ENVIRONMENTAL IMPACTS OF ACETYLENE PLANTS

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ENVIRONMENTAL IMPACTS OF ACETYLENE PLANTS

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Section | Change
---|---
Sections 2 and 4 | As indicated in text
Section 3.2 | Publication terminology added
Section 4.4.3, 4.6.2 and 4.6.3 | Some references in the text of Doc 109/11 indicated that it was acceptable to add some amounts of sulphuric acid, sodium hydroxide or sodium carbonate to a lime pond. EIGA has concerns about the acceptability of these practices and has revised the text in the current document to make it clear that it is not acceptable to add anything to a lime pond or pit other than carbide lime except under controlled and permitted conditions.
Section 5 | References added
Main text | Editorial changes in line with EIGA style manual
1 Introduction

This document details the environmental impacts of the management of acetylene plants and gives guidelines on how to reduce those impacts.

2 Scope and purpose

2.1 Scope

The document concentrates on the environmental impacts of acetylene plants. This document does not give specific advice on health and safety issues. On these issues the relevant EIGA documents, and or national legislation should be consulted for advice and these shall be taken into account before undertaking any activity.

2.2 Purpose

This document is intended to serve as a guide for Acetylene Plant operations to assist in putting in place a formal environmental management system that can be certified by an accredited third party verifier. It aims to provide a guide for operations managers to identify and reduce the environmental impacts of these operations. It also provides the basis for establishing the Best Available Techniques for the purposes of the Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (Recast) [3]. This covers acetylene production in Annex I Section 4.1a Production of organic chemicals, simple hydrocarbons.

3 Definitions

3.1 Environmental aspects

Elements of an organisation’s activities, products or services that can interact with the environment. For example, use of energy or transportation of products.

3.2 Environmental impacts

Any change to the environment, whether adverse or beneficial, wholly or partially resulting from an organisation’s environmental aspects. (Source ISO14001:2004[4]). For example, the contamination of water with hazardous substances, the reduction of air emissions.

3.3 Publication terminology

3.3.1 Shall

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

3.3.2 Should

Indicates that a procedure is recommended.

3.3.3 May

Indicates that the procedure is optional.

3.3.4 Can

Indicates a possibility or ability.
4 Acetylene plants environmental impacts

4.1 General environmental aspects and impacts and links to other EIGA documents

This document covers the environmental impact of acetylene plants which are summarised in Appendix 2.

There are several linked EIGA publications that provide more details on general environmental issues, legislation for the gas industry and operational good environmental practices. A list of these linked documents and their links to the ISO 14001 environmental management systems standard is provided in Appendix 1. Appendix 1 also shows which of these documents are relevant to acetylene plant operations.

4.2 Introduction

The basic philosophy is the minimisation of wastes, emissions and nuisances of any kind and their safe and clean disposal. By considering the potential wastes which a new process could generate when engineering a plant, future problems can be avoided. This analysis is a crucial element of Environmental Impact Assessment and is strongly recommended before any decision on industrial plant investment.

Wastes should not be mixed but should be collected separately to aid further recycling, reuse or recovery.

Material safety data sheets for all chemical substances shall be held on site and used to determine the best way to handle the chemical substances.

Acetylene is produced by two different methods:
- reaction of calcium carbide with water in special generators, and
- as a gaseous by-product from cracking crude oils.

The main method of production for the gas industry is by the first method. This is due to the lack of availability of the by-product material where the acetylene is required and the economics of production. The second method is generally used for production of acetylene as a chemical intermediate.

Consequently, this document describes only the first process mentioned, i.e. the exothermic reaction between calcium carbide and water:

\[ \text{CaC}_2 + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_2 + \text{Ca(OH)}_2 + 27000 \text{ cal.} \]

Hydrated lime, \( \text{Ca(OH)}_2 \), is also produced as a by-product. After separating from the carbide lime, excess water can be reused in the process and the lime can be recovered for use in various industrial or agricultural activities according to applicable local legislation.

