

CALCIUM CARBIDE

HOT METAL DESULFURIZATION GRADE

HEALTH & SAFETY INFORMATION

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EMERGENCY PHONE NUMBERS

Carbide Industries - 24 Hour Emergency Response

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HEALTH & SAFETY INFORMATION

HOT METAL DESULFURIZATION GRADE CALCIUM CARBIDE

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NOTE: This Health & Safety Information Booklet replaces previous Hot Metal Desulfurization Grade Booklets.

1. PRODUCT SUMMARY

A. *Product Description*

Carbide Industries' hot metal desulfurization reagents comprise a series of fine mesh products, with 95% typically passing through 105 microns. Each reagent is composed of powdered commercial grade calcium carbide and may contain additional components to enhance its effectiveness in the removal of sulfur from iron and steel. Additionally, all Hot Metal Desulfurization reagents from Carbide Industries have a flow enhancing coating to insure trouble free pneumatic transport & sub-surface injection.

B. *Calcium Carbide Reagent Chemistry*

Calcium carbide is a gray to dark gray granular solid made commercially by the reaction of coke and quicklime in a submerged arc electric furnace. Calcium carbide itself is noncombustible, but reacts readily with water to form acetylene, calcium hydroxide and heat according to the following reaction:

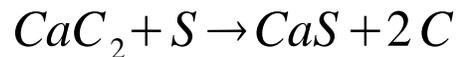


Acetylene is a highly flammable gas with a wide explosive range and a low ignition temperature. Acetylene is also pressure sensitive and can decompose explosively in the absence of air at pressures slightly above atmospheric.

The reaction of calcium carbide and water yields calcium hydroxide, also known as carbide lime. This material is caustic and may irritate exposed skin, eyes, nose and throat. Calcium carbide is classified as a

hazardous material due to the generation of acetylene gas, and as a result, strict safety precautions must be used in handling the product. Per D.O.T. classification, calcium carbide is listed as ‘Dangerous when Wet’ and carries the UN1402 designation.

In the typical desulfurization process, solid calcium carbide is added to liquid metal at temperatures above 2,650(F). Sulfur is removed from the mixture according to the following formula:



The reaction products are entrained a solid slag which is typically removed from the melt.

Typical Commercial Calcium Carbide Composition

	Weight %
CaC ₂	78.0
CaO	15.0
CaS	1.2
Ca ₃ P ₂	0.05
C (Free)	1.0
Si as SiO ₂	1.5
Al & Fe as R ₂ O ₃	1.5

To enhance the performance of Carbide Industries Desulfurization Reagents, specially prepared additives such as powdered quicklime (calcium oxide) and Gilsonite (a non-oxidizing gasifier) may be blended with the calcium carbide

2. PACKAGING AND HANDLING

A. *Tanker / Railcar Overview*

Carbide Industries Desulfurization Reagents are typically shipped in pressure differential (PD) tankers and railcars. These vehicles are equipped with suitable piping for the pneumatic transfer of the reagents using pressured dry nitrogen.

NOTE: Under no circumstances should any tanker or railcar be pressurized above 14.7 psig.

All desulfurization tankers and railcars should be inspected before and after use. Inspection should include the following items:

- All valves should be tightly closed with shipping locks intact
- The body of the container should be free of open seams and evidence of in-transit damage which might affect water tightness.

Containers failing to meet these standards should be set to one side for special handling. Refer to Carbide Industries railcar & tanker unloading booklets for detailed instructions covering proper procedures. Contact Carbide Industries for further information.

B. Handling Recommendations

The fine size and excellent flow characteristics of Carbide Industries desulfurization reagents provides for excellent performance in the removal of unwanted sulfur in iron and steel. However these properties also enhance the reactivity of these materials with all forms of moisture to produce acetylene gas as

well as their propensity to spread over large areas when spilled. It is therefore recommended that Carbide Industries desulfurization reagents are only handled in fully enclosed, nitrogen purged, moisture free systems. The shipping vessels (both tankers and railcars) are filled under a nitrogen blanket and purged prior to shipment. All reagent containers meet D.O.T. requirements under 49 CFR 172.101 and DOT SP-14659, as well as all relevant Transport Canada regulations.

C. *Storage Recommendations*

Outdoor storage areas should be located at least 20 feet from any line of adjoining property. The area should be posted with the notice:

**"CALCIUM CARBIDE - DANGEROUS WHEN WET -
KEEP WATER AND OPEN FLAMES AWAY - NO SMOKING IN AREA"**

Carbide containing vehicles stored outdoors should be placed on a concrete pad or on firm, well drained ground.

