



CALCIUM CARBIDE STORAGE AND HANDLING

TD 32/19 /E

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Figure 1 Typical production process for 1 tonne of calcium carbide 3

1 Introduction

This publication reviews the essential safety procedures associated with calcium carbide and general recommendations for calcium carbides storage areas. Additionally there is a section on the handling of typical emergency situations.

2 Scope and purpose

2.1 Scope

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

2.2 Purpose

To provide guidance on the storage and handling of calcium carbide at acetylene plants such that safe conditions are maintained.

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 Definitions

3.2.1 Calcium carbide containers

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

- intermediate bulk container (IBC) with a capacity up to 3 m³ or 2,5 t
- other containers up to 22 m³ or 20 t

3.2.2 Drums

Vessels 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.

3.2.3 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.

3.2.4 Hot spots

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

3.2.5 Transport containers (Capacity 20 t)

Containers that are used only for the transport of calcium carbide.

NOTE 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)

3.2.6 Turn bins and flow bins

3.2.6.1 Turn bin

Bulk container (approximately 1.5 t) 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.

3.2.6.2 Flow bin

Bulk container (approximately 1.5 t) 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.

4 Calcium carbide general information

4.1 Physical and chemical properties

Calcium carbide is a grey rock-like solid that comes in irregular sized pieces, typically ranging from 5 mm to 80 mm depending on customer specifications. 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. As long as it is kept dry, Calcium carbide is a stable, safe substance. Calcium carbide reacts rapidly with water or even moisture in the

atmosphere to generate acetylene and a carbide lime residue. This reaction creates considerable heat (exothermic reaction). Calcium carbide shall be kept dry, to avoid unwanted reactions generating uncontrolled acetylene.

4.2 Specific precautions

Calcium carbide is an irritant to the eyes, skin and respiratory system and can cause serious eye damages. Always wash thoroughly with water any skin that could have come in contact with calcium carbide granules or dust. Calcium carbide dust in contact with the skin can react with moisture, creating heat and caustic carbide lime that could cause severe burns.

4.3 Calcium carbide production

Calcium carbide is produced by a reaction between coke and burnt lime in an electric furnace at a temperature of 2000°C. Molten carbide is tapped from the furnace and run into moulds where it is left to solidify. When it cools it is crushed and screened by size. The manufacturing process requires large amounts of electricity.