Due to the fact that technical grade \( \text{CaC}_2 \) contains various impurities from the raw products used in its manufacture, coal and limestone, acetylene also contains impurities such as ammonia and phosphine.

The generated acetylene is purified, compressed, dried and filled into gas cylinders that are stored on site prior to distribution.

The main environmental impacts from acetylene plants are described below, following step by step the production process. A simplified drawing in Appendix 3 illustrates the acetylene production process. Technical details on acetylene production are described in EIGA Doc. 123, Code of Practice – Acetylene \([1]\).
4.3 Raw material storage

4.3.1 Calcium carbide

4.3.1.1 Calcium carbide containers

Calcium carbide is transported and stored in weatherproofed containers (drums, bags or returnable bins) to keep the carbide dry and prevent the conversion of calcium carbide to acetylene.

Where these containers are reused they need to be regularly inspected to ensure they are in good condition, in line with good practice or national regulations. They shall be stored in the correct location so as to prevent corrosion or damage.

Even when containers have been mechanically emptied they always contain carbide residuals (dust). Calcium carbide dust will generate acetylene when in contact with moisture.

Where containers are reused the small amounts of residual carbide are a potential safety and environmental hazard.

If a calcium carbide container has to be disposed of it should be clearly marked and segregated and the following procedure should be adopted.

One acceptable method to remove the dust from the container is to wash it out with sufficient water and to leave the container open for some days to vent with air. This water has to be disposed of to the lime pit. Before the container is sent for disposal it should be checked to ensure that no acetylene is left in it. The container may then be reused or recycled as scrap metal.

4.3.1.2 Calcium carbide drums

Drums that have been emptied should be stored without their tops for at least 24 hours in a designated area either outside or under cover or roof.

Returnable drums and barrels should preferably be sent back without the tops refitted. If however the top is replaced, great care is needed to ensure that no acetylene is present or can be generated.

Non-returnable drums will have a scrap value and should be recycled as scrap metals.

4.3.1.3 Calcium carbide dust

Disposal of pure dust directly into water in the lime pit is extremely hazardous and has been known to cause explosions. Carbide dust should be disposed of by spreading it thinly on an open surface and allow it to air slake (react with moisture in the air). Alternatively it may be hosed down with copious amounts of water. The residues must be drained into the lime pit.

4.3.2 Chemicals

4.3.2.1 Purifier materials

Sulphuric acid and sodium hydroxide shall be stored in dedicated containers on an impervious surface with secondary containment. Dry purifiers contain ferric/ferrous chloride and traces of mercury. The spent chemicals require disposing of by an approved contractor.

4.3.2.2 Solvents

Acetone or DMF (Dimethylformamide) shall be stored in above ground or underground storage tanks that are regularly inspected and maintained by qualified personnel.
4.3.2.3 Storage tanks

Storage tanks should be designed to be fit for purpose to the appropriate national or international standard and shall be regularly inspected and maintained by competent personnel.

When filling a tank the operator shall attend the filling at all times. By installing overfill alarms; the risk of major spills may be further reduced. Minor spills can occur when filling or emptying the tank and proper precautions such as using spill plates over drains should be taken to avoid any environmental damage caused by this.

4.3.2.4 Underground storage tanks

These should be avoided on new facilities and the more details can be found in the EIGA document Doc. 106, Environmental issues guide [5].

4.3.2.5 Above ground storage tanks

Above ground storage tanks also risk contamination of soil and water if the tank starts to leak although the control of tank leakage is less complicated than for underground tanks. Even a dripping valve could easily contaminate several cubic meters of soil. Spill plates should be used.

Large storage tanks are frequently used for fuel while the smaller ones may contain oil, antifreeze and other substances. It is important to avoid spills and to label the tanks regardless of the size.

4.4 Acetylene generator

4.4.1 General

The procedure for charging the generator depends upon the type of system and shall be laid down in specific working manuals and instructions. Two types of generator are used:

- the ‘open’ generator, where acetylene escapes from the generator during carbide charging, and
- the ‘closed’ generator, where the charging system is sealed.

The open generator causes more emissions of acetylene and other gases (see section 4.13).

