GUIDE TO CARBIDE LIME APPLICATIONS

Doc 143/17

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Table of Contents

Tables

Figures

Amendments to 143/08

Section	Change
All	Editorial changes in line with current EIGA style manual
All	Consistent use of terminology for product
4.3	New section: Carbide lime as a by-product
4.4	New section: Transport of carbide lime

NOTE Technical changes from the previous edition are underlined

1 Introduction

This publication describes some of the beneficial uses of carbide lime.

2 Scope

This publication is intended for use by the EIGA members as a guide to which applications of carbide lime can be used to demonstrate that the carbide lime can be used directly without further processing and should not be considered a waste.

3 Definitions

3.1 Publications terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May and need not

Indicate that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definition

Carbide lime or 'carbide lime slurry' is a suspension of calcium hydroxide in water produced when water is added to calcium carbide to make acetylene.

Carbide lime is also referred to as carbide slurry, carbide sludge generator slurry, lime slurry, lime sludge, lime hydrate, lime water, or activated lime.

Hydrated lime or slaked lime is a soft, white, crystalline, very slightly water-soluble powder, Ca(OH) 2, obtained by the action of water on lime.

4 Beneficial uses of carbide lime

4.1.1 Background

Carbide lime slurry is a suspension of calcium hydroxide in water produced when water is added to calcium carbide to make acetylene. The slurry is formed as a by-product of acetylene production, and, where allowed by local regulation or technical standards, can be used directly in many applications, without the need for further reprocessing or purification of any sort. This means that it is not classified as a waste if it has a beneficial application under the definition of waste in Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 *on waste* [1] [1].

[1] References are shown by bracketed numbers and are listed in order of appearance in the reference section

Carbide lime that goes into beneficial applications shall be considered a by-product if it meets the tests under the EU commissions by-products (See 4.3]. This Classification of carbide lime as by-product ensures its recovery through diverse industries as alternative neutralization agent for liquid discharges and fumes, which represents 70% of the market for this by-product.

Carbide lime has identical properties to calcium hydroxide obtained from natural limestone and therefore its use is environmentally beneficial.

4.2 Production process

Calcium carbide (CaC_2) reacts with excess water (H_2O) to form gaseous acetylene (C_2H_2) and liquid calcium hydroxide ($Ca(OH)_2$).

$$CaC_2 + 2H_2O \Rightarrow C_2H_2 + Ca(OH)_2$$

The production of carbide lime slurry is directly linked to the acetylene production and is around 500 thousand metric tons per year globally

In most acetylene plans that use this process the carbide lime slurry is at least settled in tanks. The clarified water is then pumped to the acetylene generator where it is recycled. The carbide lime slurry thus becomes more concentrated in dry matter (from 25% to 30%), which makes it easier to reclaim.

Considering the initial content in water of the carbide lime slurry, a long-term stocking is not compatible with the imperatives of production: regular removals with the aim of recovery are thus necessary.

Generally, the removals of settled carbide lime slurry take place several times a week, according to the importance of the plant of production of acetylene.

4.3 Carbide lime as a by-product

The *Communication from the Commission to the Council and the European Parliament on the Interpretative Communication on waste and by-products* (COM/2007/0059) provides a series of tests to show if a by-product is a waste or a non-waste by-product [2]. Where carbide lime is used for beneficial applications it would normally pass these tests and become a non-waste by-product.

Carbide lime is typically classified as a by-product as demonstrated by applying the tests from EU waste jurisprudence and the Commission guidance on by-products. It is demonstrated that carbide lime is typically classified as a by-product. In fact:

- The intention is not to 'discard' the carbide lime from the process but to market it; the carbide lime is produced to a specification and has a safety data sheet according to product legislation and REACH registration.
- Carbide lime can be used directly without further processing, which should mean it is not classified as a waste if it has a certain beneficial application. (*Case C- 416/02* [3] and *Case C - 121/03* [4]).

