LIME SLUDGE APPLICATIONS

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TABLE OF CONTENTS

1. INTRODUCTION

What is lime?

Acetylene gas (C2H2) is widely used in the fabrication industry along with Oxygen gas for welding of metallic structures. Production of Acetylene gas is accomplished by the reaction of Calcium Carbide with water in properly designed Acetylene generating equipment. The chemical equation for this reaction is as follows:

$$CaC2 + 2H2O \longrightarrow C2H2 + Ca(OH)2$$

The Carbide Lime [Ca(OH)2] is produced as a by-product of acetylene manufacturing process. It is slurry of Calcium Hydroxide (Calcium Hydrate). The usual solid concentration is from 10 – 12 %. The by-product Hydrate has a grayish color and a characteristic Acetylene garlic odor as it comes from the generator. The grayish color results largely from the very small percentage of combined Sulphur contained in the slurry. Also contained in the slurry are small amounts of Ferrosilicon and Carbon.

The disposal problem:

The disposal of the manufacturing process by-product in the form of slurry poses a serious problem for the acetylene producers. The slurry need to be stored in an underground tank and later on pumped into a custom built tanker for transportation. In a day’s production, an average of 1 ton of waste is generated. The messy nature of the waste makes it difficult to dispose off normally. The municipalities restrict the disposal within city limits. A piece of land is usually designated outside the city for dumping the waste. Producers have to maintain the validity of permission for hazardous waste disposal. Sometimes due to bureaucratic procedures, the permission gets expired and the production has to be stopped due to limited space in storing the waste while waiting the renewal of permission.

The truck and tanker used for transporting the slurry used to get deteriorated in a short span of time due to corrosive nature of the waste. The acetylene producers spend large sums of money maintaining two such vehicles, one regular and the other stand by. A driver is usually designated to run the operation.

MEGA has taken up this important issue in order to educate the Industrial Gases community and other stake holders in particular and public in general to educate about the applications and uses of the carbide lime. This technical paper contains information that will help the Industrial Gases community to deal with authorities in their respective countries about the nature and characteristics of acetylene by product as well as find some end users who could use the material in a productive way.

2. DEFINITIONS

Biosolid : Biological solid waste

CaO: Calcium Oxide

Mercaptan: A sulfur-containing organic compound with the general formula RSH where R is any radical, especially ethyl mercaptan, C_2H_5SH. Also called thiol.

EPA: Environmental Protection Agency

CAFO: Concentrated Animal Feeding Operation

Pozzolan: A pozzolan is a siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value but which will, in finely divided form and in the presence of water, react chemically with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties

SO2: Sulphur Dioxide

FGD: Flue Gas Desulfurization

CaCO3: Calcium Carbonate

Calcining: Calcining is a thermal treatment process in presence of air or oxygen applied to ores and other solid materials to bring about a thermal decomposition, phase transition, or removal of a volatile fraction. The calcination process normally takes place at temperatures below the melting point of the product materials.

AWWA: American Water Works Association

3. ENVIRONMENTAL APPLICATION

3.1. Treatment of Biosolids and Sludges

Lime can be used for effective treatment of sewage biosolids, as well as industrial sludge and petroleum wastes.

How Lime Treatment Works -- Lime treatment controls the environment needed for the growth of pathogens in biosolids and converts sludge into a usable product. Lime stabilization is a cost-effective option that generally has lower capital costs than alternative treatment options. The mechanism of lime treatment of biological wastes is based on several chemical reactions:

- Calcium hydroxide is an alkaline compound that can create pH levels as high as 12.4. At pH levels greater than 12, the cell membranes of harmful pathogens are destroyed. The high pH also provides a vector attraction barrier, preventing flies and other insects from infecting the treated biological waste. Because lime has low solubility in water, lime molecules persist in biosolids. This helps to maintain the pH above 12 and prevent regrowth of pathogens.

- When quicklime (CaO) is used, an exothermic reaction with water occurs. This heat release can increase the temperature of the biological waste to 70ºC, which provides effective pasteurization.

- The high pH also will precipitate most metals that are present in the waste and reduces their solubility and mobility. Lime will also react with phosphorus compounds.

