CALCIUM CARBIDE SPECIFICATION, STORAGE AND HANDLING

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Disclaimer

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1 Introduction

This publication is the updated version of the previous document 196 Calcium Carbide Storage and Handling, integrating the previous document 205, Calcium Carbide Specifications.

This publication has collected information from calcium carbide manufacturers, withdrawn national standards and gas companies experience to establish an updated and current standard for calcium carbide. It also gives guidance on the relevant properties of calcium carbide to be used for the production of acetylene.

This publication reviews the essential safety procedures associated with calcium carbide and general recommendations for calcium carbides storage areas.

2 Scope and purpose

2.1 Scope

This publication covers specification and requirements for the safe storage and handling of calcium carbide at acetylene plants.

2.2 Purpose

To provide guidance to EIGA Member Companies when they specify calcium carbide for acetylene production and to provide guidance on the storage and handling of calcium carbide at acetylene plants such that safe conditions are maintained.

3 Definitions

3.1 Publication 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 definitions

3.2.1 Calcium carbide briquette

Compressed block of calcium carbide dust.

3.2.2 Calcium carbide containers

Vessels normally made of sheet steel with a rectangular or cylindrical shape. They are water-tight and are handled either by forklift or crane. The containers can be classified into:

- intermediate bulk container (IBC) with a capacity up to 3 m^3 or 2,5 t
- other containers up to 22m^3 or 20 t

  Containers that are used only for the transport of calcium carbide. The calcium carbide is transferred to a charging skip or charging container. The 20 t containers have ventilation systems with drying absorbents and connections for purge and analysis or are under a light pressurization with nitrogen (e.g. 50 mbar)

3.2.3 Drums

Packages manufactured from sheet steel with a capacity up to 400 kg but usually not exceeding 110 kg. They are water-tight and, depending on the design, drums can be used for one or multiple trips. Larger drums are sometimes referred to as barrels.

3.2.4 Dust

Calcium carbide that passes through a test sieve having a mesh width of 1 mm.

3.2.5 Grain size

Defines the dimension of the calcium carbide pieces. The specification for the grain size of calcium carbide will depend upon the requirements of the generator system.

- Oversize of a given graded size calcium carbide

  Calcium carbide retained on coarser sieves.

- Undersize of a given graded size calcium carbide

  Calcium carbide that passes through the finer sieves. Any needle like pieces remaining after the sieving operation are to be counted as part of the next finer size provided that they can be pushed through the holes by hand.

3.2.6 Hot spots

Locally overheated (glowing) areas of calcium carbide. These can be identified by hot surfaces on the calcium carbide package or generator system.

3.2.7 Turn bins and flow bins

3.2.7.1 Turn bin

Bulk container (approximately 1.5 t carbide content) that has only one opening at the base that is used for filling and emptying. The bin is turned at the carbide manufacturers to enable it to be filled.

3.2.7.2 Flow bin

Bulk container (approximately 1.5 t carbide content) which is filled from the top and emptied from the bottom.

Both systems reduce the amount of handling required when recharging the generator hopper and can be fitted with a pull-out slide valve or with flaps to release the calcium carbide. The container is normally sealed to the plant hopper by a soft seal to ensure that there is no release of gas or dust.

Both flow bins and turn bins are fitted with quick connectors to allow a nitrogen supply and a vent line to be connected for the purpose of purging the container.

3.2.8 Gas yield

Number of litres of crude acetylene obtained from a 1 kg calcium carbide sample.

Gas yield is determined in l/kg and is corrected to 15°C and 1013 mbar, that is saturated with water vapour.

4 Properties of calcium carbide

DIN 53922, *Calcium carbide* is used for the purchasing of calcium carbide [1][1].

The standard is withdrawn, but the methods specified in it are still valid and compatible with current practices. It is not covering the sedimentation of lime.

4.1 Physical and chemical properties of calcium carbide

The bulk density of calcium carbide is approximately 1100 kg/m3; however it varies with particle size.