4.4 Transport of carbide lime

When loading carbide lime slurry into non-dedicated tankers, there are precautions that should be taken to minimize the risk of a reaction between the carbide lime slurry and any residual product in the non-dedicated tanker: Carbide lime slurry contains small quantities of dissolved acetylene, which can be released if vacuum pumping systems are used to load road tankers. This requires careful consideration as part of the task risk assessment (using a flammable zone rated vacuum pump. Reference should be made to EIGA Doc 134 Potentially Explosive Atmospheres - EU Directive 1999/92/EC [5] if required.

- The tanker to be used for transport of carbide lime slurry should be internally cleaned before use and a valid certificate of cleaning should be produced. On arrival of the road tanker at site, the certificate of cleaning should be checked by site personnel. If documentation or other evidence is not available, the tanker shall not be filled; and
- before the transfer of the carbide lime slurry, the carrier should visually inspect the tanker and the hoses to confirm there is no residual product.

The chemical name of carbide lime is 'calcium hydroxide'. It not classified as 'Dangerous Goods' under *ADR, (European Agreement Concerning the International Carriage of Dangerous Goods by Road)* [6].

The responsibilities that are laid down in ADR are not required for carbide lime slurry. For example, the requirements to load dangerous goods are detailed in Chapter 1.4 of ADR, 'Safety obligations of the participants', but do not apply to carbide lime slurry. However, it is recommended that EIGA members and those who carry carbide lime slurry consider applying the principals of Chapter 1.4 of ADR. Refer to EIGA Safety Alert SA 28 *Hazards of Transport of Lime Slurry in Non-Dedicated Road Tankers* [7].

4.5 Technical characteristics

Carbide lime slurry is usually under liquid state with at least 50% water. It is easily handled using heavy liquid pumps when it contains more than 65% of water (liquid carbide lime) or with a mechanical digger when the water content is less than 60% (solid carbide lime). Water can also be easily withdrawn down to 30% using mechanical means, such as press filter.

The main composition of the carbide lime slurry is detailed in Table 1.

Table 1: Composition of carbide lime slurry

Parameter	Unit	Result
Density (after simple decanting)	-	1.2
pH	-	12.6-12.8
Dry matter	-g/l	239.8-643
$CaCO_3$	% on dry matter	16.3-22
Lime (CaO)	% on dry matter	48.86-59.7

4.5.1 Quantified data on carbide lime recovery

Analyses of carbide lime slurry have been done and these analyses can be summarized as follows:

- 25% to 30% of lime in weight ($Ca(OH)_2$); liquid state (with carbide lime deposit);
- mean pH between 12 and 12.6;
- it can contain some impurities such as metals (Cu, Mn, Ni, Ba, Al, Cr), salts (chlorides, sulfates), aluminium, ammonium, etc.;
- significant COD (>2000 mg/l); and
- the composition may slightly differ from one plant to another (especially concerning the impurities) depending on the origin of the calcium carbide.

4.6 Applications

The following applications use lime or lime slurry in their processes and may use carbide lime or carbide lime slurry as the source of that lime or lime slurry.

The selection of an industrial application will depend on the following criteria:

- the industry's foreseeable need for the reclaimed product (future development of the industry or the industrial processes);
- foreseeable changes in the regulatory environment (new regulations or stricter application in the near future);
- the amounts that can be reclaimed; and
- the time required to set up reclaiming 'chain'.

4.6.1 Carbide Lime slurry containing 25-30% of hydrated lime

When the carbide lime slurry has settled in the settling tank, the potential uses of the reclaimed product depends on its liquidity (which enables it to be conveyed with a slurry pump) and its primary chemical characteristic, which is its alkalinity, with a value of 12 pH to 13pH.

The main uses for reclaimed carbide lime slurry are:

- to neutralize effluent acidity through an acid-base reaction;
- to precipitate and flocculate impurities; and
- to treat wastewater treatment plant sludge.

4.6.1.1 Use in production processes

Large amounts of lime slurry are used in *sugar plants* during various steps of the sugar production process.

The largest amounts are used to *clean beet juice*. Mixing the lime slurry with the beet juice first causes its impurities to flocculate. Then carbon dioxide added to the juice combines with the lime to form calcium carbonate, a precipitate which may then be removed through filtration or settling, along with the clusters of impurities that have formed.