Operating details such as

- working pressure
- temperature range
- carbide charging capacity, and
- maximum production rate

are laid down in both the design documentation and the operation manuals. Also refer to EIGA Doc. 123, Code of Practice – Acetylene [6].

All generator systems contain an interceptor that is generally fitted between generator and gasholder. It consists of a small tank containing water through which acetylene is bubbled. It is used as a hydraulic non-return valve as well as a device to prevent a flame travelling back from the gasholder to the generator.
4.4.2 Calcium carbide residuals

Calcium carbide residuals normally contain non-reactive materials e.g. stones, iron, ferrosilicon, coke, etc which are infused with lime. Carbide should be purchased in consistent quality to reduce impurities. Difficulties in disposal of calcium carbide residuals arise from the lime. Due to the alkaline properties of lime it may not be possible to dispose of calcium carbide residuals on normal landfills without special treatment. This is due to the very high pH values and conductivity of the residual-water mixture.

To dispose of calcium carbide residuals on a landfill, permission from the competent authority may be necessary. Alternatively the material can be used for road and parking place construction by mixing it into the concrete and thus encouraging recycling.

4.4.3 Lime

Lime storage and loading areas shall always be watertight (basins, tanks, silos etc.) to avoid soil and groundwater contamination. Additionally they shall be open to the atmosphere to avoid the hazard of generation of explosive air/acetylene mixtures.

Using a filter press or a centrifuge to remove excess water can reduce the volume of lime, which makes transport easier and more economical.

Examples of uses include:

- In industries where spent acids and waters with low pH-value need to be neutralised (lime is an excellent neutraliser).
- Sewage water treatment.
- Flue-gas purification.
- Use as corrector of pH-value of soil (agriculture).
- Building trade (mortar processing).
- Chemical processes.

Sulphuric acid from the acetylene purification may be neutralised in the lime pits under certain conditions (see 4.6.2). In this case the content of calcium-sulphate must not exceed approximately 2% $\text{SO}_4$ in solid Ca(OH)$_2$.

If the concentration is greater than 2% the lime cannot be used in sewage water treatment and the construction industry. If this activity is to be carried out specific authorisation is required in the site regulatory permit for this activity.

Lime slurry should be considered as a product and not as a waste, because it is possible to market it for different uses (See EIGA Doc. 143, Guide to lime applications [5] and ASTM Special Technical Publication STP 931, Lime for Environmental Use [7] for reference). Regular analysis should be carried out to promote lime as a product.

Lime can be classified as a by product and not a waste provided if it meets the tests in EU commission guidance COM 2007/56 [8], for example when:

- The intention is not to ‘discard’ the lime from the process but to market it, the lime is produced to a specification and has a safety data sheet according to product legislation (registered or pre-registered under REACH).
- Lime can be used directly without further processing, which should mean it is not classified as waste if it has a certain beneficial application.
In the unlikely event that there is no available use for the lime, it has to be disposed of as waste according to amending Decision 2000/532/EC \cite{9} as regards the list of wastes (Waste number 06 02 01 for Ca(OH)$_2$). Permission from competent authorities is required.

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.

### 4.4.4 Generator water

Water that is used in the acetylene generator (excluding the water that remains with the lime) should be re-circulated after separation from lime. Rainwater can also be used as generator water after having been properly filtered and checked.

The lime-water must never be drained uncontrolled into the sewage water system or ground water. Releasing limewater into the drainage or public sewage water system will cause problems due to its high pH-value.

Before draining the water, the local sewage water authorities shall be asked for permission and a proper method (depending on the sewage water composition) shall be agreed. This water can also contain ammonia, which is highly toxic to fish, so it also shall not be discharged directly to rivers.

### 4.4.5 Generator cleaning residuals

The generator may be cleaned mechanically or by using acids. Solid residuals of mechanical cleaning consist of slaked lime and can may be disposed of in the lime pits. If acids are used for cleaning the spent mixture must be disposed of by an authorized waste disposal contractor or can be neutralized in the lime pits under the same circumstances as spent sulphuric acid (see sections 4.4.3 and 4.6.2).