Calcium carbide is a grey, brown, or black granular solid that reacts with water to form acetylene and carbide lime. The colour can differ depending on the impurities, e.g. if there is a high content of ferrous oxide the colour can be a deeper brown.

Calcium carbide typically contains between 15% to 20% impurities.

The main impurities is un-reacted burnt lime (7%-14%)

Additionally, there is a minor amount of chemical compounds containing iron, silicon, aluminium and magnesium. E.g.

- Coke: Should be less than 1% by weight;
- Ferrosilicon compounds: Should be less than 1,5% by weight; and
- Aluminium oxide derived from the limestone used to produce the calcium carbide affects the sedimentation rate.

Calcium carbide has a unique odour that has been described as garlic-like, due primarily to trace impurities. These impurities include phosphine, ammonia, hydrogen sulphide, and organic sulfides.

As long as it is kept dry, calcium carbide is a stable, safe substance. Calcium carbide itself will not burn or explode. Calcium carbide reacts readily with water, water-moistened materials, or moisture in any form (fog, mist, spray or vapor) to form acetylene and calcium hydroxide. This reaction liberates heat and expands the volume of the reactants.

When moist air contacts calcium carbide dust, the acetylene-air mixture generated can combust spontaneously due to the heat generated when the moisture reacts with calcium carbide.

4.2 Production of calcium carbide

Calcium Carbide is made in an electric furnace by combining burnt lime (CaO) and coke (C). It is a white hot liquid taken from the furnace at a temperature greater than 2000°C into moulds open to the air. When calcium carbide has cooled down, it is broken down and the irregular sized pieces are graded,

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

typically ranging from 5 mm to 80 mm depending on customer specifications. When crushed, calcium carbide is a rock-like solid with sharp, angular surfaces representing irregular fracture planes.