Proper stock turnover is recommended. It is suggested that a regular schedule of **STOCK INSPECTION** be set up to check condition of containers. In this manner, excessive rusting or other damage to a container that might affect its water and air seal will be recognized and the defective container removed within a reasonable period of time.

All applicable federal, state, and local regulations or ordinances governing storage of calcium carbide must be observed. Reference should also be made to the provision of insurance coverage. Contact local Fire Marshall and your insurance carrier.

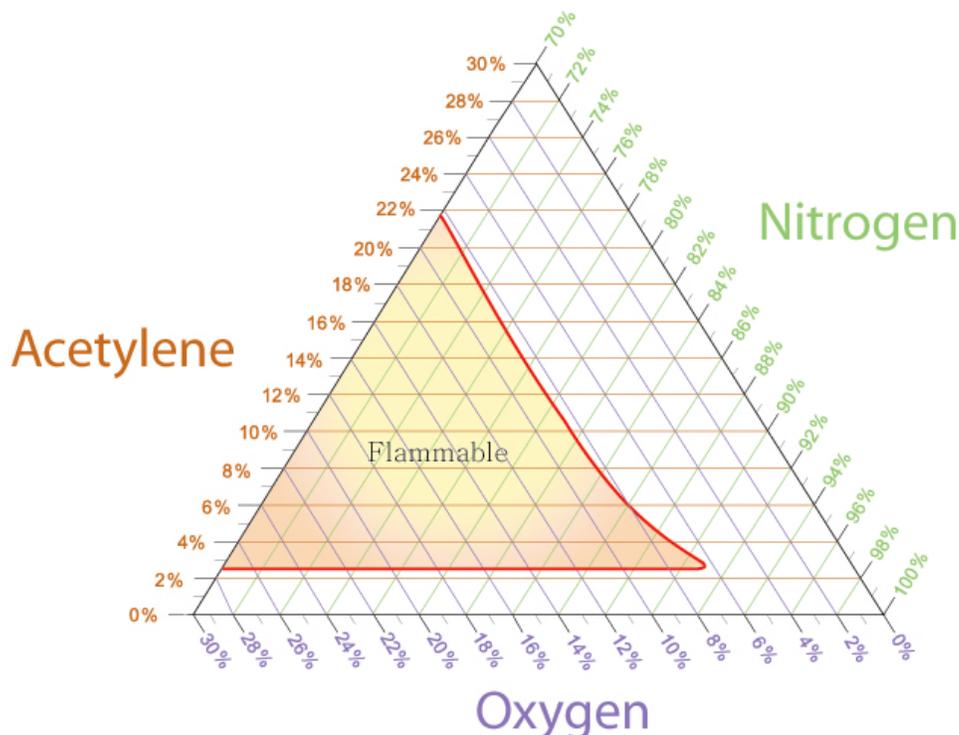
3. FIRE & EXPLOSION HAZARDS

Calcium carbide in a dry state is non-combustible. Dusts of calcium carbide are classified as nuisance dusts and do not constitute a fire or explosion hazard except in the presence of moisture or at temperatures in excess of 1,000°C. Calcium carbide will react with ANY form of moisture (e.g. rain, dew, perspiration, condensation, atmospheric humidity etc.) to generate highly flammable acetylene gas. As a consequence, every precaution should be taken to ensure that materials containing calcium carbide do not come into contact with any form of water and that water sources, open flames, and smoking are prohibited in areas where calcium carbide is used or stored.

A. Explosive Limits of Acetylene

Shown below is the ternary $C_2H_2-O_2-N_2$ system, highlighting the nitrogen rich corner.

Acetylene Flammability Chart



Data from Gliwitzky; Autogene Metallbearbeitung 33, 2-6 (1940)

It can be seen that explosive acetylene mixtures cannot be produced in atmospheres containing more than 91% nitrogen, irrespective of the actual oxygen or acetylene levels. Similarly, explosive mixtures cannot be formed at oxygen levels below 6% (with nitrogen levels above 50%) or at acetylene levels below 2.5%

As such, the safety of the desulfurization reagent handling system can be enhanced by controlling both the oxygen and acetylene levels present.

B. *Analysis of Gaseous Atmospheres for Acetylene*

By convention, low concentrations of combustible gases are measured in terms of their Lower Explosive Limit (or LEL). For acetylene in air mixtures the LEL is 2.5% acetylene gas (on a volume basis). At this concentration the acetylene level would be reported as 100% LEL. Similarly, absolute acetylene gas concentrations of 0.5%, 1%, and 2% (by volume) are reported as 20% LEL, 40% LEL, and 80% LEL respectively. It is important to remember that when measuring combustible gas concentrations, the analysis usually reports the concentrations as a percentage of the lower explosive limit, meaning that any concentration below 100% LEL is non-explosive.