Lime slurry can also be used to *wash beets* (it increases wash water density which enables the beets to float), or in the plant's *water treatment unit* (same use as in a municipal water treatment plant), or to *facilitate cake pressing*.

4.6.1.2 Surface treatment

Lime slurry can also be used in plants that use acid baths and phosphate baths for *surface treatment*. It is added to wastewater treatment plants to neutralize acids and precipitate phosphates. Although most plants that use lime slurry for neutralization prepare it from powdered hydrated lime, some already procure carbide lime slurry directly (such as the Renault plant in Douai).

4.6.1.3 Wastewater treatment

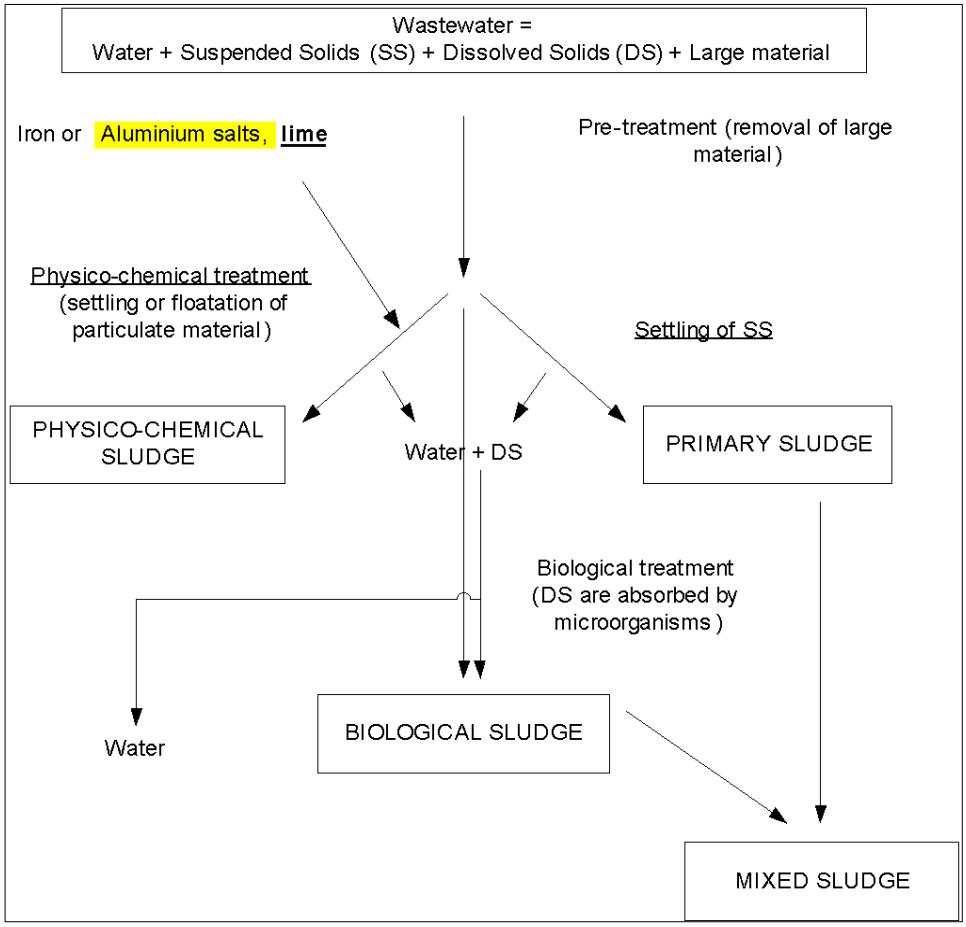
Lime may be used at various phases of the *water treatment* and *sludge treatment* processes.

It is used in so-called '*physico-chemical'* plants where flocculating agents (lime slurry or aluminium or iron salts) are added to flocculate suspended solids. These plants, built in the 1970s, are currently used in tourist and resort areas that are subject to large seasonal variations in the local population.