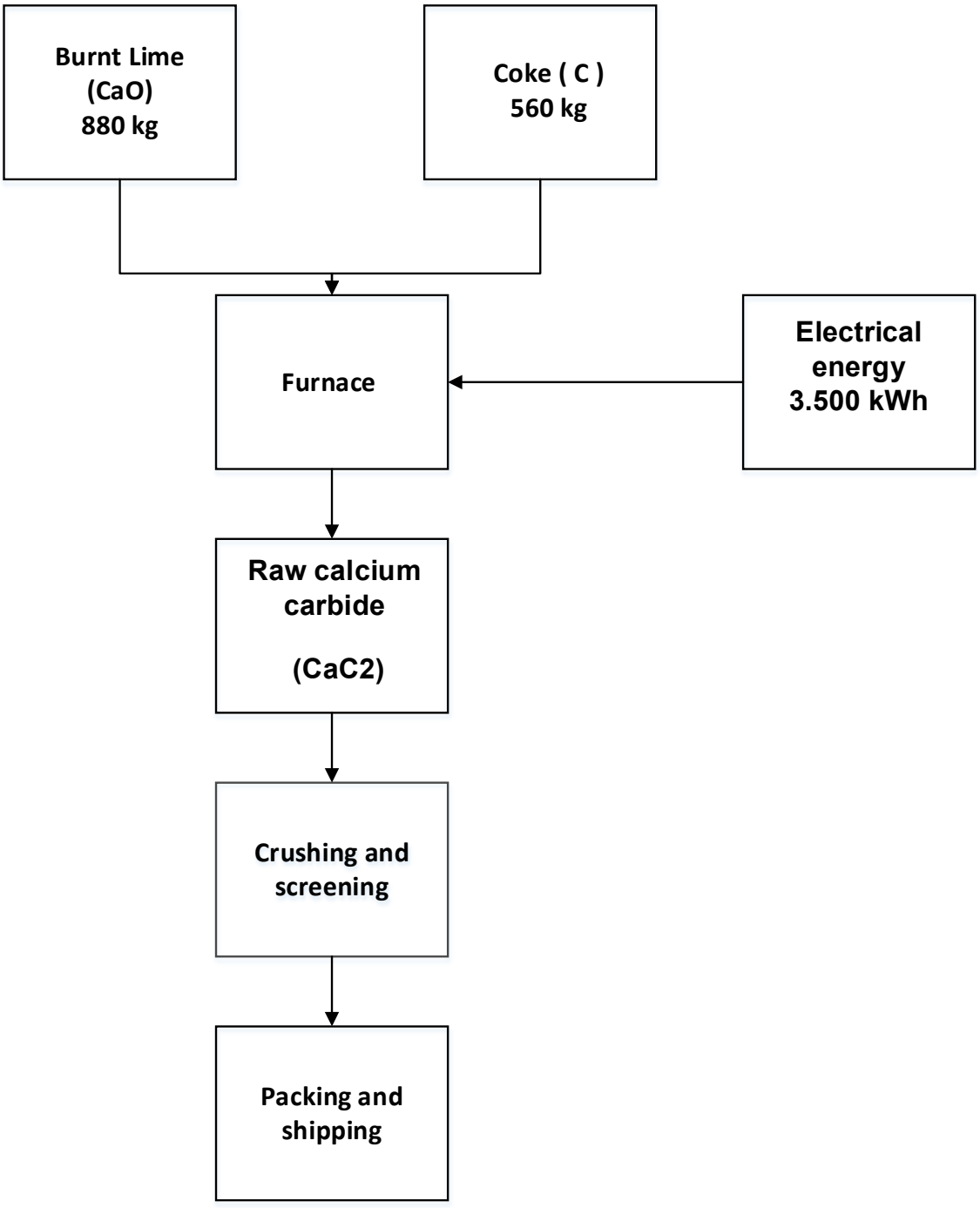

Figure 1 Typical production process for 1 tonne of calcium carbide

4.3 Commercial sizes and dust content

Calcium carbide is manufactured in the following graded sizes and designated accordingly:

Size	Particle size (mm)
2/4	2 to 4
4/7	4 to 7.1
7/15	7.1 to 16
15/25	16 to 25
25/50	25 to 50
50/80	50 to 80

Table 1: Graded sizes of calcium carbide

Other intermediate sizes are possible, for example 15/50, 15/80, 25/80.

For some graded sizes there are specifications other than the simple particles size:

- Calcium carbide of a size 2/4 or above should not contain more than 5% by weight of oversize, and not more than 15% by weight of undersize, including dust. Furthermore, of this 15% by weight of undersize, at least 70% by weight should consist of the next finer size.

  The oversize should belong only to the next coarser size. Needle-like pieces should not, in a longitudinal direction, be more than 1 1/2 times the length of the corresponding upper limit of the particle size.

- Oversize pieces of calcium carbide size 50/80 must pass through a test sieve of 90mm hole size.

Calcium carbide can exhibit the following dust content on delivery to the acetylene plant:

- For sizes 4/7 to 15/25 maximum of 2% by weight; and
- For sizes 25/50 and 50/80 maximum of 1% by weight.

Some processes use small size calcium carbide with the addition of oil to reduce the blockages in calcium carbide feeders.

4.4 Briquettes

The use of briquettes will impact the rate of reaction in comparison with a normal grade calcium carbide.

One advantage of briquettes is the possibility to insert additives to modify the sedimentation rates.

4.5 Porosity

The porosity of the calcium carbide will impact the reaction in the generator. Increasing the porosity will increase the reaction speed and possibly introduce air into the generator.

There is no specification for porosity, but this parameter should be considered when:

- Trying to find a reason for a fast, unexplained reaction speed in the generator; and
- Changing calcium carbide supplier.

4.6 Acetylene Gas yield from calcium carbide

The yield from the acetylene production process is expressed in terms of the volume of acetylene gas recovered from the weight of calcium carbide used. The maximum yield is maintained by ensuring the generator water reaction temperature is kept between 70°C and 80°C.

Calcium carbide for acetylene gas production should show the following minimum average gas yields:

- Sizes 25/50 and 50/80: 300 l/kg
- Size 15/25: 280 l/kg
- Sizes 4/7 and 7/15: 260 l/kg

The deviation of the individual sample values should not be more than 3% below these figures; this is to take account of variations in sampling and in the analysis of the calcium carbide.