### 4.5 Gas holder

Some generation systems use a gasholder. The purpose is to match the production of acetylene from the generator to the compressor demand. A gasholder usually consists of a rising bell that is immersed in water that forms a gas seal. The bell rises and falls to balance the production by controlling the calcium carbide feed to the generator.

#### 4.5.1 Water

Gasholder water contains small amounts of acetylene and ammonia that should be taken into consideration when emptying the gasholder for maintenance or other reasons. Gasholder water should be emptied into the lime pit.

#### 4.5.2 Oil

In some cases oil is used as fluid in gasholders instead of water. If, due to contamination, oil cannot be reused in the gasholder it should be handled according to the recommendations in sections 4.7.1 and 4.7.2.

### 4.6 Purification

Acetylene contains impurities, i.e. phosphine, ammonia, hydrogen sulphide and organic sulphides. Purification involves the removal of these components by scrubbing and/or oxidation. Purification takes place in relatively narrow and tall washing towers to ensure an intensive contact between cleaning agent and gas or by passing the gas through beds of solid purification material. Sulphuric acid, sodium hydroxide and sodium carbonate are mostly in use as purification agents.
4.6.1 Chromic acid

Chromic acid is generally no longer used due to the difficulties to disposing of it correctly and should be replaced with less hazardous materials, such as sulphuric acid.

Spent chromic acid is considered as hazardous waste and should be disposed of only by an authorised waste disposal contractor.

4.6.2 Sulphuric acid

Spent sulphuric acid must never be drained into the sewage water system. Sulphuric acid should either be:

- Returned back to the producer of sulphuric acid for purification and reuse.
- Neutralized in the lime pits.
- Disposed of by a specialist.

When neutralizing the acid with lime the following has to be considered:

- This activity must be included in the site regulatory permit (IED/IPPC)

- Only small amounts of acid should be neutralized in large amounts of lime to avoid emissions of hydrogen-sulphide and phosphine and to prevent foaming in the generator when water from the lime pits is reused for acetylene generation.

- The sulphuric acid must be fed into the lime such that both substances are mixed instantaneously, e.g. into the lime pipe between the generator and the lime pit, or underneath the surface of the lime in the pits. The neutralization in the lime pipe, between the generators and the lime pit, is possible only when the generators are in use.

4.6.3 Sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃)

The sodium hydroxide and sodium carbonate can be diluted in the lime pits, provided this activity is included in the site regulatory permit. The concentration shall be kept low.

4.6.4 Solid purification media

Solid purification media that use ferric chloride (FeCl₃) and ferric oxide (Fe₂O₃) as active agents often contain catalysts such as mercuric chloride (HgCl₂) or cupric chloride (CuCl₂). These materials must be disposed of in accordance with relevant waste regulations.

4.7 Compression

Acetylene is compressed in multi stage compressors. The compression is also an important stage in the drying process because most of the water separates out. Despite acetylene being dry when leaving the sulphuric acid cleaning device it becomes moist again after having passed the cleaning tower containing sodium hydroxide or sodium carbonate, which are dissolved in water.

During compression a small quantity of acetylene emission is possible. It can be reduced by regular inspection and maintenance of the compressor equipment. Acetylene is dried by passing through vessels containing drying material such as calcium chloride, in some plants of an older design, or silica gel, alumina gel, molecular sieve or similar which can be regenerated. Maximum operating pressure is 25 bar gauge.
4.7.1 Oil

Precautions must be taken to prevent oil from entering drainage systems.

- Oil shall not be mixed with other substances if it can be avoided e.g. water, soil, and solvents.
- Oil shall always be collected in a barrel or drum and be delivered for recycling.
- A bund (or secondary containment system / pit) on each compressor or transformer installation should be installed to collect potential leaks and purges.
- Oil drums should be stored above a catch pot.

4.7.2 Water-oil mixtures

When using water-soluble emulsifiers for cleaning purposes the water emulsions have to be disposed of in a way acceptable to the authorities in the particular countries. Sometimes it may be possible to dispose of the emulsion by draining it into a suitable sewage water drainage system.

