DRAFT HUMAN AND ENVIRONMENTAL RISK ASSESSMENT OF CALCIUM HYDROXIDE

Prepared by the Washington State Department of Ecology
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Fact Sheet

Project Title:	State of Washington Aquatic Plant Management Program
Proposed Action:	The Proposed Action is review of calcium hydroxide for phosphorous management in lakes. The action is defined as a nonproject proposal under State Environmental Policy Act (SEPA) rules such that the Environmental Impact Statement (EIS) will be integrated with on-going agency planning and permitting procedures for aquatic herbicides. The Final Supplemental Environmental Impact Statement for Freshwater Aquatic Plant Management was completed by Ecology's Water Quality Program February 2001 (Publication # 00-10-040). The current evaluation for calcium hydroxide is a supplement to that Environmental Impact Statement. The recommended alternative is an integrated aquatic plant management approach using the most appropriate mix of vegetation control methods that may include biological, manual/mechanical, and chemical methods. Other alternatives analyzed include no action, which is the continuation of current policy.
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Responsible Official:	Duane Weaver, Program Development Section, Technical Services Unit Supervisor
Licenses, Permits:	Not all permits listed below are required. Requirements may change; please check with resource agencies to determine permit requirements for a particular project.
Ecology:	Coverage under the Aquatic Nuisance Plant and Algae Control Permit No. WAG-994000 .
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Executive Summary

Calcium hydroxide is a compound most commonly used in the production and manufacturing of building materials, but is also used extensively for the treatment of wastewater and biosolids. Calcium is the fifth most abundant element in the Earth's crust, and is therefore found in almost every. Production in the United States alone exceeds one million pounds annually.

Environment

Calcium hydroxide dissociates slowly in water into form calcium oxide and water. When calcium hydroxide comes into contact with carbon dioxide it creates an insoluble form of calcium carbonate. Acute ecotoxicity tests with fish showed LC_{50}'s ranging from 33.9 mg/L to 240 mg/L. The lower level toxicity values can be attributed to some fish species sensitivity to hydroxides (Note: the 33.9 mg/L value was obtained at 96 hours.). Because of the lack of data available on calcium hydroxide, a great deal of the risk assessment information is focused on the toxicity and potential effects of calcium.

After calcium hydroxide is used in the treatment of wastewater and biosolids, a great deal of it will be discharged with the remaining wastewater into natural aquatic ecosystems. Calcium hydroxide would inevitably come in contact with carbon dioxide during this process and leave behind an insoluble form of calcium carbonate. In aquatic ecosystems, calcium hydroxide binds to phosphorous, making it unavailable in the system. This lowers the risk of large scale algae blooms in lakes. Calcium has a very low toxicity, and the amount being emitted is relatively low in comparison to the natural background of calcium in water.

Based on the available data, the use of calcium hydroxide in the treatment of wastewater has no adverse effect on the aquatic ecosystem.

Human Health

There is very little data available on the toxicity of calcium hydroxide. It does have a low acute oral toxicity (LD50 >7000 mg/kg bodyweight). There is very little existing animal data, but is has been shown that chronic exposure to calcium hydroxide in drinking water can cause aggression, restlessness, reduced food intake and blood changes in rats. Changes have also been observed in the liver, kidneys, stomach and small intestine. In animal tests there was no reported skin irritation in rabbits exposed to calcium hydroxide, and eye irritation studies reported a high possibility of corrosiveness and permanent eye damage when exposed to thick, pasty compounds containing calcium hydroxide.

When consumers are exposed to calcium hydroxide, neither hydroxide nor calcium carbonate should cause any permanent or lasting physical effects. Calcium carbonate should precipitate out, and hydroxide will combine with available oxides to form water, which would also be flushed from the system. In regards to genotoxicity, carcinogenicity, and developmental toxicity, calcium is already present in the body and essential to bone

density and production. It can be concluded that there is concern for humans with regard to possible genotoxicity, carcinogenicity or developmental toxicity of calcium hydroxide. The only critical endpoint for calcium hydroxide exposure seems to be the potential for eye irritation.

Consumers and workers can be exposed to substances containing calcium hydroxide via skin contact. However, the estimated concentrations and mixtures of calcium hydroxide are too low to cause skin irritation.