No figures for the gas yield can be guaranteed for sizes under 4 mm.

5 Calcium carbide containers design

Calcium carbide shall be contained in packages of sufficient strength to permit handling without rupture. There are two basic types of calcium carbide vessels used for transport and storage: drums and containers (see definitions)

Each design of calcium carbide package shall be approved for transport, for example for road transport, ADR, *European Agreement on the Carriage of Dangerous Goods,* [2] and, depending on the type approval includes:

- material identification;
- dimensional checks;
- bottom lift integrity;
- top lift integrity;
- stacking limitations;
- leak proof-test; and
- drop test.

All containers in which calcium carbide is supplied shall be closed so that they are air and water tight and be filled as full as possible.

For dispatch, the regulations appropriate to the means of transport employed shall be observed.

According to United Nations Manual of Test and Criteria [3] packing group I shall be assigned for this product.

The container shall be marked with the following details:

- Designation of the size grading;
- The manufacturer's name or symbol;
- ADR marks according Packing Group I; and
- Hazard label according to GHS.

6 Reception and inspection at the plant

6.1 Reception and inspection of drums

Drums can be delivered either on pallets or individually. If drums are delivered on pallets, they shall be secured against falling.

Drums shall be conveyed from the transport vehicle to the calcium carbide store with the minimum of delay. On receipt at the calcium carbide store, drums shall be inspected prior to storage. The inspection shall cover the following:

- Excessive moisture (e.g., snow, ice): any excessive moisture shall be removed before storage.

- External damage, such as dents, holes, etc. Any drum found damaged shall be quarantined for examination.

- Any sign of swelling, bulging or heat. If the vessel shows signs of swelling, bulging or heat it could be in a dangerous state and additional precautions are required.

    - A hot drum shall neither be cooled with water nor shall it be moved until it is cold and remains cold; the surrounding area should be cordoned off and entry restricted.
    - Any pressure shall be released from the drum only by experienced people, wearing appropriate PPE based on a risk assessment.
    - If there is a seal tightening bar, slackening the clamping can be the safest way to release the pressure.

- External labelling and stencilling: the labelling on the drums should be verified to ensure compliance with grain size. Drums with incorrect grain size should either be returned to the supplier or used under supervision.

  If the drum has been opened, the contents shall not be used without supervisory approval. If it is decided that the calcium carbide cannot be used, and that the drum cannot be resealed, it shall be placed into a suitable calcium carbide vessel and sealed. The vessel shall be placed in a separate area of the calcium carbide store to await collection by the supplier.

6.2 Reception and inspection of containers

On arrival at an acetylene plant, the calcium carbide containers shall be visually checked during unloading for swelling or physical damage. Containers with defects shall be brought immediately to the attention of the supervisor.

Bulk containers that have seals broken or opening mechanisms loose could have been opened during transit by shipping or customs authorities. These containers could no longer be gas-tight or nitrogen purged. Such containers should be dried (if wet), purged and used as soon as possible.

If the container is suspected of overpressure (e.g. swelling) it shall not be moved and it shall be checked for hot spots. If a hot spot is found, the container shall neither be cooled with water nor shall it be moved until it is cold and remains cold; the surrounding area should be cordoned off and entry restricted.

Any pressure can be released by slowly opening the purge valve or slackening the clamping ring of the lid, provided that this does not completely release the lid.

If the container is damaged, it should be purged. In case of a punctured container, the hole should be temporarily sealed (e.g. with dry rags, mastic) before starting to purge it. The calcium carbide should be used as soon as possible. The container shall be clearly marked for repair.

External labelling, stencilling or accompanying documentation shall be checked, to ensure that the grain size is correct. If labelling, stencilling or accompanying documentation do not comply, the containers should either be returned to the supplier or used under supervision.

6.3 Reception and inspection of 20 t transport calcium carbide containers

The 20 t containers are purged during transport with dry air or with nitrogen. They shall be checked on arrival for the acetylene content. If the acetylene content exceeds 1% the container shall be re-purged. For containers under pressurization, they shall be safely depressurized before unloading.

