

“Achieving consensus on the science of food regulations and legislation to ensure the global availability of safe and wholesome food products for all consumers”

GHI Working Group Chemical Food Safety

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Possible health problems associated with the use of calcium carbide as a source of the ripening gas acetylene (GHI, June, 2022)

Acetylene

The acetylene that is produced does not present a serious toxicological problem. The lowest published lethal concentration for rats is 9 vol%. Dogs are less sensitive: 80 vol% acetylene in the air is necessary to produce a narcosis accompanied by an increased blood pressure and a decreased pulse frequency (stimulation of vasomotor and vagus centres). In humans, the inhalation of air containing 10 vol% acetylene has a slight intoxicating effect, marked intoxication occurs at 20 vol %, incoordination at 30 vol %, and unconsciousness within 5 min on exposure to 35 vol %. Inhaling 35 vol.% for 5 – 10 min or 10 vol% for 30 – 60 min is lethal. Symptoms of intoxication are excitement, coma, cyanosis, weak and irregular pulse, and memory failure (Ullman, 2002).

Note: Acetylene in mixtures with air is explosive.

Calcium carbide

Calcium carbide itself, however, is a toxicologically relevant substance (Hüseyin, 2007). Calcium carbide enters the human system mainly through its consumption of fruits quick-ripened with CaC_2 and by inhaling aerosols, powders, and gaseous products of CaC_2 residues on fruits (Okeke et al, 2022).

Direct consumption of acetylene gas released by calcium carbide can reduce oxygen supply to the brain and can cause prolonged hypoxia. Calcium carbide in general is alkaline in nature and can cause irritation in the mucosal tissue in the abdominal region. Arsenic and phosphorous found in industrial grade calcium carbide can cause dizziness, frequent thirst, irritation in mouth and nose, weakness, permanent skin damage difficulty in swallowing, vomiting, skin ulcer.

Accessory minerals of calcium carbide may include arsenic and/or phosphorous – esp. industrial grade qualities. If calcium carbide is contaminated with arsenide, a reaction with water will occur meaning that arsenic hydride (AsH_3) will be formed. This AsH_3 as well as similar organic derivatives are highly toxic. It is also known that PH_3 is also formed during this reaction which is also highly toxic.

Concentration ($\mu\text{g/g}$) of all analysed metals in calcium carbide samples (Saqib et al, 2019):

Metals	Without Air Treatment Mean \pm SD	With Air Treatment Mean \pm SD
^{52}Cr	60.9 \pm 1.9	52.5 \pm 2.1
^{55}Mn	92.4 \pm 6.7	86.8 \pm 2.8
^{56}Fe	540.9 \pm 69.6	396.4 \pm 32.1
^{59}Co	11.2 \pm 0.9	10.0 \pm 0.6
^{60}Ni	12.1 \pm 2.0	11.8 \pm 1.2
^{63}Cu	47.8 \pm 2.6	38.8 \pm 2.0
^{66}Zn	355.5 \pm 20.4	264.1 \pm 13.0
^{75}As	19.5 \pm 2.6	16.8 \pm 2.4
^{107}Ag	11.3 \pm 0.5	11.5 \pm 0.4
^{111}Cd	0.6 \pm 0.2	0.6 \pm 0.2
^{208}Pb	54.0 \pm 2.1	38.9 \pm 3.5

As early as in 1913 the problem of phosphine formation was mentioned in the literature. Calcium phosphide is a common impurity in calcium carbide, which may cause the resulting phosphine-contaminated acetylene to ignite spontaneously (Witherspoon, 1913):

...Phosphorus occurs as calcium phosphate, which is reduced at the temperature of the electric arc, and in the presence of carbon, to calcium phosphide, which when brought into contact with water, gives off phosphoretted hydrogen. This gas mixes with the acetylene, and when burners are lighted, causes a haze of phosphorus pentoxide, which is objectionable. So carefully, however, are the raw materials selected, that to-day, all commercial carbides are practically free from phosphorus, the average content of phosphine in acetylene being less 0.002 per cent, by volume....