When no emulsifiers are used oil and water must be separated in special oil-water separators. Water can then be discharged into the drainage water system, and the oil should be recycled, see section 4.7.1.

4.8 Dryers

4.8.1 Silica gel / Alumina gel

Used gel should be checked for oil contamination. Uncontaminated gel can be disposed of as non hazardous waste. Consideration should be given to return it to the supplier.

4.8.2 Calcium chloride

The normal way to dispose of the calcium chloride is to dilute it with the lime sludge in the lime pits, but when the lime is delivered to a water treatment plant the calcium chloride shall be diluted to a level of the chlorine ion concentration that does not adversely affect the functioning of the water treatment plant. The maximum level has to be agreed upon with the treatment plant operator.

4.8.3 Sodium hydroxide

See section 4.6.3.

4.8.4 Packing materials

Packing materials (Raschig rings, Berl saddles, etc.) should be rinsed, where practicable, with suitable cleaning agent before being reused or disposed of on a normal landfill. The cleaning agents should be disposed of according to their properties and in accordance with this document.

4.9 Cylinder filling

Acetylene is dissolved under pressure in cylinders, which contain porous mass and a solvent that is either acetone or DMF (dimethylformamide). During cylinder filling no significant emission of acetylene occurs. For safety reasons every cylinder is weighed after filling to ensure that it is correctly filled.

4.9.1 Cooling water

Recycling of cooling water is recommended.
As long as cooling water does not contain any impurities it is allowed to drain it into the rainwater drainage or sewage water system in accordance with national or local regulations, e.g. requirements for pH-value or temperature. (Companies in various countries need permission for this).

If cooling water is contaminated with oil or other chemicals (closed circuit cooling system) the procedure of draining the cooling water into the sewage water system has to be arranged in accordance with methods accepted by the local authorities.

Often chemicals such as biocides are added to prevent the development of legionella and other anti fouling chemicals may also be added. Care shall be taken to prevent operator exposure to breathing overspray water containing these biocides, as they are hazardous to health.

Additionally, rainwater can be used for cooling water.

### 4.9.2 Ethanol / Glycol

Cooling waters containing ethanol or glycol shall comply with local authority requirements before drainage into the sewage water system.

### 4.9.3 Acetylene emissions

Acetylene is an organic gas that contributes to the formation of photochemical oxidants and predicted warming of the atmosphere. It is therefore classified as a Volatile Organic Compound (VOC). Specific legal requirements on VOC emissions reporting may exist depending on the country.

Acetylene from overfilled cylinders, or from cylinders being prepared for testing, should always be discharged into a closed piping system and returned to the gasholder or compressor.

As a general principle of environmental protection and for safety reasons only very small amounts of acetylene should be allowed to escape into the atmosphere. When starting the generator, acetylene emissions to the atmosphere due to quality specifications have to be kept at the minimum.

### 4.9.4 Acetone from return gas

In some plants the acetone from the return gas is washed out with water in a scrubber. This water may be drained into the lime pits.

### 4.10 Cylinder maintenance

#### 4.10.1 Scrap metals

It is necessary to separate different scrap metals. Steel, copper alloys and other nonferrous metals must be separated. Scrap metals should be sent to a specialised dealer for recycling.

#### 4.10.2 Scrap cylinders

Scrapped acetylene cylinders should be treated in accordance with the EIGA Doc. 05, Guidelines for the management of waste acetylene cylinders [10].

#### 4.10.3 Paint

Paint, solid or liquid, is normally considered hazardous waste and consequently it should be disposed of in accordance with national regulations.

#### 4.10.4 Porous mass / material

Refer to the EIGA Doc 05, Guidelines for the management of waste acetylene cylinders [10].
4.10.5 Acetone and DMF

Refer to the EIGA Doc. 05, Guidelines for the management of waste acetylene cylinders \(^{[10]}\).