7 Storage of calcium carbide full packages

7.1 General recommendations

Calcium carbide should be kept in a specific storage area. The store shall be well ventilated, dry, and the ingress of water to the area shall be prevented. Ventilation shall be provided by openings near the floor and in the roof.

Calcium carbide storage areas shall be provided with an adequate supply of dry sand or dry powder extinguishers or both.

Water, lime, condensate or steam pipes shall not pass through the area used for full packages.

Calcium carbide areas shall not be used for the storage of flammable materials or cylinders of compressed or liquefied gases. Ideally other chemicals such as acids and corrosives should be kept out of calcium carbide storage areas. If these materials have to be stored in the same area they should be separated by an adequate distance or a wall. Precaution shall be taken to prevent contact with the calcium carbide.

When storing calcium carbide vessels, ensure enough room is left to allow forklift trucks to manoeuvre safely and without causing damage.

Carbide drums and containers shall be stored in a manner to prevent damage and to enable visual inspection and easy removal of any leaking or damaged containers/drums.

The store shall be organised such that rotation of the stock is possible, to ensure the oldest carbide is used first, i.e. first in, first out (FIFO).

The store shall be regularly cleaned to prevent the accumulation of carbide dust.

No open flames or smoking shall be permitted in the storage area.

The permanent electrical equipment in the carbide store shall be to a classification that allows for a very occasional release of acetylene into the atmosphere (see EIGA doc 134, *Potentially Explosive Atmospheres EU Directive 1999/92/EC* [4]). No portable unclassified electrical equipment shall be allowed inside the store. The passage of electrical power lines in the store is permitted if they are protected against mechanical damage (e.g. forklift, etc.).

Notices shall be clearly displayed reading as follows (or equivalent):

CALCIUM CARBIDE

DANGEROUS WHEN WET

IN THE EVENT OF FIRE DO NOT SPRAY WITH WATER

NO NAKED FLAMES OR SMOKING ALLOWED

7.2 Storage of full drums at the acetylene plant

Drums shall be stored under a roof and always in a designated area (carbide store). They can be stored either on the ground or in stacks. The height of the stack will depend upon the dimensions and strength of the drum, the weight of calcium carbide and the suitability of equipment for storage and removal.

Stacks should be separated to allow for access and be kept clear of all entrances and exits.

When drums or barrels are removed from stacks for use, they shall not be dropped from the stack directly on the floor.

7.3 Storage of full containers at the acetylene plant

Full containers shall be stored inside unless the container design allows for external storage. They may be stored in stacks, if designed to do so; stacks should be separated to allow adequate access and be kept clear of all entrances and exits.

7.3.1 Outside storage of containers

Containers designed for outdoor storage shall be placed on concrete or asphalt pads or on dry well-drained ground using timbers, pallets, gravel or other structures to prevent container contact with the ground. During heavy rains or flash floods, containers should be kept above accumulated surface water.

8 Purge procedures

There are requirements for purging the equipment to prevent the development of hazardous atmospheres during the transport of calcium carbide, the transfer to the generator system, and in the return of vessels to the manufacturer.

Typically, nitrogen is used for inerting and purging the calcium carbide packages. The exposure to an oxygen deficient atmosphere shall be prevented.

Purge gas requirements can be controlled either by the use of exhaust gas analysers or by pre-determined control of time and/or flow rate. It is extremely important that when the purge is based on time and flow that the settings used have been determined by experiments using an analyser, or calculation based upon the volume of equipment to be purged and the dilution required

Finally given the critical importance of the purge systems to process involving calcium carbide and acetylene it is essential that the equipment and instruments associated with purge gas flows are checked and maintained regularly.

9 Handling

9.1 Handling of drums at the acetylene plant

Whilst handling full or empty calcium carbide vessels the development of an explosive air-acetylene mixture shall be prevented. Explosive mixtures unavoidably formed are to be kept away from ignition sources. Purging with dry gas, earthing and the use of non-spark tools, will help prevent ignitions.

