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FLAMMABLE AND TOXIC MATERIALS WHICH ARE NOT ALLOWED TO GET IN CONTACT WITH WATER - A CALCIUM CARBIDE CASE

Abstract: *The paper presents materials which in contact with water emit flammable and toxic gases. Their classification according ADR and identification according NFPA 704 standards are presented. The physical-chemical, toxic, flammable and reactive properties of calcium carbide are shown. Also, first aid and fire fighting measures are given. Regular handling of flammable and toxic materials is conditioned by the knowledge of their properties. Regular handling reduces the risk of chemical accident followed by a fire and explosion.*

Key words: dangerous material, water, toxicity, fire, explosion.

INTRODUCTION

Production and consumption of hazardous materials is continuously increasing. A large number of organic and inorganic chemical compounds are produced and used in many industries. Many chemical compounds, particularly those in concentrated form, can be dangerous to people. People, who come in contact with chemical substances, often know little or nothing about the hazardous properties of substances and their influence on the human body. This is confirmed by many accidents of dangerous substances, various acute and chronic diseases, disabilities and even deaths. The potential risks of adverse effects of hazardous materials threaten the wider environment.

The world's attention has been focused to potential risks that hazardous materials are carrying. International Programme on Chemical Safety (IPCS) is constantly improving [1]. The main elements of Programme are: evaluation of chemical risks to human health (preparation and publication of chemicals assessments, development of scientific methods for chemicals assessment, evaluating the safety of food components); poisons information, prevention and management; chemicals incidents and emergencies.

Hazardous materials are divided into nine classes on the basis of the specific chemical characteristics which are producing the risk [2]:

- Class 1 - Explosive substances and articles (1.1 - 1.6);
- Class 2 - Gases:
  Class 2.1. - Flammable gas,
  Class 2.2. - Non-flammable, non-toxic gas,
  Class 2.2. - Toxic gas;
- Class 3 - Flammable liquids;
- Class 4 - Flammable solids:
  Class 4.1 - Flammable solids, self reactive substances and solid desensitized explosives,
  Class 4.2 - Substances liable to spontaneous combustion,
  Class 4.3 - Substances which, in contact with water, emit flammable gases;
- Class 5 - Oxidising substances:
  Class 5.1 - Oxidizing substances,
  Class 5.2 - Organic peroxides;
- Class 6 - Toxic substances:
  Class 6.1 - Toxic substances,
  Class 6.2 - Infectious substances;
- Class 7 - Radioactive substances;
- Class 8 - Corrosive substances;
- Class 9 - Miscellaneous dangerous substances and articles.

In international classification of hazardous materials there is class of materials which are not allowed to get in touch with water. Solid substances that emit a flammable gas when wet or react violently with water emit flammable gases can form explosive mixature with oxygen from the surrounding air or other oxidizing substances.

All chemicals that react violently with water or in contact with water liberate toxic gas are included in the list of substances covered by the majority of the international legislation on major hazards. The toxicity and the effects of water reactive materials on humans and on the environment are highly variable, depending not only on their properties, but also on the properties of their products on reaction with water or the atmosphere or the substrate. This category includes a large number of chemicals that are used widely in the process industries.

Knowledge of the reactivity of any substance with water is especially important when water is present in the spill area or a fire takes place and firefighters do not wish to make the situation worse by applying water to the flames or chemicals.

MATERIALS WHICH REACT WITH WATER

There are many water reactive chemicals of significance in major hazards. The main ones have

been categorized as follows: inorganic acid halides (such as POX_3, SOX_2, SO_2X_2); organic halides (such as CH_3COX, CH_2COX); sulphonic acids (such as HSO_3X); halides of non-metals (mainly phosphorus-halogen, silicon-halogen and boron-halogen compounds such as PX_3, PX_5, SX_2, SiX_4); a number of silanes (such as HX_3Si, CH_3X_3Si); non-metal oxides, such SO_3 and oleum (mainly sulphur and phosphorus oxides); anhydrous metal halides (such as AlX_3, TiX_4, ZrX_4, SnX_4); radioactive materials (such as UF_6) [3].

Many materials violently react (burst, explode or ignite) in contact with water. Two categories of these materials exist, as follows:

- Materials which react with water releasing the heat;
- Materials which in contact with water, decompose in flammable gases that are prone to form explosive mixtures with the surrounding air.

Some of the most basic types of exothermic reactions occur when certain materials are dissolved in water.