The testing of gaseous atmospheres for acetylene is suggested whenever there is the potential for explosive mixtures of acetylene to collect in equipment. In closed conveying systems, it is also advisable to monitor the oxygen content. This is due to the importance of assuring that the oxygen content stays below the minimum concentration required for acetylene ignition – typically 6% at atmospheric pressures.

In order to limit the reaction with atmospheric moisture, all Carbide Industries desulfurization reagents are prepared and transported under a 100% nitrogen

atmosphere. The manufacturing process is continuously monitored by automated test instruments that detect both oxygen and acetylene.

For measuring acetylene levels in oxygen deprived atmospheres, such as in nitrogen-purged containers and storage bins or enclosed conveying equipment, Carbide Industries recommends using an infrared monitor, as these instruments do not require oxygen for accurate readings. For area monitoring or measurements where at least 20% oxygen is present, electrochemical based units may be used. Additionally, It is important that any gas atmosphere being sampled is at atmospheric pressure for the measurement to be correct.

For further information, please contact Carbide Industries LLC.

C. *Managing Spills and Leaks*

If the spill is dry and free from contaminants, sweep up the material immediately. Transfer to a dry, open top metal container in a covered, ventilated area, and consume in the process as soon as possible. The material should be clearly labeled as **calcium carbide - water reactive solid - acetylene hazard**. Personnel should not use compressed air to blow down or maneuver spills as this generates airborne dust. Spills of calcium carbide should be swept or shoveled during clean-up. The use of vacuum systems to address spills is discouraged, as there is the potential for developing an explosive atmosphere in such equipment.

If the spilled material is damp or contaminated, the area should be cordoned off to prevent unauthorized access. Contact with water should be minimized. The material should not be disturbed until the residual lime is free of calcium carbide. It is important that the area of the spill be isolated and unauthorized personnel kept out. The clean-up team should

have proper protective clothing including goggles, full face shields, and dust masks. The operation should be performed under close supervision with water-less fire extinguishing equipment maintained near-by.

Spills to the environment of ten pounds or greater require notification of the National Response Center (1-800-424-8802) as well as appropriate state and local authorities. The following information should be provided:

1. Name of reporter
2. Address of company represented by reporter
3. Phone number where reporter can be contacted
4. Date, time, and exact location of incident
5. Description of incident, quantity spilled
6. Extent of injuries, if any
7. Possible danger to public

The National Response Center will make the necessary follow-up to ensure proper handling and clean-up procedures were followed.

In the event of a large spill, Carbide Industries LLC should be contacted immediately. THE CARBIDE INDUSTRIES EMERGENCY RESPONSE NUMBER 502-775-4123 is answered 24 hours a day.

IF THERE IS ANY DOUBT ABOUT HOW TO PROCEED, Carbide Industries SHOULD BE CONTACTED.

D. *Fighting Calcium Carbide Fires*

If for any reason the calcium carbide spill contacts water (e.g., material spilled onto a wet floor) and the acetylene gas ignites, the first formed fire may die out due to a protective crust of carbide lime formed at the surface which prevents the further ingress of oxygen. Disturbance of the crust

may then be followed by re-ignition.

Once a fire begins, it can only continue to burn as long as acetylene is being produced. Calcium carbide fires are unusual because they can only be fought by PREVENTING WATER FROM CONTACTING THE CALCIUM CARBIDE. Provided that the fire is away from buildings and people, the easiest and safest course of action is to isolate the fire and allow it to continue to burn until acetylene is no longer produced. At this stage either the carbide is fully reacted or the moisture is consumed. This will prevent the accumulation of unburned acetylene, which could lead to re-ignition and resultant explosion.

If an acetylene fire must be put out, this should only be accomplished by eliminating the source of water. The spill should be contained by encircling with sandbags or similar inert material, such that running surface water is deflected from the spill. If rain is a problem, corrugated steel sheets can be used to cover the spill. The spill should then be covered with dry inert materials such as dry sand, dry chemical, or by using ABC type fire extinguishers. Apply the extinguishing media over the top of the burning material to blanket it. Once a crust has formed over the burning material, do not disturb or walk through it. Breaking the crust will allow air to get to the carbide and may re-ignite the acetylene. Once the fire is out, the spill should be left until cold and then cleaned up (once weather conditions permit). An ample supply of the fire protection and extinguishing equipment should be maintained and be conspicuously identified so that it is readily available and accessible in an emergency.