4.11 General

Any material containing oil, oil binders and oily cloths shall be disposed of as hazardous waste in accordance with local regulations, e.g. burning in an incinerator plant or deposition on a licensed landfill site.

Valves, membranes, metallic packing materials, flame arrestors etc. should be handled as scrap metals.

4.12 Noise

The main sources of external noise at an acetylene site are:

- Manual handling, use of vehicles
- Compressors and pumps

The EIGA Doc. 85, Noise Management for the Industrial Gases Industry \(^{[6]}\) gives a comprehensive review of noise management and the actions which should be considered.

4.13 Air emissions

Methods for estimating the air emissions from an acetylene plant are given in EIGA Doc 84, Calculation of air emissions from an Acetylene Plant \(^{[11]}\).

4.14 Emergency plan

The main hazards of acetylene are

- the extremely high flammability,
- the possibility to form explosive mixtures with air in a wide range and
- its property of decomposition under various circumstances with the consequence of a fire or an explosion.

To prevent such an event all acetylene plants shall be equipped with an emergency shut down system to stop all electrical machinery. An emergency water deluge system must also be provided to cover the cylinder filling and indoor storage areas. Water deluge systems must be designed to avoid oil and chemical storage areas so that their operation does not spread contamination. They must not be installed over the generators or in the carbide storage areas. Their purpose is to cool hot cylinders in the event of a fire or internal decomposition.

The gas company employees and contractors must be aware of the site emergency plans, trained and competent in the requirements. The emergency plan should contain, as examples:

- Actions in the event of the emergency shutdown system activating.
- Actions in the event of environmental events such as major leakage of lime, chemicals or oil in the emergency plan.
• The location of absorption material to clean up spills on the floor.

• Actions in the event of a major gas leak.

• Actions in the event of fire in the carbide store, the generator, the compressors and filling plant, the solvent bulk storage area and the cylinder storage areas.

• Actions to contain contaminated fire water run-off.

• Action in the event of dispersal of hazardous materials e.g. asbestos.

The emergency plan should be regularly tested with drills and simulations etc.

5 References

[4] ISO 14001 Environmental management
[10] EIGA Doc. 05, Guidelines for the management of waste acetylene cylinders
## APPENDIX 1: EIGA Document Links to ISO 14001

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<td>Environmental auditing guide</td>
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### What Documents are relevant to me?

For Acetylene plants the relevant documents specific documents are highlighted in bold, and useful general documents in italics. There is an EIGA Training Package on Acetylene plant Environmental Issues. Other EIGA documents are obtainable from the EIGA web site.
## APPENDIX 2: Acetylene Plants Environmental Impacts

<table>
<thead>
<tr>
<th>INPUTS</th>
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<td><strong>DUST CONTAINERS</strong></td>
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<td><strong>WATER</strong></td>
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<td><strong>(HEAVY METALS)</strong></td>
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<td><strong>WATER EMISSIONS</strong></td>
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<td><strong>CONSUMABLES</strong></td>
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<tr>
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<td><strong>CYLINDERS</strong></td>
<td><strong>WATER</strong></td>
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<td><strong>LIME PITS</strong></td>
<td><strong>PERSISTENT PERIODIC OCCASIONAL OR ACCIDENTAL</strong></td>
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</table>

Diagram:

- Calcium carbide → Storage → Air Emissions, Dust, Containers
- Water → Generator → Air Emissions, Lime, Generator Residuals, Generator Water
- Consumables, Water → Gas Holder → Oil, Solvents, Water
- Chemicals, Purification Media → Purification → Chemicals, Purification Media (Heavy Metals), Water Emissions
- Consumables → Compression → Oil, Noise, Water
- Adsorbents → Dryers → Adsorbents, Packaging
- Water, Chemicals, Cylinders → Cylinder Filling → Water, Air Emissions
- Water, Consumables → Cylinder Maintenance → Paint, Scrap Cylinders, Porous Mass
- Lime Pits → Air Emissions, Lime, Water

Persistents: •
Periodic: △
Occasional or accidental: ■
APPENDIX 3: Simplified drawing for acetylene production process