- The solubility of calcium hydroxide also provides free calcium ions, which react and form complexes with odorous sulfur species such as hydrogen sulfide and organic mercaptans. Thus the biological waste odors are not covered over but actually destroyed.

- The addition of lime also increases the solids content of the waste, making it easier to handle and store.

For biosolids that are to be beneficially used, lime stabilization is one of the technologies identified to meet the requirements to address pathogens. Class A and B biosolids - that specify performance goals and the degree of treatment biosolids must receive before beneficial use or disposal:

- Class B biosolids contain higher pathogen concentrations than Class A, but have levels low enough for some beneficial uses, such as land application with restrictions. To meet Class B requirements using lime stabilization, the pH of the biosolids must be elevated to more than 12 for 2 hours and subsequently maintained at more than 11.5 for 22 hours.

- Class A biosolids contain extremely low pathogen concentrations and have few or no use restrictions. To meet Class A requirements using lime stabilization, the Class B elevated pH requirements are combined with elevated temperatures (70°C for 30 minutes).

In addition to regulating pathogen concentrations, it reduces the tendency of biosolids to attract disease vectors such as rodents and insects. Lime treatment is one of the methods sanctioned in the regulations. To meet vector attraction reduction requirements using lime, the pH must be raised to 12 or higher for 2 hours and subsequently maintained above pH 11.5 for another 22 hours without further alkali addition. Most lime treatment facilities have the flexibility to produce either Class A or Class B biosolids, thus increasing disposal and recycling options.

Lime-treated biosolids can be re-used -- Lime-treated biosolids are safe and promote recycling. Properly prepared biosolids provide a rich source of the essential fertilizer elements needed by plants to produce food. “Biosolids Recycling is a Beneficial Technology for a Better Environment”. Reuse of lime-stabilized biosolids is not limited to use on farmland. Biosolids have also been used as a soil substitute for landfill cover, and in reclamation of mining-disabled land. Exceptional quality biosolids can also be sold for public use as a commercial fertilizer or soil conditioner.

Lime use is cost-effective -- Lime stabilization is generally more cost-effective than alternative biosolids options. A series of studies comparing lime stabilization to composting, thermal drying, and digestion technologies found that lime stabilization has unit costs as much as 60% lower than alternatives. Reduced capital cost requirements of lime stabilization are even more dramatic – particularly important for municipalities with limited capital budgets. In general, lime stabilization is a non-proprietary process, although patented processes are available

3.1.1. All Sewage Biosolids

Sewage Biosolids - Quicklime and calcium hydroxide (hydrated lime) have been used to treat biological organic wastes for more than 100 years. The treatment of human wastewater sludge (i.e., biosolids) by lime treatment is specifically prescribed in U.S. EPA regulations (40 C.F.R. 503). There are many examples of wastewater treatment systems using lime stabilization.

3.2. <u>Treatment of Animal Waste</u>

The Animal Waste Problem -- An emerging issue is the growing environmental threat caused by animal wastes. Current management practices have begun to create environmental problems because of the consolidation of the livestock industry into much larger facilities, and the resulting concentration of waste-producing activities. Concentrated animal feeding operations (“CAFOs”) for beef cattle, swine, and poultry can create numerous problems, including excess nutrient loading of agricultural land, eutrophication of surface waters, groundwater contamination, pathogen release, and offensive odors. There have been a number of incidents in which large numbers of people have been sickened by water or food contaminated by animal wastes. These problems will only get worse—the amount of animal manure produced annually is estimated to be 10 times the amount of municipal sewage—and much of that manure currently receives little or no treatment. In addition to solid animal manure, there are large amounts of other animal wastes, such as poultry bedding, urine, and carcasses which also are environments problems and are estimated to total up to 100 times the amount of human wastewater biosolids.

EPA’s CAFO rule -- The Environmental Protection Agency (USA) is in the process of developing a new rule to regulate concentrated animal feeding operations. If the final rule resembles the proposed rule, many more of these 40,000 facilities will be required to institute effective treatment of animal wastes than presently do. When this happens, the need for cost-effective treatment methods will become acute.