These impurities – being gaseous compounds – might find its way into the fruits that are ripened with calcium carbide. It was published that e.g. As concentrations range from 30 – 70 ppm. However, it is possible to reduce the As concentrations in e.g. artificially ripened mangoes by dipping the fruits into Na_2CO_3 solutions (Chandel and Sharma, 2017).

Another publication showed that especially the workers are exposed to PH_3 (Shaeda et al, 2019). Direct exposure and also indirect exposure of persons who handle the contaminated products are relevant. The time-weighted average (TWA)¹ was determined as 0.033 ppm for workers. The evaluation of the occupational exposure limit² showed that there is a significant risk for workers.

¹ An occupational exposure limit is an upper limit of the acceptable concentration of a hazardous substance in workplace air. This limit is set by national authorities to protect occupational safety.

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Although banned in many countries, CaC_2 is still used in the Philippines because equally inexpensive and effective alternatives are lacking³.

Some selected countries that have banned the use of calcium carbide for artificial fruit ripening are mentioned here:

- **Pakistan** (<https://www.dawn.com/news/1369816>)
- **India**
(<https://agricultureandfoodsecurity.biomedcentral.com/articles/10.1186/s40066-016-0057-5>)
- **Bangladesh** (ibid)
- **Sri Lanka** (The Gazette of the Democratic Socialist Republic of Sri Lanka: The Food Act, No. 26 of 1980. 1990, The Ministry of Health: Colombo, Sri Lanka.)
- **Nepal** (The Nepal Food Regulation 2027, To prohibit the use of carbide gas for fruit ripening)

Production of calcium carbide

Calcium carbide is a basic chemical that is mainly used for production of fertilizers and in welding for production of acetylene. The synthesis is done in an endothermic reaction from highly purified calcium oxide and coke. Burnt lime is produced from limestone which is heated to 900 – 1,000 °C. Coke is formed during heating and dry distillation of coal under exclusion of air. In an electric resistance furnace, arc furnace, or carbide furnace the two components (calcium oxide, coke) are transformed into calcium carbide at temperatures between 1,800 and 2,300 °C. The product is a solid mixture with crystalline structure that contains 80 – 85 % calcium carbide. The remaining part comprises calcium oxide, calcium sulphide, calcium nitride or silicon carbide which contribute to the brownish colour. Pure calcium carbide is also crystalline.

Because of the high energy input, which is necessary for the production of calcium carbide, the production is very cost intensive and uneconomical. Therefore, calcium carbide is increasingly substituted by alternative substances.

Table 1: Specific energy requirement for production of 1,000 kg of calcium carbide.

Electric power consumption	8.3 GJ/t
Fuel and steam	6.1 GJ/t
Total energy consumption	14.4 GJ/t
Primary energy requirement	26.6 GJ/t

³ <https://www.seniorcareto.com/is-calcium-carbide-illegal/>

Occupational exposure standards

	Long-term Exposure (8 h TWA reference period) ppm (mg/m ³)			Short-term Exposure Limit (15 min reference period) Ppm (mg/m ³)		
	UK	USA	Germany	UK	USA	Germany
Calcium carbide			Not stated			
Acetylene			Simple asphyxiant			
Phosphine	0.3 (0.4)	0.3 (0.42)	0.1 (0.15)	1 (1)	1 (1.4)	- (-)
Arsine	0.05 (0.2)	0.05 (0.16)	0.05 (0.2)	- (-)	- (-)	- (-)
Hydrogen sulphide	10 (14)	10 (14)	10 (15)	15 (21)	15 (21)	- (-)
Ammonia	25 (18)	25 (17)	50 (35)	35 (27)	35 (24)	- (-)
Calcium hydroxide	- (5)					

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