Such substances have what is called a positive heat of solution. They do not transform to a different material, but simply generate heat while mixing. Some examples are sodium hydroxide (also called caustic soda) and sulfuric acid, which generates considerable heat to the point of causing some degree of "violence" when concentrated or pure materials are spilled into water.

An example is quicklime (calcium oxide - CaO) which exothermically reacts with water while developing a high temperature, as follows:

$$CaO + H_2O = Ca(OH)_2 + Q \quad (1)$$

Because of vigorous reaction of quicklime with water, quicklime causes severe irritation when inhaled or placed in contact with moist skin or eyes. Although quicklime is not considered a fire hazard, its reaction with water can release enough heat to ignite combustible materials.

Other materials may ignite, evolve flammable gases, or otherwise react violently when in contact with water.

Materials which in contact with water, decompose in flammable gases that are prone to form explosive mixtures with the surrounding air. This group of materials include alkali metals (Na, K, Li), carbides of calcium and alkali metals, alkali metal chlorides, etc. When these compounds interact with water, they then create flammable gases that are lit at the expense of the heat released during a chemical reaction.

Elementary sodium reacts strongly with water, according to the following reaction mechanism:

$$2Na + 2H_2O = 2NaOH + H_2 + Q \quad (2)$$

A colorless solution is formed, consisting of strongly alkalic sodium hydroxide (caustic soda) and hydrogen gas. Sodium metal is heated and may ignite and burn with a characteristic orange flame. Hydrogen gas released during the burning process reacts strongly with oxygen in the air. A number of sodium compounds do not react as strongly with water, but are strongly water soluble.

Potassium reacts rapidly and intensely with water, forming a colorless basic potassium hydroxide solution and hydrogen gas, according to the following reaction mechanism:

$$2K + 2H_2O = 2KOH + H_2 + Q \quad (3)$$

This is an exothermal reaction and potassium is heated to such an extent that it burns a purple flame. Additionally, hydrogen released during the reaction strongly reacts with oxygen and ignites. Potassium reacts with water more slowly than rubidium, but it reacts with water more rapidly than sodium.

CLASSIFICATION OF MATERIALS WHICH IN CONTACT WITH WATER EMIT FLAMMABLE AND TOXIC GASES

Given the fact that there are many hazardous materials, their classificaton has been made in the world. The classification was done according to analogous properties of hazardous materials which enable the use of identical protection measures when handling certain classes.

According ADR [2], materials which in contact with water emit flammable and toxic gases are classified into class 4.3. of dangerous substances. Those substances are classified, as follows:

- **W -** substances which, in contact with water, emit flammable gases, without subsidiary risk, and articles containing such substances:
  W1 - liquid,
  W2 - solid,
  W3 - articles;
- **WF1 -** substances which, in contact with water, emit flammable gases, liquid, flammable;
- **WF1 -** substances which, in contact with water, emit flammable gases, solid, flammable;
- **WS -** substances which, in contact with water, emit flammable gases, solid, self-heating;
- **WO -** substances which, in contact with water, emit flammable gases, oxidizing, solid;
- **WT -** substances which, in contact with water, emit flammable gases, toxic:
  WT1 - liquid,
  WT2 - solid;
- **WC -** substances which, in contact with water, emit flammable gases, corrosive:
  WC1 - liquid,
  WC2 - solid;
- **WFC -** substances which, in contact with water, emit flammable gases, flammable, corrosive.

IDENTIFICATION OF WATER REACTIVE MATERIALS

Water reactive chemicals are generally aggressive materials with complicated properties. The hazardous nature of these substances is recognized in various items of legislation relating to industrial safety. Under the Seveso II EU Directive, all substances that attract the risk phrases R14 "reacts violently with water" (including R14/15 "reacts violently with water liberating highly flammable gases") or R29 "in contact with water, liberates toxic gas" are described as major hazards and are included in the list of chemicals [4].

According to ADR, UN hazard warning diamond of materials which react with water is shown in Figure 1 [2].

Figure 1. *UN hazard warning diamond*

NFPA 704 [5] presents a system to simplify determining the degree of health, flammability and instability hazards of chemical materials. The objectives of the system are: to provide an appropriate signal or alert and on-the-spot information to safeguard the lives of emergency response personnel (e.g., fire fighters, HAZMAT responders); to assist in planning effective fire and emergency control operations, including clean up; to assist all designated personnel, engineers, plant and safety personnel in evaluating hazards.

The NFPA 704 ratings are displayed in markings that are commonly referred to as the NFPA hazard diamond (Figure 2).