Lime Treatment for Animal Wastes -- Lime treatment is a multi-functional, cost-effective, politically acceptable option with respect to many of the challenges posed by animal wastes, just as it has played an important role in biosolids (sewage) treatment.

Lime Can Help Control Excess Nutrients -- Animal wastes contain phosphorus and nitrogen, and these nutrients can be returned to the soil as fertilizer. However, the quantities of animal wastes produced means that there is an excess of these nutrients for the soil and crops to absorb, and runoff causes damaging eutrophication of surface waters. Lime will volatilize the nitrogen (and with the use of new technology, convert it into a usable concentrated fertilizer), and can precipitate the phosphorus to an insoluble form, reducing the excess nutrient problem. Lime can also be used to precipitate most metals that are present in the waste and reduce their mobility.

Lime Can Help Control Pathogens -- Lime inhibits pathogens by controlling the environment required for bacterial growth. Calcium hydroxide (hydrated lime) is an alkaline compound that can create pH levels as high as 12.4. At pH levels greater than 12, the cell membranes of harmful pathogens are destroyed. The high pH also provides a vector attraction barrier (i.e., prevents flies and other insects from infecting the treated biological waste). Because lime has low solubility in water, lime molecules persist in biosolids. This helps to maintain the pH above12 and prevent regrowth of pathogens. In addition, when quicklime (calcium oxide or CaO) is used, an exothermic reaction with water occurs. This heat release can increase the temperature of the biological waste to 70°C, which provides pasteurization and also helps dry out the solid waste.

Lime Can Help Control Odors -- Lime treatment also reduces odors, particularly hydrogen sulfide, which is not only a nuance odor but also can be very dangerous if localized high concentrations build up. In addition to high pH, lime provides free calcium ions, which react and form complexes with odorous sulfur species such as hydrogen sulfide and organic mercaptans. Thus the biological waste odors are not ‘covered over’ but actually destroyed.

Lime Treatment is Cost-Effective -- Lime treatment of animal wastes is economically attractive. For biosolids, lime treatment is often a least cost alternative—for example, unit treatment costs of lime stabilization of biosolids have been estimated to be less than half the costs of aerobic and anaerobic digestion. There are a number of innovative technologies that use lime or lime-derived materials to treat animal wastes and generate a usable agricultural product. Because of the versatility of lime it can be used for the treatment of most animal wastes, including hogs, cattle, dairy, and poultry.

3.3. Industrial Sludges and Petroleum Waste

Industrial Sludge and Petroleum -- Quicklime and hydrated lime can be used in the treatment of many industrial sludge by correcting pH for further treatment, neutralizing acidic wastes, and removing or immobilizing contaminants. Specific examples include sulfite/sulfate sludge and petroleum waste.

Calcium sulfite/sulfate waste -- Calcium sulfite and sulfate wastes from desulfurizing stack gases, lime neutralization of acid waste effluent, and waste accumulated in the manufacture of superphosphate fertilizers, when untreated, are lacking in bearing strength and are prone to leach objectionable amounts of the sulfate ion into the ground water. However, this material, when mixed with 2-3% lime and 15-30% pozzolan--such as fly ash, volcanic ash, pulverized slag, etc.--develops considerable bearing strength, erosion resistance and is non-leaching. The stabilized material can be used in constructing embankments and earth dams. In addition, synthetic gypsum can be crystallized from sulfite sludge from wet scrubbers. The gypsum produced from hydrated lime in this manner is very white and is a saleable product.

Petroleum wastes -- Restoration of waste oil ponds to environmentally safe land for beneficial uses has been achieved using either commercial lime (mainly quicklime) or lime kiln dust. Either material is used to dewater the oily waste to the extent that the dried sludge can be compacted and the pond area converted to useful land.

3.4. Waste Water Treatment

Lime is used as an active ingredient in Municipal as well as Industrial Waste Water treatment.

3.5. Flue Gas Treatment

Lime plays a key role in many air pollution control applications. Lime is used to remove acidic gases, particularly sulfur dioxide (SO2) and hydrogen chloride (HCl), from flue gases. Lime-based technology is also being evaluated for the removal of mercury.