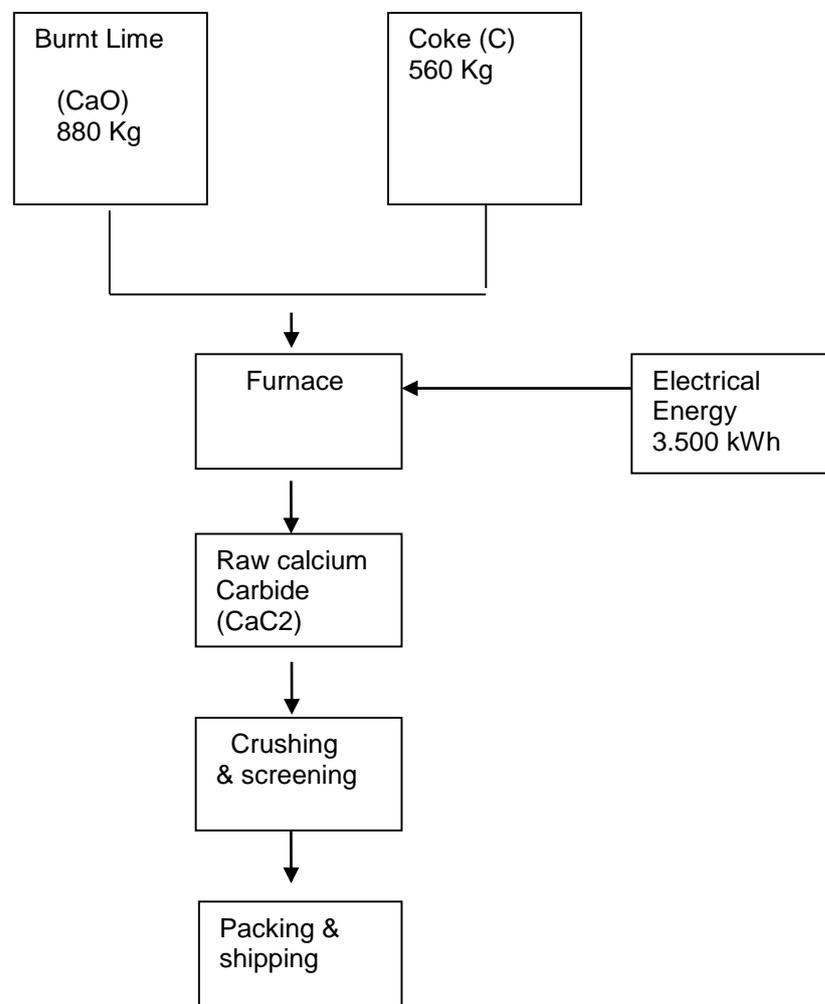


Figure 1 Typical production process for 1 tonne of calcium carbide

The calcium carbide typically contains between 15% to 20% impurities. The main impurities are un-reacted lime (7%-14%) and coke (0,4%-3,0%). Additionally there is a minor amount of chemical compounds containing iron, silicon, aluminium and magnesium. Impurities such as phosphine, ammonia, hydrogen sulphide and organic sulphides give calcium carbide and acetylene their distinctive garlic-like smell. The impurities present depend on the source and quality of the raw materials used.

4.4 Calcium carbide yield

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. The yield also depends on the grade size of the calcium carbide, in general the greater the size the higher the yield. Typical yields are between 265–300 litres of gaseous acetylene per kilogram of solid carbide.

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 size typically 50 kg - 400 kg
- Containers size typically 1 t - 2,5 t and 20 t

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*, [1]¹ 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.

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.

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

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 stenciling: 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, stenciling or accompanying documentation shall be checked, to ensure that the grain size is correct. If labelling, stenciling 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 acetylene plant store shall be to a classification that allows for a very occasional release of acetylene into the atmosphere. 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

e.g.



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 Handling

8.1 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.

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).

8.2 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.

9 Storage of empty packages

9.1 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.

9.2 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.

10 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 should be marked in accordance with procedures agreed with the calcium carbide manufacturer.

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

11 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. It is implicit that a factor of safety of at least two shall be included in the calculation.

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.

12 Emergency procedures for calcium carbide storage and handling

12.1 General considerations

Calcium carbide drums or containers can become hot if they are damaged and there is any ingress of water. Emergency procedures and equipment shall be in place to safely deal with such situations.

As a general precaution, the following actions should be taken:

- Ensure that the area where the emergency is occurring is cordoned off.
- The container should not be moved until the reaction has ceased and the surface is cool. If possible any further contact with water should be eliminated.

12.2 Hot calcium carbide drum

Before taking any action, allow the drum to cool naturally by ambient air until cold to the touch then move it to a designated safe location. This location shall be:

- dry;
- well ventilated; and
- as far as practical from objects of concern (people and equipment).

When the drum is cold, it is possible to move and start to purge it.

The following procedure shall be followed only by competent and trained personnel; always ensure a competent second person is present and that a dry powder fire extinguisher and dry sand are available.

Purging reduces or eliminates potentially flammable acetylene-air mixtures from calcium carbide drums. Nitrogen is passed through the drum to dilute and displace any potentially flammable acetylene-air mixtures. It also dries the carbide, stopping the generation of acetylene. Nitrogen is used because it is an inert, non-reactive gas.

The nitrogen purge equipment should be able to provide a controlled flow of nitrogen at low pressure (typically <100 mbarg), through a small bore tubular probe, which can be inserted in to a pierced hole in the drum if the inlets not available.

Hold a non-sparking tool against the drum and pierce one hole in the lid of the drum, and one near the drum base.

Insert a nitrogen purge line into the hole near the base.

Slowly turn the nitrogen on and purge the drum until cool. Ensure that the purge gas is vented to a safe location.

Continue purging, checking periodically that it is not re-heating, until the drum is opened for the next generator recharge.

12.3 Hot carbide containers

Containers of calcium carbide are normally fitted with purging connection points.

Any container showing signs of heat should be purged with nitrogen until the external surface of the container is cold and the gas venting off is less than 25% LEL (acetylene in nitrogen).

The container may then be used in the normal manner.

12.4 Carbide spillage

12.4.1 Equipment

The following equipment is required for cleaning up calcium carbide spills:

- non-sparking shovel (full shovel with long handle);
- non-sparking bucket, natural bristle broom (not nylon which could generate static electricity);
- steel drum without a lid;
- drum containing dry sand (in the event of a fire); and
- personal protective equipment (refer to EIGA Doc 136 *Selection of personal protective equipment* [2]).