Accidental exposure of the eyes to pasty, dry, or mixed solutions of calcium hydroxide could result in eye irritation. Only if the calcium hydroxide concentration in the product exceeds 10% could irreversible eye damage occur if the eyes are not rinsed immediately. There is less likelihood of damage from a clear liquid (such as lime water) than a more pasty substance (cement, plaster, or mortar).

Acute cases of oral poisoning or effects on human eyes, due to accidental or intentional overexposure to calcium hydroxide, have not been found in the literature.

Based on the available data, the use of calcium hydroxide in environmental process has no adverse effect on the public.

Effect of carbon dioxide on the aquatic environment

Research shows that there should be little to no adverse effect from the addition of carbon dioxide to aquatic ecosystems. The combination of calcium hydroxide and carbon dioxide to form calcium carbonate has the potential to control algae blooms in lakes. The addition of carbon dioxide may increase plant growth within the system, given that carbon is a limiting factor in aquatic environments.

Contents

Fact Sheet _____ ***2***

Executive Summary _____ ***4***

Contents _____ ***6***

1. Introduction _____ ***8***

Identity and physical/chemical properties _____ **8**

Production _____ **9**

Use _____ **9**

Regulatory History _____ **10**

Classification _____ **10**

2. Environmental Assessment _____ ***11***

Environmental exposure assessment _____ **11**
Seawater Challenge 11
Environmental Fate 11
Monitoring Data 12
Predicted Environmental Concentrations 13

Environmental effects assessment _____ **14**
Toxicity 14

3. Human Health Assessment _____ ***15***

Consumer Exposure_____ **15**
Skin contact 15
Inhalation 15
Oral uptake 15

Hazard Assessment_____ **16**
Toxicokinetics, metabolism and mechanism of action 16
Skin Irritation 16
Eye Irritation 16
Repeated Dose Toxicity 16
Genetic toxicity 17
Carcinogenicity 17
Toxicity to Reproduction 17
Developmental Toxicity / Teratogenicity 17
Experience with human exposure 17

Identification of critical endpoints 18

3.3 Consumer Risk Characterisation 18

References 19

DRAFT RISK ASSESSMENT OF CALCIUM HYDROXIDE

1. Introduction

Calcium hydroxide, or hydrated lime, is being investigated for its potential use in controlling phosphorous in Washington lakes, rivers, and streams. Phosphorous is the limiting nutrient for algae, and with the amount of phosphorous entering lakes via stormwater runoff and groundwater seepage, phosphorous problems have quickly led to algae problems.

Algae has become more of a problem in Washington lakes in recent years, primarily because many of our lakes are shallow and hypereutrophic, and many lie in residential areas, making algae blooms very visible to the public. Washington has also begun to have more toxic algae blooms, making the water unsafe for drinking, recreation, irrigation and any other use.

There are very few tools available for algae control in Washington State. As a result of the 2001 *Headwater Inc. v. Talent Irrigation District* ruling in the Ninth Circuit Court of Appeals, Washington now regulates aquatic pesticide use via one of seven aquatic pesticide NPDES permits. The Nuisance Weed and Algae Control General NPDES Permit regulates algae control activities. We currently allow the use of three products for algae control: Green Clean (active ingredient sodium carbonate peroxyhydrate), Hydrothol® 191 (active ingredient endothall) for filamentous algae control only, and aluminum sulfate is allowed for nutrient control (either through an injection system or a whole lake application).

Calcium hydroxide has been used for algae control and lake purification throughout Europe, the northeastern United States and northern Canada. Normally, these are hard water, highly eutrophic systems suffering from alkalinity changes due to acid rain or other pollution sources.

Identity and Physical/Chemical Properties

Calcium hydroxide is a dry powder that is obtained by adding enough water to calcium oxide to covert the oxides into hydroxides. There are three different chemical formulations of calcium hydroxide, all dependent upon the type of calcium oxide used and the way the product is hydrated.

High calcium hydrated lime generally contains 72 to 74 percent calcium oxide and 23 to 24 percent water. *Dolomitic hydrated lime (normal)* is formed when under atmospheric hydrating conditions only the calcium oxide fraction of the dolomitic quicklime hydrates, producing a hydrated lime that contains 46 to 48 percent calcium oxide, 33 to 34 percent magnesium oxide, and 15 to 17 percent water. *Dolomitic hydrated lime (pressure treated)* is produced from dolomitic quicklime under pressure, which results in hydrating almost

all of the magnesium oxide as well as all of the calcium oxide, producing a compound that is 40 to 42 percent calcium oxide, 29 to 30 percent magnesium oxide, and 25 to 27 percent water.