Lime is more reactive than limestone, and requires less capital equipment. SO2 removal efficiencies using lime scrubbers range from 95% to 99% (at electric generating plants). HCl removal efficiencies using lime range from 95% to 99% (at municipal waste-to-energy plants).

There are two main methods for the removal of acidic gases - dry scrubbing and wet scrubbing where both methods are used for cleaning flue gases from the combustion of coal to produce electric power. Dry scrubbing is also used at municipal waste-to-energy plants and other industrial facilities, primarily for HCl control. Lime is used in both systems.

3.5.1. Dry Lime Scrubbing

In dry scrubbing, lime is injected directly into flue gas to remove SO2 and HCl. There are two major dry processes: “dry injection” systems inject dry hydrated lime into the flue gas duct and “spray dryers” inject an atomize lime slurry into a separate vessel.

A spray dryer is typically shaped like a silo, with a cylindrical top and a cone bottom. Hot flue gas flows into the top. Lime slurry is sprayed through an atomizer (e.g., nozzles) into the cylinder near the top, where it absorbs SO2 and HCl. The water in the lime slurry is then evaporated by the hot gas. The scrubbed flue gas flows from the bottom of the cylindrical section through a horizontal duct. A portion of the dried unreacted lime and its reaction products fall to the bottom of the cone and are removed. The flue gas then flows to a particulate control device (e.g., a baghouse) to remove the remainder of the lime and reaction products.

Both dry injection and spray dryers yield a dry final product, collected in particulate control devices. At electric generating plants, dry scrubbing is used primarily for low-sulfur fuels. At municipal waste-to-energy plants, dry scrubbing is used for removal of SO2 and HCl. Dry scrubbing is also used at other industrial facilities for HCl control. Dry scrubbing methods have improved significantly in recent years, resulting in excellent removal efficiencies.

3.5.2. Wet Lime Scrubbing

In lime wet scrubbing, lime is added to water and the resulting slurry is sprayed into a flue gas scrubber. In a typical system, the gas to be cleaned enters the bottom of a cylinder-like tower and flows upward through a shower of lime slurry. The sulfur dioxide is absorbed into the spray and then precipitated as wet calcium sulfite. The sulfite can be converted to gypsum, a salable by-product. Wet scrubbing is used primarily for high-sulfur fuels and some low-sulfur fuels where high-efficiency sulfur dioxide removal is required. Wet scrubbing is a primary use for magnesium-enhanced lime (containing 3-8% magnesium oxide), which provides high alkalinity that increases SO2 removal capacity and reduces scaling potential.

COMPARING LIME AND LIMESTONE SO2 WET SCRUBBING PROCESSES:

Over ninety percent of U.S. flue gas desulfurization (FGD) system capacity uses lime or limestone. This trend will likely continue into the next phase of federally mandated SO2 reduction from coal burning power plants. In 2003, the National Lime Association sponsored a study by Sargent and Lundy to compare the costs of leading lime and limestone-based FGD processes utilized by power generating plants in the United States. The study included developing conceptual designs with capital and O&M cost requirements using up-to-date performance criteria for the processes. The results of the study are summarized in two reports: Wet FGD Technology Evaluation and Dry FGD Technology Evaluation. The reports present the competitive position of wet and dry limestone and lime-based processes relative to reagent cost, auxiliary power cost, coal sulfur content, dispatch, capital cost, and by-product production (gypsum and SO3 aerosol mitigation chemicals), as summarized in technical paper presented in May 2003.

HCl REMOVAL:

Because lime also reacts readily with other acid gases such as HCl, lime scrubbing is used to control HCl at other types of municipal and industrial facilities:

- At municipal waste-to-energy plants, dry lime scrubbing is used to control emissions from about 70 percent of the total U.S. capacity (as of 1998). HCl removal efficiencies using lime range from 95 to 99 percent.

- At secondary aluminum plants, for example, the U.S. Environmental Protection Agency identifies lime scrubbing as a maximum achievable control technology for HCl. EPA tests demonstrate removal efficiencies greater than 99 percent.