Elsewhere, these plants have been widely replaced by biological plants that enable more effective purification in areas where the volume of wastewater to be treated does not vary substantially throughout the year. It should be noted however that municipal treatment plants that treat urban effluent and industrial effluent (such as the Limay plant) must maintain a physico-chemical process since the change in pH is quite effective in killing microorganisms. This process is shown in Figure 1 below.

Lime may be used to treat both physico-chemical and biological plant sludge. When mixed into sludge before or after dehydration it serves four purposes: it stabilizes the sludge, by reducing its fermentability and therefore unpleasant odour; it facilitates the separation of the liquid and solid phases and thus dehydration; it sanitizes the sludge, by increasing its pH and destroying microorganisms (and, if lime slurry is used, by drying out the sludge from the exothermic reaction); and lastly it increases the sludge's fertilizer value if the sludge is used for this purpose. This process is shown in Figure 2 below.

Figure 1: Wastewater treatment processes



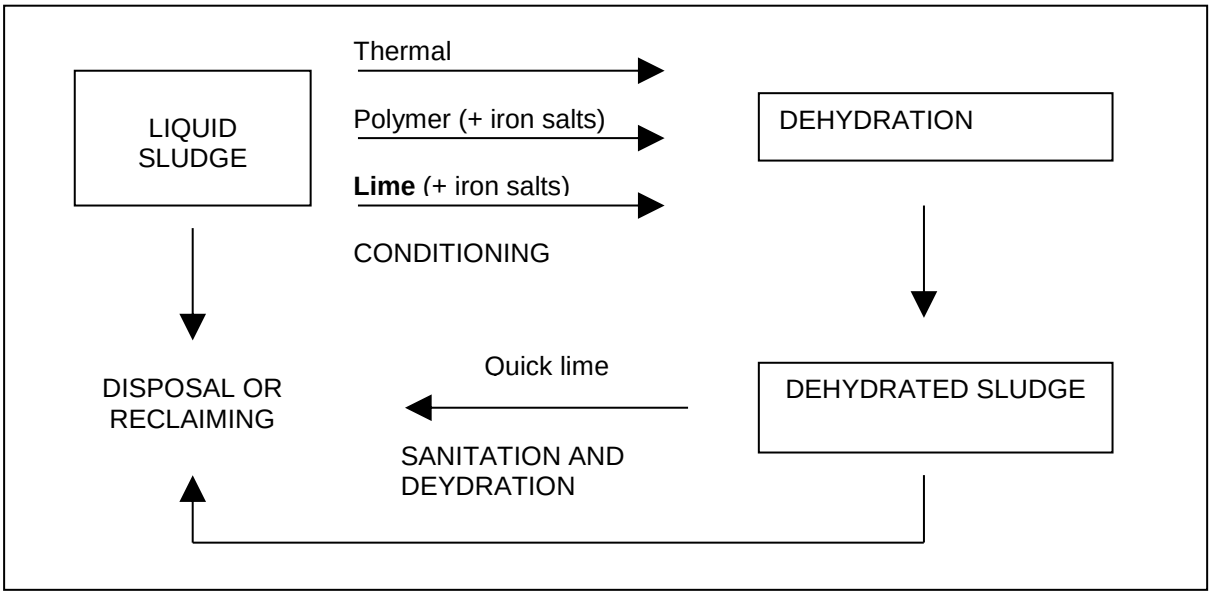


Figure 2—Sludge treatment processes

4.6.1.4 Smoke treatment

This mainly involves the *scrubbing of incinerator smoke*. Generally, powdered lime is stored at the incineration facility and is used to make lime slurry which is added to the process. The replacement of hydrated lime with carbide lime slurry requires the installation of storage tanks.

Lime is also used to *scrub thermal power plant smoke*. There are two possibilities, either:

- the power plants are equipped with fluidized beds, in which case the lime is used in the form of dry limestone and carbide lime slurry therefore cannot be used. However, *lime cakes can be mixed in with the coal*; or
- plants use limestone milk, which can be replaced with carbide *lime slurry*.