A boiling point could not be determined for calcium hydroxide because it disassociates when heated to the melting point of 580° C. Calcium hydroxide has very low solubility, but when mixed with carbon dioxide creates a insoluble form of calcium carbonate. The particle size of calcium hydroxide is irrelevant, because it is usually prepared as a powder or liquid. Hydrated lime, or calcium hydroxide, is strongly alkaline, possessing a pH of 12.4. The identity and several physical/chemical properties are summarized in Table 1.

Table 1. Identity and physical / chemical properties of calcium hydroxide

Property	**Results / Remarks**	**Reference**
Molecular Formula	$Ca(OH)_2$	
Molecular Weight	74.09	
CAS Number	1305-62-0	
EINECS Number	215-137-3	
Average Particle Size		
Melting Point	580° C	ESIS (2000)
Density	2.343 @ 25° C	
Odor	Odorless	
Water Solubility	0.185g / 100 cc water @ 0° C	
Vapor Pressure	Negligible	

Production

Calcium is the fifth most abundant element in the Earth's crust. Because of this, calcium hydroxide is produced at over one hundred locations worldwide, predominately in manufacturing communities. More than one million pounds are produced annually in the United States alone.

Calcium hydroxide is one component of a cyclical process, where calcium carbonate ($CaCO_3$) is either heated or calcinated to a temperature of 1100° C, forming calcium oxide (CaO). Through the addition of water via hydration or slaking, calcium oxide becomes calcium hydroxide ($Ca(OH)_2$). The final piece is when carbon dioxide is added to the calcium hydroxide, reproducing calcium carbonate and starting the whole cycle over.

Use

Worldwide, calcium hydroxide has a number of uses. It is often use in steel manufacturing, magnesium manufacturing, alumina manufacturing, ore flotation and non-ferrous metal smelting. In the pulp and paper industry, it is used in the sulfate process, sulfite process, bleaching, strawboard manufacturing, and in the treatment of pulp and paper mill liquid wastes, as a coagulant in color removal. It is also used in the

purification of citric acid, glucose, and dextrin; metallic calcium, and for soda-lime, and absorbent.

Calcium hydroxide is used heavily in the environmental arena. This includes uses in air pollution control to remove acidic gases, particularly sulfur dioxide (SO_2) and hydrogen chloride (HCl), from flue gases. Lime-based technology is also being evaluated for use in the removal of mercury. Lime can be used for effective treatment of sewage biosolids, as well as industrial sludges and petroleum wastes. (National Lime Association, 2002)

Calcium hydroxide and quicklime have been used for over 100 years to treat biological organic wastes. The U.S. EPA specifically prescribes the use of lime treatment for the treatment of human wastewater sludges. In this environment, lime treatment is used to control the environment needed for the growth of pathogens in biosolids and converts biosolids into a usable product. (National Lime Association, 2002)

It is extensively used to neutralize phosphorous and nitrogen in wastewater and animal wastes. Not only is it a cost-effective option, but it also means that the treated biosolids and other waste products can be reused in agricultural and urban areas as a soil supplement.

Calcium hydroxide also plays a huge role in the manufacturing process for concrete products, calcium silicate bricks, miscellaneous building materials, insulation products, pigments, water plaints, varnish, petroleum, leather and rubber. It is also used by the dairy industry, the sugar industry, animal glue and gelatin industries, baking industry and in the controlled atmospheric storage of fresh fruit and vegetables. All tortillas are made with lime treatment.

Regulatory History

Calcium hydroxide is not now, nor has it ever been officially registered as a pesticide by the U.S. EPA. It is registered on list 4, the EPA's list of inert pesticide ingredients of minimal concern (U.S. EPA, 2002). Calcium hydroxide is used extensively in wastewater, industrial, and drinking water treatments. This is all done using approved EPA methods.

This is a regulated chemical in Europe, and there is extensive monitoring and product information available through the European Commission's Chemical Bureau.

Classification

Calcium hydroxide is not currently classified in any of the four toxicity categories used by U.S. EPA.

EPA currently uses the following criteria to determine the toxicity category of pesticides. The criteria are based on animal studies done in support of the registration of the product.