MERCURY REMOVAL:

Many different methods for controlling mercury emissions are being evaluated in the U.S. One control technology being evaluated combines hydrated lime with activated carbon. The reagent, a registered product, consists of 95-97 percent lime and 3-5 percent activated carbon. Other calcium-based sorbents are also being evaluated as cost-effective alternatives for combined SO2 and mercury removal

4. CONSTRUCTION APPLICATIONS

4.1. Portland Cement

CaCO3 is the major raw material for the clinker-making process (to form CaO).

Calcium carbonate decomposes into calcium oxide at 900 °C

- $CaCO_3 \rightarrow CaO + CO_2$ $\Delta H = +1700$ kJ/kg

Calcium hydroxide decomposes into calcium oxide at 600 °C

- $Ca(OH)_2 \rightarrow CaO + H_2O$ $\Delta H = +1300$ kJ/kg

4.2. Mortar Applications/ Brick/ Blocks Manufacture Industry

Early mortars were produced by calcining limestone in a kiln and slaking it for long periods of time in water creating lime putty. This was necessary to enhance the workability and the soundness of the mortar. Locally available sand was added to the slaked lime putty to create lime mortar. These mortars were used to construct masonry walls containing brick, block or stone. The lime in these mortars absorbed carbon dioxide from the air to convert it back to its original chemical form (limestone). This process was slow and further inhibited in underwater applications.

To increase the speed of construction, pozzollans such as brick dust and volcanic ash were added to lime. Natural cements and hydraulic lime products were produced by calcining limestone high in silica content or with clay. These products would develop strength without the addition of pozzollans and would set under water.

In the early 1870's Portland cement was introduced in the United States. Portland cement provided a more uniform alternative to pozzollans, natural cement and hydraulic lime and became widely used. Combinations of lime and cement were developed using alternate letters of the phrase MASON WORKS. Type M mortar is the strongest mortar with the least lime and Type K is the weakest mortar with the most lime. In these formulations, lime enhances workability, water retention and bond strength. The carbonation of lime also enhances long term strength development.

4.3. Product Application

There are several types of hydrated lime products defined for masonry applications as follows.

Type N, or Normal hydrated lime, products are only partially hydrated and/or have poor workability. Additional additives and/or long soak periods are required for these products to perform effectively in masonry applications.

Type S, or Special hydrated lime products are a combination of calcium and magnesium hydroxides. In building applications, Type S dolomitic hydrated lime products have high hydration levels and controlled plasticity (water retention). This allows for minimal soak periods prior to application.

Both Type N and Type S hydrated lime products can contain air entrainment additives. Air-entrained lime products must have a minimum air entrainment level of 7% and a maximum air level of 14%.

Modern cement-lime mortars can be specified by the properties (air content, compressive strength and water retention) of the mortar or by volume proportions of cement, lime and sand.

4.4. Graymont

Graymont is considered to be one of the best dolomitic limestone for the production of building lime products in the world. Located in North West Ohio, the purity of Graymont products is evident in the white color of the masonry products. Graymont masonry products also offer exceptional plasticity for increased water retention and workability in mortar applications

Lime Mortar is a mixture of lime and sand used to bed stones in walls. Over time lime mortar reacts with carbon dioxide to form calcium carbonate which hardens to hold the stones in place.

4.5. Asphalt

Calcium hydroxide is used as a multi-functional filler/anti-strip agent in asphalt mixtures.

5. TREATMENT OF HAZARDOUS WASTE

Lime is widely used to treat hazardous wastes both currently generated process wastes and previously disposed or abandoned materials. Lime stabilizes most metals by converting them to more chemical stable forms that are less likely to leach. In addition, lime can react with soils to solidify materials, further reducing the leaching of hazardous wastes. Lime can also be used to neutralize acidic materials.

Under the U.S. EPA's land disposal restrictions regulations, currently generated hazardous wastes that are to be land disposed must be pretreated using the best demonstrated available technology. For hazardous wastes containing metals, metals stabilization or metals precipitation is frequently required, and lime is identified by EPA as suitable to treat these wastes (see 40 C.F.R. Part 268.42).