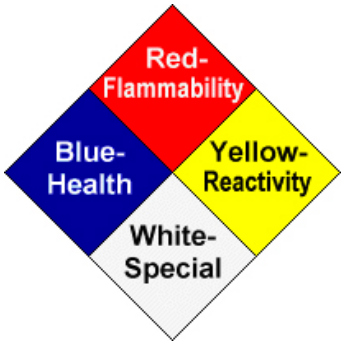

Figure 2. *NFPA hazard diamond*

The hazard diamond comprises four sections. Each section of the diamond contains a number from 0 (minimal hazard) to 4 (severe hazard) that indicates the relative degree of risk presented by the material.

The red section indicates flammability, or the susceptibility of a material to burning:

- A "0" rating indicates a non-combustible material, or a material that will not burn, such as water;
- A "1" rating indicates that a material must be pre-heated before it will ignite. The flash point or the lowest temperature at which a liquid produces sufficient vapor to form an ignitable mixture with air near the liquid's surface, of a liquid rated "1" is over 93°C;
- A "2" rating indicates that the material must be heated or exposed to relatively high ambient temperature before it will ignite. The flash point of a liquid rated "2" is between 38°C and 93°C;
- A material rated "3" is a liquid or solid that can ignite regardless of ambient temperature. The flash point of a liquid or solid rated "3" is between 23°C and 38°C;
- A material rated "4" is a material that will vaporize at normal temperatures and atmospheric pressure or that will readily disperse in air and burn easily. The flash point of a material rated "4" is below 23°C.

The blue section conveys information on health hazards to people exposed to the material:

- A "0" rating indicates no hazard other than that of a combustible material, such as peanut or vegetable oil;
- A "1" rating indicates potential irritation or minor injury if not treated;
- A "2" indicates temporary incapacity or potential injury. Exposure requires medical treatment;
- A "3" rating indicates that serious temporary or residual injury may occur even with medical treatment;
- A material rated "4" may cause death or major residual injury even with medical treatment.

The yellow section indicates chemical reactivity or stability:

- A material rated "0" is normally stable even when exposed to fire and does not react with water;
- A material rated "1" is normally stable but becomes unstable at high temperature and pressure and will react with water;
- A material rated "2" is normally unstable, will explode when mixed with water, or will undergo violent chemical reactions under elevated temperature and pressure, but will not detonate;
- A material rated "3" may detonate or explode when exposed to an initiating force or when heated, and reacts explosively with water;
- A material rated "4" detonates or explodes readily at normal temperature and pressure.

The white section indicates required protective equipment and other special considerations:

- "W" denotes materials that react with water;
- "OX" denotes materials with oxidizing properties.

These materials may decompose to yield oxygen and may cause fire when exposed to combustible materials.

A CALCIUM CARBIDE CASE

Pure calcium carbide is a colorless solid with a characteristic garlic-like odour. The pure material is colorless, but most samples have a color ranging from black to grayish-white. Its main use industrially is in the production of acetylene and calcium cyanamid [6].

Physical and chemical properties

The most important physical and chemical properties of calcium carbide are shown in Table 1.

Table 1. *Properties of calcium carbide*

Property	Value
Chemical formula	CaC_2
Molecular weight	64.1 (g/mol)
Melting point	1700÷2300 (°C)
Density	2.22 (g/cm^3)
Vapour density (air = 1)	2.2

Chemical dangers

Calcium carbide decomposes violently on contact with moisture and water producing highly flammable and explosive acetylene gas and corrosive calcium hydroxide solution, as follows:

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2 + Q \qquad (4)$$

Even very small amounts of water will react with calcium carbide developing sufficient heat to make the acetylene gas ignite spontaneously. Simultaneously, very small amounts of poisonous phosphine and hydrogen sulphide gas are set free.

Calcium carbide is a reducing agent. It may react vigorously with oxidizing materials. The powdered mixture of the acetylide and iron oxide and iron chloride burns violently upon ignition, producing molten iron. Calcium carbide incandesces with chlorine, bromine, or iodine at 245, 350, or 305°C, respectively. The carbide burns incandescently when mixed and heated with lead difluoride, magnesium, hydrogen chloride, and tin (II) chlorid. Interaction of calcium carbide with methanol to give calcium methoxide is vigorous, but subject to an induction period of variable length. Once reaction starts, evolution of acetylene gas is very rapid. Mixing calcium carbide with silver nitrate solutions forms silver acetylide, a highly sensitive explosive. Copper salt solutions would behave similarly. The mixture of calcium carbide and sodium peroxide is explosive, as is calcium carbide and perchloryl fluoride as gases at 100-300°C.