	I	II	III	IV
Oral LD50	Up to and including 50 mg/kg	From 50 thru 500 mg/kg	From 500 thru 5000 mg/kg	Greater than 5000 mg/kg
Inhalation LC50	Up to and including 0.2 mg/liter	From 0.2 thru 2 mg/liter	From 2 thru 20 mg/liter	Greater than 20 mg/liter
Dermal LD50	Up to and including 200 mg/kg	From 200 thru 2000 mg/kg	From 2,000 thru 20,000 kg/mg	Greater than 20,000 mg/kg
Eye effects	Corrosive: corneal opacity not reversible within 7 days	Corneal opacity reversible within 7 days; irritation persisting for 7 days	No corneal opacity; irritation reversible within 7 days	No irritation
Skin effects	Corrosive	Severe irritation at 72 hours	Moderate irritation at 72 hours	Mild or slight irritation at 72 hours

2. ENVIRONMENTAL ASSESSMENT

Available LC50 values are normally used to identify the hazards associated with a product. In the case of calcium hydroxide, there are no LC50's available because this product has not been registered as a pesticide in the past.

Seawater Challenge

A Seawater challenge has not been completed for calcium hydroxide. Given the abundance of calcium in the natural environment, there seems to be little risk associated with its presence in seawater.

Environmental Exposure Assessment

After use in manufacturing and environmental processes (like sewage sludge stabilization), calcium hydroxide is discharged into aquatic ecosystems (rivers, lakes, estuaries, and the sea).

Environmental Fate

Calcium hydroxide is slightly water soluble and when mixed with carbon dioxide will form an insoluble form of calcium carbonate.

$$\mathbf{Ca(OH)_2 + CO_2 = CaCO_3}$$

Calcium carbonate does not adsorb to sediment. There is no transfer of this substance into the atmosphere and therefore the environmental risk assessment can be focused on the potential aquatic effects. The environmental fate of calcium carbonate will be discussed below.

Calcium Carbonate

When calcium carbonate is brought in contact with powerful oxidizing agents such as fluorine, boron triflouride, and oxygen diflouride, the reaction may cause fire and/or explosions. Calcium carbonate is also incompatible with acids, alum, ammonium salts and magnesium when presented in the form of limestone (would contain crystalline silica). This type of contact would cause the limestone to ignite.

Buffering

When used in a lake setting to inactivate total phosphorous, calcium hydroxide should be buffered to avoid the pH rising above 10. Under most conditions, a pH over 10 will cause increased mortality rates for aquatic organisms. By including carbon dioxide (CO2) soon after the calcium hydroxide enters the system, it is possible to control the pH and keep it below ten, but high enough for efficacy, for an extended period of time.

Breakdown

When dissolved in water, hydroxides dissociate to produce free hydroxide ions (thus raising the pH of the solution) and the counter metal cations:

$$\mathbf{Ca(OH)_2 = CaO + H_2O}$$

The hydroxide ion may then react with any free H+ or any acidic species in the system, forming water:

$$OH^- + H^+ = H_2O$$

The solubility of $Ca(OH)_2$ in solution is 1.85 g/L H_2O; this solubility is affected by pH, temperature, and the presence of aquatic species in the solution. Increased pH lowers solubility because a higher OH- concentration lowers the available solid hydroxide that can dissociate into free OH- ions and metal ions. With increased temperature, the calcium hydroxide solubility decreases (ESIS, 2000).

Monitoring Data

There is no available data for any aquatic or groundwater sampling for the presence of calcium hydroxide in the United States. However, there is natural background data for calcium taken from surface waters in Europe. Background was taken in various cities throughout Belgium in 1993, with the results shown below.

Location	**Calcium concentration (mg/L)**	**pH**
Jambes	65.7	8.41
Nameche	75.3	8.21
Liege	74.1	8.08
Gorbbendonk	71.6	8.19
Lier	70.6	8.23

Broechem	69.6	8.22

*Data submitted to the European Chemicals Bureau of the European Commission by Solvay S.A. Brussels

There is also data from 1983, collected by Solvay S.A. of Brussels showing natural background levels of calcium and the corresponding pH from various European countries. That information is shown below.

Country	**Location**	**Calcium concentration (mg/L)**	**pH**
France	Remilly	77	8.1
Belgium	Hastiere	66	8.2
Belgium	Tailfer	65	8.1
Belgium	Nameche	73	8.2
Belgium	Liege	74	8.0
The Netherlands	Eijsden	76	7.8
The Netherlands	Belfeld	72	7.7
The Netherlands	Heusden	70	7.7
The Netherlands	Keizersveer	68	7.8

*Data submitted to the European Chemicals Bureau of the European Commission by Solvay S.A. Brussels

Information for natural background of calcium in different aqueous systems has also been calculated, including the type of rock in the freshwater systems. This information is presented below.