In either case, a considerable amount of lime is used (from 25 000 to 75 000 metric tons a year). This industrial application has the following characteristics:

- the product must be of guaranteed uniform quality with few impurities since the burnt ash by-product is reclaimed; and
- a large supply is required on a continuous basis.

It should be noted that plants that use oil coke use up to three times more lime.

4.6.2 Lime paste containing 50% hydrated lime

Water can be removed from carbide lime slurry relatively easily through conventional filtration or using a filter-press to obtain a paste-like product that contains no more than 50% water.

This product is suitable for various industrial applications. Its key characteristics are its mineral composition and its capacity to absorb water and therefore act as a drying agent:

4.6.2.1 Liming soil to correct pH

Acidic soils must be limed regularly to enable them to be farmed. There are two types of liming:

- *maintenance liming* (about every three years); or
- *corrective liming* (about every 10 years).

The specific amount of lime required depends on the soil's characteristics. Generally, the following average amounts are required for:

- *Maintenance liming* – about 500 units of CaO, or *two metric tons of lime slurry containing 25% CaO per hectare (2.5 acres)*; or
- *Corrective liming* – about 1000 units of CaO, or *four metric tons of lime slurry containing 25% CaO per hectare (2.5 acres)*.

The carbide lime slurry is spread on land that is not being cultivated at a time when the soil is dry and firm enough to enable this. This is generally during the *summer*, but *may be during the winter* if the soil is sown in the spring and there is little rain. Only fallow land may be limed at any time during the year, provided it is firm enough.

4.6.2.2 Road construction work

Lime may be used to:

- stabilize clay through dehydration – quick lime is mostly used to enable a sufficient exothermic reaction.
- improve the soil's firmness (load-bearing capacity) – generally quick or hydrated lime is used for this purpose. In some regions subject to draught (such as southern France) quick lime may cause too much dehydration and carbide lime slurry may be used.

It should be noted that the only equipment that road construction companies have for this purpose are lime sprayers. Lime cakes cannot be used since they would have to be broken up. Carbide lime slurry could be used directly in that form but a mobile carbide lime slurry tank would have to be installed (these are used for contaminated soils and sites) and spraying equipment would also be necessary.

Furthermore, this equipment must be used in a variety of worksite environments.

5 References

Unless otherwise specified, the latest edition shall apply.

[1] *Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste*. OJ L 312, 22.11.2008

[2] *Communication from the Commission to the Council and the European Parliament on the Interpretative Communication on waste and by-products*. COM/2007/0059 final. 21.2.2007

[3] Case C - 416/02 - - Commission v Spain. Judgment of the Court (Third Chamber) of Justice of the European Union of 8 September 2005. http://curia.europa.eu

[4] Case C - 121/03 - Commission v Spain. Judgment of the Court (Third Chamber) of Justice of the European Union of 8 September 2005. http://curia.europa.eu

[5] EIGA Doc 134 Potentially Explosive Atmospheres - EU Directive 1999/92/E. www.eiga.eu

[6] ADR *European Agreement Concerning the International Carriage of Dangerous Goods by Road*

[7] EIGA Safety Alert SA 28 Hazards of Transport of Lime Slurry in Non-Dedicated Road Tankers. www.eiga.eu

6 Additional references

EIGA Doc 109 *Environmental Impacts of Acetylene Plants*. www.eiga.eu

CGA G1.5 *Carbide Lime: Its Value and Uses*. www.cganet.com

The following are company publications, not publically available:

- Report on potential use of waste carbide lime from Messer Company, Ljubljana – Messer – 2006
- 'Chauxal' APV - French Ministry of Agriculture – 1992 – 1996
- Supplier Lime /lime slurry Safety Data Sheets
- Study to have lime slurry sludge approved as a reclaimed product – Astradec / Air Liquide – September 2005
- Feasibility study to find sustainable applications for reclaimed lime slurry – Eko Consulting - co-financed by ADEME and Air Liquide – June 2004
- Study organized by the Morbihan Farming Bureau on using lime slurry produced by Air Liquide's Lanester facility for agricultural purposes – 1999