Calcium carbide identification

Identification of the chemical substance can be made based on relevant numbers. Identification numbers of calcium carbide are shown in Table 2 [1,2,7,8].

According to the standard NFPA 704 hazard diamond of calcium carbide is shown in Figure 3 [5].

Table 2. *Identification numbers of calcium carbide*

CAS number	75-20-7
RTECS	EV9400000
UN number	1402
EINECS	200-848-3
EC	006-004-00-9
Hazard class	4.3
Kemler number	X423

Figure 3. *Calcium carbide hazard diamond*

A "3" health rating indicates that exposure of calcium carbide may result in serious temporary or residual injury, even with medical treatment. A "3" flammability rating indicates that calcium carbide is material which can ignite regardless of ambient temperature. A calcium carbide reactivity rated with "2" means that it is normally unstable, will explode when mixed with water, or will undergo violent chemical reactions under elevated temperature and pressure, but will not detonate. "W" denotes calcium carbide as material that reacts with water or with it forms explosive mixture. Fire extinguishing of this material should not be used with water.

According to ADR hazard symbols of calcium carbide are shown in Figure 4 [2].

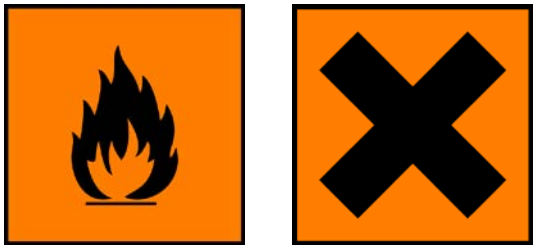

Figure 4. *Hazard simbols of calcium carbide*

Risk phrases of calcium carbide are:

- R15: Contact with water liberates extremely flammable gases.
- R37/38: Irritating to respiratory system and skin.
- R41: Risk of serious damage to eyes.

Safety phrases of calcium carbide are:

- S2: Keep out of the reach of children.
- S8: Keep container dry.
- S24: Avoid contact with skin.
- S26: In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
- S39: Wear eye/face protection.
- S43A: In case of fire, use dry chemical (never use water).

Toxicity

Toxicity of calcium carbide and its decomposition products during the chemical reaction with water are shown in Table 3 [6].

Table 3. *Toxity of calcium carbide and its products*

Chemical name	Chemical formula	Max allowable concetration, (mg/m^3)	Degree of health hazard
Calcium carbide	CaC_2	-	3
Acetylene	C_2H_2	2662	1
Calcium hydroxide	$Ca(OH)_2$	5	2

Calcium carbide in contact with eyes causes its severe burns. It may cause blindness and opacity and scarring. In contact with skin it causes irritation and possible burns, especially if the skin is wet or moist. When in contact with moist skin, caustic lime is formed, which can lead to ulceration and scarring. If ingested, it causes gastrointestinal tract burns. During inhalation calcium carbide may cause severe irritation of the upper respiratory tract with pain, burns, and inflammation. It can produce delayed pulmonary edema. During chronic exposure repeated inhalation may cause chronic bronchitis.

Acetylene may cause central nervous system depression with nausea, headache, dizziness, vomiting, and in coordination or difficult breathing. It may cause skin and eye irritation.

Calcium hydroxide is harmful if swallowed or inhaled**.** It is gastric irritant. Ingestion may be followed by severe pain, vomiting, diarrhea, and collapse. Calcium hydroxide causes irritation of the respiratory tract. Symptoms may include coughing, shortness of breath. It can cause chemical bronchitis. In contact with skin and eyes it is corrosive. It causes burns and blistering of skin. It may produce severe irritation and eyes pain and induce ulcerations of the corneal epithelium.

Flammability and explosiveness

Dry calcium carbide is not inflammable. Contact with humidity and water liberates acetylene gas which is highly inflammable and can form explosive mixtures with air.

Acetylene requires very low ignition energy. Its ignition temperature is 305°C. Acetylene explosion limits in the air are 1.5÷82vol%. The gas is lighter than air. Its vapor density is 0.9.

Acetylene may cause flash fire. Its hazardous combustion products are carbon monoxide and carbon dioxide.

Calcium carbide is also flammable in presence of acids. Contact with acid or acid fumes evolves heat and flammable vapors. Some metallic oxides may occur as combustion products of calcium carbide.

Stability and reactivity

Calcium carbide is stable under normal temperatures and pressures. It reacts vigorously with water to form highly flammable acetylene gas. Lime may also be formed raising the pH of the solution and causing a white precipitate.