Aqueous System (rock type drained if known)	**Calcium concentration (mg/L)**
Seawater	412
Groundwater (limestone)	80
Stream (granite)	4
River/unpolluted	13.4
River/including contribution of human activities	14.7
Public water supply/ 100 U.S. cities	26 (mean) ; 0-145 (range)

*Data submitted to the European Chemicals Bureau of the European Commission by Solvay S.A. Brussels

Predicted Environmental Concentration

Both calcium and hydroxide should be extremely abundant in natural water systems. Calcium will be present in organisms, plants, and sediments, as well as possibly dissolved in the water column. Hydroxide ions, or hydrogen and oxygen should also be easily found throughout the natural environment. Because none of these breakdown products are unnatural, there addition to the environment should cause little to no environmental change.

Environmental Effects Assessment

Toxicity

Effects on fish
There is information available on acute toxicity in fish. The data was collected in Europe, and is summarized below. (Note: most of this data was not collected in methods consistent with EPA standards and would therefore not meet compliance for product registration through the Office of Pesticide Programs).

Acute Toxicity Data

Species	**Exposure period**	**Value**
Gambusia affinis	24 hour	240 mg/L
Gambusia affinis	48 hour	220 mg/L
Gambusia affinis	96 hour	160 mg/L
Clarius gariepinus	96 hour	33.9 mg/L
Micropterus sp.	7 day	100 mg/L
Goldfish, bass, sunfish	5 hour	100 mg/L (these species have survived 50 mg/L for 7 or more days)

* This data was submitted to ESIS by Solvay S.A., Brussels. It should also be noted that any LC50 greater than 100 mg/L declares the substance is non-toxic (for European standards).

Effects on invertebrates

Chironomids and amphipods are known to move through the water column to feed. They would potentially be affected by any calcium hydroxide treatments applied on a lake. In a study conducted in five naturally eutrophic lakes in eastern Canada, macroinvertebrate samples were taken at three-week intervals between May and August 1991 to 1993. Additions of 225 and 295 g $Ca(OH)_2 \cdot m^{-2}$ (74 and 107 $mg \cdot L^{-1}$) to two lakes resulted in the water pH remaining within its natural range (<10) and had no significant impacts on macroinvertebrate density or biomass for up to two years after treatment. (Yee et al., 2000)

Effects on aquatic plants and algae

Calcium hydroxide should have little or no direct effect on aquatic plants or algae. There are some indirect effects on aquatic plants and algae when calcium hydroxide is added to lake systems. Calcium hydroxide has long been used as a stabilization tool and nutrient management tool in lakes.

Lime in the form of calcium hydroxide ($Ca(OH)_2$) and calcium carbonate ($CaCO_3$) have been used extensively during the past twenty years to increase the alkalinity and pH of acidified lakes in eastern Canada and Europe. It is just in the last 15 years that lime has been used to inactivate P in eutrophic hard waters (Prepas et al., 1990). Studies have shown that multiple treatments with lime were sufficient to reduce mean total phosphorous and chlorophyll *a* concentrations by as much as 70 and 88% (Yee et al., 2000).

Effects on microorganisms

Calcium hydroxide should have little effect on microorganisms given its use in maintaining pH levels in sewage sludge and treated wastewater.

HUMAN HEALTH ASSESSMENT

Consumer exposure

Given that calcium hydroxide is used in so many building products as well as food production, data is available on the potential effects on consumers.

As relevant consumer contact scenarios, skin contact, inhalation, oral uptake and accidental or intentional overexposure of calcium hydroxide were addressed.

Acute Toxicity

Inhalation

Inhalation of calcium hydroxide dust can cause discomfort to the upper respiratory tract, which means that some type of protective mask should be worn during activities using $Ca(OH)_2$ is powder form (ESIS, 2000).

Oral Toxicity

The acute oral toxicity values identified in laboratory experiments are presented below.

Species	**LD_{50}**	**Reference**
Rat	7340 mg/kg body weight	Solvay S.A. Brussels
Mouse	7300 mg/kg body weight	Minermix SRL Fasano

*This data was acquired from ESIS and provided in a report published in 2000

Given such high LD_{50}'s, if this product was being registered by the EPA, it would fall into the toxicity category IV, meaning practically non-toxic. It should also be noted that calcium hydroxide is often used in food production to maintain pH levels and act as a texturing, firming, and anticaking agent.