12.4.2 Use and maintenance of equipment

Equipment to clean up calcium carbide spills should be maintained at a designated spot in the acetylene plant and used for that sole purpose only.

Plastics or other potential spark generating equipment shall not be used.

12.4.3 Cleaning up a calcium carbide spill

Wear the following personal protective equipment:

- flame retardant gauntlets (long sleeve gloves);
- chemical resistant eye protection;
- flame retardant clothing; and
- dust mask.

If the spillage is a major loss of containment then evacuate personnel from the area to a location upwind and prevent vehicle access to the incident area in accordance with site emergency procedures.

Keep water away from spilled calcium carbide. If carbide has become wet in the vicinity of the acetylene generator, immediately stop all acetylene production operations and ensure that the area is well ventilated in the vicinity of the spillage before beginning clean up.

Isolate all sources of ignition in the area.

Check for dust / fines (small granular carbide) in the spilled calcium carbide as these residues can:

- react rapidly with moisture in the air; and
- become hot enough to ignite the acetylene produced.

If dust or fines are present:

- Use non-sparking equipment to remove calcium carbide dust, fines and residues away from the acetylene plant.
- Spread deposits thinly on a designated disposal area, and hose with large quantities of water.

Do not throw agglomerated quantities of dust, fines and residues directly into water or carbide lime settling pits as this could cause an explosion.

If the PPE has become impregnated with calcium carbide, ensure that it is removed and laundered before re-use. Personnel should ensure that they have a shower immediately after the clean-up operation to remove residual calcium carbide products.

If spilled calcium carbide has come in contact with water and become wet, eliminate hot spots by covering it with sufficient dry sand so that no calcium carbide can be seen through the layer of sand. Wait until cool and then clean up calcium carbide using the recommended equipment and place it in a transfer cart or steel drum. Then:

- transfer to a safe area away from buildings and sources of ignition,
- scatter calcium carbide and sand mixture in a thin layer on an designated disposal area and leave to react with the moisture in the air,

Alternatively, after picking up the bulk of the spillage, water hoses may be used to wash the remaining spilt residues in to the carbide lime disposal system.

If the calcium carbide has not become contaminated, e.g. with sand, it may be kept covered and be used in the first available generator charge.

12.5 Carbide fires

12.5.1 General considerations

Calcium carbide is not flammable but generates acetylene gas when in contact with water.

Therefore never apply water or use foam extinguisher to a calcium carbide fire. The water will react with the calcium carbide to produce more acetylene gas, feeding the fire.

It is preferable to let fires in carbide spills to burn out naturally. This consumes the escaping acetylene and avoids the formation of large unconfined gas clouds, which could result in an explosion.

12.5.2 Procedure

Wear the following fire retardant personal protective equipment:

- leather gauntlets (long sleeve gloves);

- leather boots;
- chemical resistant eye protection; and
- flame retardant clothing.

Evacuate personnel from the area to a location upwind and barricade to prevent access.

Isolate all sources of ignition in the area.

Re-ignition of generated acetylene could be a secondary risk, following extinguishing of the fire.

If water is present attempt to isolate the source of the water. It is best to leave the fire to burn out naturally until all of the generated acetylene has been consumed. The heat of the fire will dry out the carbide, thus stopping the generation of acetylene, which is the source of the fire.

In extreme circumstances, it is possible to extinguish the fire with a dry chemical powder but this is only necessary if the fire is creating an extreme hazard. This operation should only be carried out by the authorised emergency services trained to deal with this action for example the fire brigade.

Allow the building to ventilate freely by opening the doors and waiting for at least 30 minutes or until the atmosphere is safe.

Immediately place the spilt carbide into air tight steel drums for storage until it can be used in the next generator charge.

Drums should be purged with nitrogen before sealing the lids as acetylene could still be generated.

13 References documents

- [1] ADR, *European Agreement on the Carriage of Dangerous Goods*, www.unece.org/
[2] EIGA Doc 136, Selection of personal protective equipment www.eiga.eu
[2] EIGA Doc. 196/15 CALCIUM CARBIDE STORAGE AND HANDLING.

14 Additional references

CGA G-1.7, *Standard for Storage and Handling of Calcium Carbide in Containers*
www.cganet.com
EIGA Doc 123 Acetylene Code of Practice www.eiga.eu