For large spills and fires, it is best to withdraw from the area and allow the fire to burn until the acetylene is no longer produced. The fire fighters should be equipped with full protective clothing and self-contained breathing apparatus. Never turn your back on the fire! Only authorized personnel, trained in fighting calcium carbide fires, should be allowed in the area. Isolate the fire area and deny entry to all others.

E. *Water Penetration of Containers*

If a single container becomes contaminated with water and develops hot spots, you may first notice a very distinct acetylene odor (garlic like). There may be bulging of the container, smoking or hissing from the gas escaping. Try to remove the container from the source of moisture if you can do so without risk. If it is raining, a plastic cover or tarpaulin should be placed loosely over the top of the container; to repel rain water but still allow accumulated acetylene to escape. Allow the container to remain in a dry isolated area but do not put indoors. Do not attempt to open the top hatch or jar the container in any way until it is cool, as this could cause the acetylene to explode. Once the container has cooled and there is no further indication of acetylene generation, the container should be purged with nitrogen or other inert gas. In case there is a spillage in the carbide storage area and fire results, *DO NOT ATTEMPT TO USE WATER OR FOAM TO EXTINGUISH THE FIRE*. These will only cause more acetylene to be generated.

4. *HEALTH & HYGIENE*

A. *Health Hazards*

Calcium carbide is neither toxic nor carcinogenic (it does not cause cancer). There are no long-term effects of exposure to calcium carbide, and there are no existing TLV (threshold limit values) for exposure to calcium carbide or calcium hydroxide. Although practically inert, fine particles of these materials are classified as nuisance dusts, and must be treated as such. The primary effects of bodily contact with calcium carbide are related to the heat of reaction and the calcium hydroxide produced. The heat of reaction is not enough to cause harm in most cases, but the residual material (hydrate) has

the irritating effects of a strong alkali.

Inhalation

Dusts are irritating to nose, throat and lungs. Acute overexposure can result in coughing and sneezing.

Eye Contact

Dusts are irritating to eyes. Acute overexposure can cause conjunctivitis and corneal abrasions.

Skin Contact

Superficial lime burns can result if moisture is present.

Ingestion

Superficial burns to mouth and esophagus

Chronic

No systemic effects are known. Prolonged and repeated exposure may cause dry, cracked skin; eyes may show irritation around lids.

B. *Personal Hygiene*

Standard safety glasses with side shields or goggles may be worn for handling calcium carbide. In addition, eye wash fountains should be available for emergency use in areas where calcium carbide dust might enter the eye.

In areas where employees may be exposed to powdered carbide, such as when changing lances or working around lines and dispensers, goggles are suggested. Additionally, full face shields as well as head and neck hoods are recommended when performing maintenance on pressure differential dispensing equipment.

Employees should be advised to wear long sleeve shirts to protect the arms and wrists. They should change work clothes often enough to avoid wearing clothing heavily contaminated with calcium carbide dust. Work clothes should be loosely buttoned at waist or neck, and in hot weather, the use of a scarf around the neck helps to avoid chafing between the collar (which may be contaminated with calcium carbide) and moist skin.

Standard cotton work gloves may be worn to protect the hands. Calcium carbide should not be allowed to get inside work gloves. Stockinette may be wrapped around hands and wrists to prevent burns in these areas. In hot weather or after unusually heavy dust contact, the employees should be encouraged to wash face, neck, hands, and forearms to remove accumulations of carbide.

C. *First Aid*

The effects of calcium carbide are limited to local action at the site of contact with a moist surface. Therefore, first aid treatment is directed toward removal of the irritant residual lime.

Inhalation

Remove to fresh air, get prompt medical attention. If heavy dusting is a problem, the use of a nuisance dust respirator may be necessary. Any disposable respirator meeting the NIOSH N-95 standard is recommended.

Eye Contact

Flush eyes immediately with clear water, being sure to wash out all the calcium carbide particles. Continue flushing for at least 15 minutes. For more effective cleaning, a saline solution is recommended to clean around the eyes. Refer case to a physician when the person has come in contact with large amounts of carbide or the irritation persists.

Skin Contact

All of the calcium carbide should be dusted or wiped off the skin before first aid is attempted. Wash the skin with vinegar to neutralize any adhering lime and then flush with copious amounts of water. Wash clothes thoroughly to remove any residual carbide before wearing again. If skin irritation results from the calcium carbide contact, cover with sterile dressing. A topical antibiotic ointment may be used if deemed necessary. No other drug should be used without medical authorization.

Ingestion

Dilute by drinking water or milk. Do not induce vomiting. Get prompt medical attention.

This information should be used as general guidelines until Carbide Industries LLC is contacted. Since each emergency is different, this information should not be used as a substitute for calling Carbide Industries LLC for expert technical information and assistance.

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