The number of drums withdrawn from the carbide store at any one time should not exceed that required for charging a generator. The drums markings shall be checked for correct specification of calcium carbide.

Drums shall be opened in a designated area and not until immediately before the calcium carbide is required for use.

The operator shall wear the correct protective clothing (e.g. gloves, helmets, face shields), when opening the calcium carbide drums and filling the charging skip.

Drums can be opened either by removing the lid or by cutting out the entire top. When cutting out the top the initial opening shall be made using a non-sparking tool. Lids should not be replaced on the empty drums or barrels but should be stored separately.

The calcium carbide can be transferred to the generator system either using a charging skip or directly using a special adapter. The charging skip shall be earthed during its refill and whilst it is used on the generator.

Additionally, the charging skip should be equipped with purging facilities. The capacity of the skip shall be less than the capacity of the generator feed hopper or open charging hopper. If the charging skip is

lined internally with a sound insulating material, the material shall be electrically conductive bonded to the shell and fire-resistant.

Precautions should be taken with plastic materials, to avoid the generation of electrostatic electricity.

Drums shall be emptied of calcium carbide to prevent subsequent generation of acetylene.

Spillages of calcium carbide during transfer from the drums to the charging skip should be swept up using a natural fibre brush and non-sparking tools. For more information see EIGA doc 231, *Response to Operational Issues in Acetylene Plants* [5]

The residual calcium carbide dust can either be transferred to the charging skip awaiting calcium carbide transfer to the generator hopper, or if the transfer has been completed the calcium carbide should be disposed in a safe manner. Calcium carbide dust floating on the surface of the water is likely to ignite. It should therefore always be immersed below the water surface (e.g. lime pit).

9.2 Handling of containers at the acetylene plant

The methods of transferring the calcium carbide from the container to the generator will depend on the generator charging system. This can be done either using a charging skip or directly from the container itself or with special adapters. In all cases the container and the charging skip or hoppers shall be earthed and electrically connected to each other and whilst being used on the generator.

10 Storage of empty packages

10.1 Storage of empty drums at the acetylene plant

Drums that have been emptied should be stored without their lids for at least 24 hours in a designated area either outside or under cover to ensure that any residual carbide in the dust dissipates.

Returnable drums should preferably be sent back without the lids refitted. If the lid is replaced great care is needed to ensure that no acetylene is present or can be generated.

Drums may be disposed either by crushing or sale to a third party.

10.2 Storage of empty containers at the acetylene plant

Empty containers shall be purged (e.g. with cycles of pressurization with nitrogen and subsequent de-pressurization), before storing them in a dedicated area.

No special provisions apply for these storage areas.

11 Final inspection of drums and containers before return

The following checks should be made in accordance with the calcium carbide manufacturer's recommendation and include:

- verifying that the container is empty;
- visual inspection for mechanical damage, closure and purge connections; and
- defective containers shall be marked in accordance with procedures agreed with the calcium carbide manufacturer.

Empty and clean containers may be transported under ADR as empty unclean.

12 Operational issues during calcium carbide storage and handling

For more information see EIGA doc 231 [5]

13 Reference documents

Unless otherwise specified, the latest edition shall apply.

[1] DIN 53922 *Calcium carbide,* www.din.de
(withdrawn). At time of writing this publication is still available at beuth.de

[2] ADR, *European Agreement concerning the International Carriage of Dangerous Goods by Road*, www.unece.org/

[3] United Nations *Manual of Tests and Crit*eria, www.unece.org

[4] EIGA doc 134, *Potentially Explosive Atmospheres EU Directive 1999/92/EC,* www.eiga.eu

[5] EIGA doc 231, *Response to Operational Issues in Acetylene Plants,* www.eiga.eu

14 Additional references

EIGA Doc 123 *Acetylene Code of Practice,* www.eiga.eu

EIGA Doc 136, *Selection of personal protective equipment,* www.eiga.eu

CGA G-1.7*, Standard for Storage and Handling of Calcium Carbide in Containers,* www.cganet.com