Dermal toxicity

There is no data on the potential acute dermal toxicity, but was presented by European manufacturers as being not applicable. In a 1994 study, rabbits were tested for skin irritation by calcium hydroxide, and no irritation was found (ESIS, 2000).

Hazard Assessment

Toxicokinetics

Calcium hydroxide is a soluble organic compound usually obtained in either a powder or granular form. Its ionic structure is most often presented as:

Ca

OH OH

It has a low solubility (1.85 g/L H_2O), and dissociates into free hydroxide ions and the counter metal cations as discussed in a previous section.

$Ca(OH)_2 = CaO + H_2O$

Skin contact

Both consumers and workers can be exposed to calcium hydroxide via skin contact with solutions that contain calcium hydroxide. A common exposure would be during the use of calcium hydroxide in the manufacturing process. Calcium hydroxide is a relatively strong base, and as such a moderately caustic irritant to any exposed skin on humans.

There is no data on the potential acute dermal toxicity, but was presented by European manufacturers as being not applicable. In a 1994 study, rabbits were tested for skin irritation by calcium hydroxide, and no irritation was found (ESIS, 2000). There is no indication as to whether or not this toxicity study would meet EPA guidelines for registration of calcium hydroxide.

Eye Irritation

Being that calcium hydroxide is a relatively strong base, it could be seriously corrosive and can cause permanent eye damage if there is prolonged exposure (this was found with as little as a 10% solution).

Repeated Dose Toxicity

Solvay S.A. conducted a three month repeated dose toxicity test on rats. The rats were administered two different levels of calcium hydroxide (50 mg/L and 350 mg/L) in drinking water. Chronic exposure to Ca(OH)2 in drinking water led to aggression, restlessness, reduced food intake and blood changes in tested rats. Internally, changes were observed in the liver, kidneys and stomach, and some swelling in the small intestine.

Genetic Toxicity

There is no available data on the genetic toxicity of calcium hydroxide. This is a data gap that will most likely not get addressed, primarily due to the abundance of this substance and its breakdown products in the natural environment.

Carcinogenicity

There is no data available on the potential carcinogenicity of calcium hydroxide. Calcium hydroxide is used in food production, a use that would not be allowed if the substance was believed to be cancer-causing.

Toxicity to reproduction

There have been no studies conducted on the potential toxicity to reproduction of calcium hydroxide. There are some concerns, given the affect that chronic dosing had on rats in a previous study.

Developmental Toxicity/Teratogenicity

There is no data available on the developmental toxicity of calcium hydroxide.

Experience with human exposure

Acute Toxicity-Ingestion

If ingested, calcium hydroxide would cause severe pain, vomiting, diarrhea and collapse. The vomiting would contain blood and mucosal lining. If death does not occur within 24 hours, the patient may improve within 2 to 3 days (ESIS, 2000).

Eye irritation

Lime burns of the eyes have been observed in humans and are normally caused by pasty material (cement, mortar or plaster). It is less common for burns to be associated with a splash of a milky fluid. It is rare for eye irritation to occur as a result of exposure to a clear solution of calcium hydroxide (lime water). The result of the exposure is generally a particulate paste that has come in contact with the cornea and conjunctiva and adheres and dissolves slowly, creating a strongly alkaline calcium hydroxide solution. (Solvay S.A. Brussels *in* ESIS, 2000)

Because of low solubility and reports that calcium hydroxide is slow to penetrate tissues, it is not considered likely to be corrosive.

Worker exposure

It is unknown as to whether or not there are epidemiological studies related to lime exposure during production and application. Workers in lime factories for up to 40 years have shown no ill effects from exposure. The only remarkable risk with lime is potential eye exposure. To avoid the risk of eye damage from exposure, workers either applying or producing lime-based products should wear some type of protective face mask.

Identification of critical endpoints

The endpoints for critical exposure to applicators and the public would be through the eyes. One way to avoid damage would be to require some sort of protective eyewear during application, and posting of the treatment prior to and for at least one hour post application.

Consumer Risk Characterization

Given the information provided above, and the copious amounts of calcium hydroxide in everyday situations, there should be little risk to the general public from normal use of the product. There is the potential for eye damage if someone was putting up plaster or mixing cement and not wearing personal protective equipment.

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