From 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).)
Based on the intended use, no evidence distinct from that provided under Evaluation Question #9 and in Table 1 was uncovered.

<u>Evaluation Question #12:</u> Is there a wholly natural product which could be substituted for the petitioned substance? (From 7 U.S.C. § 6517 (c) (1) (A) (ii).)

This paragraph does NOT imply that the listed alternatives are either wholly natural or accepted by NOSB, but rather represent an attempt to provide a broader context for evaluation. According to a Clemson

University website (www.hubcap.clemson.edu), potential alternatives as soil amendments to adjust pH include (but are not limited to)

- Ground agricultural limestone
- Quick lime, burned lime, or oxide lime
- Hydrated lime
- Marl or Selma chalk
- ground oyster shells
- very finely ground egg shells
- basic slag or blast furnace slag
- boiler wood ash and fireplace ash
- flue dust or cement kiln dust
- grits and dregs (also pulp and paper mill by-products)
- carbide lime or acetylene lime

Of the alternatives listed above, the following appear to be potentially wholly natural (other than mechanical processing to reduce particle size): ground agricultural limestone, Marl or Selma chalk, ground oyster shells, very finely ground egg shells. Several or most of these are likely to be less efficacious than lime mud, based on information provided at www.hubcap.clemson.edu.

Physical characteristics of lime mud may be poor for agricultural use, but when it is finely ground, it may neutralize soil acidity more effectively than ground limestone or other products (www.hubcap.clemson.edu). Lime mud may be more efficacious than agricultural lime because of particle size, higher calcium content, lower magnesium content, and CCE (University of Maine 2004; University of Georgia 2004).

This TAP review does not compare the efficacy of the petitioned material to alternative approved products. In addition, the review does not necessarily identify all potential alternative products.

<u>Evaluation Question #13:</u> Are there other already allowed substances that could be substituted for the petitioned substance? (From 7 U.S.C. § 6518 (m) (6).)

According to the NOSB Materials Database, lime is allowed for use in controlled atmosphere storage to remove CO2 from the air, but prohibited for use as a fertilizer (NOSB Material Database, 1996).

Hydrated (or slaked) lime is allowed for use in livestock (NOSB Material Database, 1995). It is composed of 36% calcium, 20% magnesium, and calcium hydroxide. It is approved for the following uses:

- Pest control
- Antacid when used as limewater
- Reduces scours in young animals
- Antidote to high tannin intakes
- Topically as an irritant and caustic in dehorning pastes
- Dessicant wound treatment preparations
- Deodorant over fecal wastes

This TAP review does not compare the efficacy of the petitioned material to alternative approved products. In addition, the review does not necessarily identify all potential alternative products. Additional information is provided in Evaluation Question #12.

<u>Evaluation Question #14:</u> Are there alternative practices that would make the use of the petitioned substance unnecessary? (From 7 U.S.C. § 6518 (m) (6).)

No alternative practices were identified, other than those discussed in Evaluation Questions #12, and 13.

<u>Additional Information:</u>

According to the University of Maine (www.useit.umeciv.maine.edu/materials/limemud…), because of the small particle size and presence of hydroxides, lime mud may increase soil pH faster than dolomitic limestone does. Lime mud also rapidly increases soil levels of calcium, but not manganese. Lime mud can increase soil levels of sodium, but not to a level that would be a problem agriculturally.

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Table 1. Inorganic analytical results for Lime Mud and comparison for context.
All units in parts per million (except as otherwise noted).

Analyte	lime mud - petition (1)	lime mud - University of Georgia (2)	Agricultural lime - University of Georgia (2)	common ecological screening level for soil (4)	common human health screening levels for residential soil (5)
aluminum	630			NA (3)	78,000
antimony	<0.6			0.3	31
arsenic	1.6	1.71	<1 - 3	31	0.43
barium	260			330	5,500
beryllium	0.06			30	160
cadmium	1.2 j	bd - 0.5	<0.1 - 1.1	0.4	78
chromium (total)	10			7.9	120,000
cobalt	<6			32	1,600
copper	22			54	3,100
iron	700				23,000
lead	36	bd - 0.5	1.3 - 130	15	400 (6)
manganese	1040			152	1,600
mercury	0.11	<0.05	<0.01 - 0.02	0.1	23
molybdenum	4.1	bd - 0.1	0.3 - 0.5	2	390
nickel	9	3.3 - 71	7.0 - 17	48	1,600
selenium	0.7	bd - 7.6	<1	1	390
silver	<7			2	390
thallium	<0.7			1	6
vanadium	<50			2	78
zinc	248			120	23,000
boron	4			0.5	7,000
cyanide	<1.2				1,600
pH (standard units)	12.06				

1. The Environmental Exchange, Inc., 2004. (analyzed by Maine Environmental Laboratory)
2. University of Georgia, Cooperative Extension Program, 2004
3. aluminum not likely to be toxic unless pH is less than 5.5 (Eco-SSL, USEPA 2003).
4. USEPA Region 6. 2005. DRAFT Technical Memorandum, Selection of Chemicals of Potential Concern.
5. USEPA Region 3. Risk-based Concentration Table. April 4, 2004.
6. Not from USEPA Region 3. Common USEPA-based screen for lead in residential soil.