It extremely reacts with acids, highly reacts with alkalis and reacts with oxidizing agents.

This material is incompatible with water, moist air or moisture from any source, acids (hydrogen chloride, stannous chloride), oxidizers (sodium peroxide, potassium hydroxide), lead fluoride, magnesium, selenium, sulfur, chlorine and silver nitrate.

Impact on the environment

Calcium carbide can be found into rivers, lakes, seas, etc. By the reaction with water, the decomposition products of calcium carbide, acetylene and calcium hydroxide are harmful to fish.

Acetylene in quantity of 200 mg/l is lethal for trout fry, and of 400 mg/l is lethal for gold fish within 24 -48 hours. Calcium hydroxide in quantity of 20 mg/l is harmful to fish and 70 mg/l is lethal after 26 minutes

Calcium carbide may affect acidity (pH-factor) in water with risk of harmful effects to aquatic organisms.

First aid measures

In case of inhalation it is necessary to evacuate the victim to a safe, well ventilated area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.

In a case of ingestion do not induce vomiting. If victim is conscious and alert, give 2-4 cupfuls of milk or water. Never give anything by mouth to an unconscious person. Get medical aid immediately.

If there is contact with eyes, it is necessary immediately to flush eyes with plenty of water for at least 15 minutes, occasionally lifting the upper and lower eyelids. Get medical aid immediately.

After the contact with skin, wash immediately with plenty of water. Gently and thoroughly wash the contaminated skin with running water and non-abrasive

soap. Be particularly careful to clean folds, crevices, creases and groin. Cover the irritated skin with an emollient. If irritation persists, seek medical attention. Wash contaminated clothing before reusing

Fire fighting measures

Fire of calcium carbide shall not be extinguished with water, foam or halogenated extinguishing agents. Carbon dioxide may be ineffective.

It is necessary to use class D extinguisher or smothers with soda ash, dry sand, dry clay, dry powdered sodium chloride or dry graphite.

Small fires will be extinguished with dry chemical powder, lime or dry sand. In the case of large fires should withdraw from area and let fire burn.

Firefighters should wear full fire fighting turn-out gear and respiratory protection.

Accidental release measures

In the case of small spill should use the appropriate tools to put the spilled solid in convenient waste disposal containers. They must not be tightly closed. It should protect the spilled material from contact with water and do not allow it to enter water courses.

In case of large spill should not touch spilled material. It is necessary bulk material cover with dry earth, sand or other non-combustible material and to eliminate all ignition sources. It must be prevented his entry into sewers, basements or confined areas.

CONCLUSION

Knowledge of potential risks and dangers of hazardous materials is crucial for raising awareness of the necessity of taking certain actions for avoiding the risk of injury, or at least for reducing dangerous and harmful effects to the minimum.The aim of this paper was to highlight the importance of identifying and understanding the nature of hazardous materials.

Based on the categories and the degree of dangerousness, the transportation, storage, ventilation, operating the materials, cleaning of the tanks and equipment containing material, organizational measures of protection, personal protective equipment, procedures in case of emergency at work and in accidents in transport, fire and explosion protection, first aid, decontamination and environmental protection are determined.

Proper handling of a hazardous material reduces the risk of chemical accidents, fires and explosions. Also, knowledge of the nature of hazardous material is necessary for an adequate response in accident situations.

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BIOGRAPHY

Dušica Pesić was born in Pirot, Serbia, in 1961. She received the diploma in occupational safety engineering and the Ph.D. degree in fire protection from the University of Nis, Faculty of Occupational Safety. Her main areas of research include fire protection, environmental protection, etc.
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ZAPALJIVI I TOKSIČNI MATERIJALI KOJI NE SMEJU DOĆI U KONTAKT SA VODOM – PRIMER KALCIJUM KARBID

Dušica Pešić, Milan Blagojević, Miloš Milojević, Suad Suljović

Rezime: U radu su analizirani materijali koji u kontaktu sa vodom emituju zapaljive i toksične gasove. Prikazana je njihova klasifikacija prema ADR -u i identifikacija prema standardu NFPA 704. Analizirane su fizičko-hemijske, toksične, zapaljive i reaktivne osobine kalcijum karbida. Date su mere prve pomoći i procedure gašenja požara ovog materijala. Pravilno rukovanje toksičnim i zapaljivim materijalima je uslovljeno poznavanjem njihovih osobina. Pravilno rukovanje smanjuje rizik od nastanka hemijskih akcidenata praćenih požarom i eksplozijom.

Ključne reči: opasna materija, voda, toksičnost, požar, eksplozija.