EPA also endorses lime stabilization as a key technology for hazardous waste site cleanups (see, e.g., Handbook for Stabilization/Solidification of Hazardous Wastes (EPA/540/2-86/001, June 1986). In 1997, for example, EPA announced a proposed cleanup plan as part of the Anaconda Regional Water, Waste, and Soils Project for 14,000 acres in Anaconda, Montana. A key element of the plan is to treat arsenic-containing soils with lime and organics. Copper mining created environmental contamination in the 300 square mile area and concern about potential human exposures. EPA recommended in-place lime treatment over the option of excavating and treating the tailings and contaminated groundwater. (Nearby, the Warm Springs Pond is already being used to capture and treat water contaminated with metals (copper, zinc, and arsenic) that threaten the Clark Fork River. The contaminated waters are treated with a lime solution.)

6. TREATMENT OF DRINKING WATER

In terms of annual tonnage, lime ranks first among chemicals used in the treatment of potable and industrial water supplies—in 2001, nearly a million metric tons. It is used by many municipalities to improve water quality, especially for water softening and arsenic removal. Indeed, the American Water Works Association (AWWA) has issued standards that provide for the use of lime in drinking water treatment.

Softening -- In water softening hydrated lime is used to remove carbonate hardness (caused by bicarbonates and carbonates of calcium and magnesium) from the water. Hardness caused by other calcium and magnesium salts, called non-carbonate hardness, is generally treated by means of the lime-soda process, which entails the precipitation of magnesium by lime. The co-produced calcium salt reacts with the soda ash to form a calcium carbonate precipitate. Lime enhanced softening can also be used to remove arsenic from water. Recent changes to the national drinking water standard for arsenic have increased the need for this treatment. The U.S. EPA has issued new guidance on enhanced lime softening to remove arsenic, see http://www.epa.gov/safewater/mdbp/coaguide.pdf.

pH Adjustment / Coagulation -- Hydrated lime is widely used to adjust the pH of water to prepare it for further treatment. Lime is also used to combat "red water" by neutralizing the acid water, thereby reducing corrosion of pipes and mains from acid waters. The corrosive waters contain excessive amounts of carbon dioxide (carbonic acid). Lime precipitates the CO2 to form calcium carbonate, which provides a protective coating on the inside of water mains.

Lime is used in conjunction with alum or iron salts for coagulating suspended solids incident to the removal of turbidity from "raw" water. It serves to maintain the proper pH for most satisfactory coagulation conditions. In some water treatment plants, alum sludge is treated with lime to facilitate sludge thickening on pressure filters.

Effect on Pathogen Growth -- By raising the pH of water to 10.5-11 through the addition of lime and retaining the water in contact with lime for 24-72 hours, lime controls the environment required for the growth of bacteria and certain viruses. This application of lime is utilized where "phenolic water" exists, because chlorine treatment tends to produce unpalatable water due to the phenol present. This process, called "excess alkalinity treatment," also removes most heavy metals.

Removal of Impurities -- One of the most common methods of removing silica from water is the use of dolomitic lime. The magnesium component of this lime is the active constituent in silica removal. Lime is also used to remove manganese, fluoride, organic tannins and iron from water supplies.

7. PRODUCTION OF SODA ASH

Lime in the Soda Ash Industry

Lime plays two important roles in the production of soda ash and sodium hydroxide.

One of the major sources of soda ash ($NA2\ CO3$) and caustic soda ($NaOH$) is the refining of naturally occurring trona ores. These naturally occurring ores are mixtures of carbonates, bicarbonates and impurities that have to be refined to produce marketable products. In the production of soda ash from trona, reacting the bicarbonate containing liquid with lime is one of the processes used to convert the bicarbonates in the trona to the carbonate form.

By increasing the lime dosage either the trona or soda ash can be converted to caustic soda, a higher value product. In this process, lime is first slaked and converted to calcium hydroxide ($Ca(OH)2$). Next the lime slurry is combined with soda ash ($Ca(OH)2 + Na2CO3$). This yields caustic soda and limestone ($2NaOH + CaCO3$). The limestone from this reaction can be recycled to make lime.

Soda and caustic soda solution are essential ingredients in an array of industrial operations, including pulp and paper, glass manufacture, water treatment, flue glass treatment, soap and detergents, bleach, petroleum products and alumina, along with many other uses in the chemical processing industry.

8. BIBLIOGRAPHY

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