

Safety in Handling of Bleaching Chemicals in Pulp Mills

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ABSTRACT

Properties, safe handling, possible hazards and precautions in the use of bleaching chemicals such as chlorine, hypochlorite, chlorine dioxide, oxygen and hydrogen peroxide have been described.

With increasing demand in the brightness and whiteness of cultural papers, the bleaching operation has become very important both for large as well as small paper mills. Nearly all chemicals used in bleaching are either very corrosive such as acids, caustic soda or explosive such as chlorine dioxide, hydrogen peroxide etc. Most of them are toxic and chlorine as we know is used universally to treat and disinfect water. With these characteristics, the safety in handling of these chemicals during various stages of manufacture, storage, transport, use and disposal becomes of paramount importance. In this paper an attempt has been made to summarise the available information on safe handling of some of the commonly used chemicals in bleaching of pulps both in plants as well as laboratory experiments and trials.

The hazards caused by these chemicals can be due to their presence in air due to leaks in process, piping or transfer operation. Water may be contaminated by their presence or there may be direct contact with the solid or liquid material due to spillage. Vapours are most hazardous as it involves contact with eyes, skin and inhalation of the gas. Ingestion of liquids while pipetting the solutions or by accident is a distinct possibility. Solids harm mostly due to body contact. The worst effect is suffered by materials of construction which are slowly consumed without notice and in the event of failure lead to accidents and become a major hazard to human lives and property.

The safety aspect involves mainly a thorough knowledge of the properties and behaviour of these chemicals by users and concerned persons, an awareness of the possible hazards and a training to cope up with them during incidents. Regular maintenance and check-up of equipments, familiarity with first aids and the methods to minimize, stop or handle leaks as well as instrumental monitoring of environment in and around plant, go a long way to make it safe to work with such chemicals.

Characteristics peculiar to these chemicals have been detailed in the following whereas the pertinent physical properties, materials of construction and toxicity limits have been given in Table 1, 2 and 3.

Table - 1
PHYSICAL PROPERTIES OF
BLEACH CHEMICALS

No		Melting Point °C	Boiling Point °C	Specific gravity
1	Chlorine gas	-100	-35	2.5 times heavier than air
2	Chlorine dioxide	-59	11	2.40
3	Hydrogen peroxide 98%	-2.1	148.7	1.39
4	Sodium hydroxide solid	318	1390	2.13
5	Sodium hydroxide -50% Aq. solution)	5	148	—

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Table - 2
MATERIALS OF CONSTRUCTION FOR
BLEACH CHEMICALS

No.		
1	Chlorine-dry	Carbon steel
2	Chlorine-wet and sodium hypochlorite	Mild steel lined with PVC, Polyester, epoxy, PTFE, glass, lead, S.S., copper, Hastelloy, Karbate stoneware, Titanium, Tantalum, zirconium.
3	Chlorine dioxide	Acid proof bricklining, UPVC, lead, glass, FRP., high molybdenum S.S. Porcelain, S.S. with anodic protection, Titanium, Hastelloy C.
4	Oxygen	Carbon steel, S.S. -304
5	Hydrogen peroxide	Aluminium and its alloys, S.S., Polyethylene polyesters, PTFE
6	Sodium Hydroxide	Cast iron, Mild steel, S. S., PVC, epoxylining.

Table - 3
TOXICITY OF BLEACH CHEMICALS^{11,12}

No.	Chemical	Toxicity limits*	ppm-concentration in air to cause		
			Irritation-harm-fatal		
1	Chlorine gas	TLV-1 ppm	3	60	1000
2	Sodium Hypo-chlorite	LC 50 - 8.9 g/kg	—	—	—
3	Chlorine-dioxide	TLV - 1 ppm	15	50	500
4	Hydrogen peroxide 90%	TLV - 1 ppm	—	—	—
5	Sodium Hydroxide	LC ₅₀ — 0.5 g/kg	—	—	—

*1. TLV value is the concentration in air that can be breathed for five working days without adverse effect.

2. LC₅₀ Means that about 50% fish will die under the conditions of this concentration.

Handling of Chlorine and Hypochlorite :

Chlorine the most commonly used bleach chemical is a greenish yellow gas with a characteristic irritating odour. It is non explosive and non inflammable but is capable of supporting combustion of hydrogen and hydrocarbons. Liquified and compressed gas is stored in cylinders for transport and use. One volume of liquid when vaporised gives 460 volumes of gas. Expansion chambers must be provided at the end of long pipe lines in its transport. Shut off valves at intermediate points are good means to isolate leaks in a long line¹⁻³.

Chlorine containers should be stored in a shade and prevented from exposure to water, steam, sun, heat or direct flame. It is advisable to use a barometric leg or vacuum breaking to avoid back suction of water or reaction medium into the cylinder while passing chlorine.

Titanium is very good material of construction for wet chlorine but it reacts with dry chlorine even at ambient temperature. Carbon steel or copper pipes should be preferred over rubber hoses in transferring chlorine.

Leakage of chlorine can be tested with ammonia swab as it gives a thick white cloud of ammonium chloride. The gas can be emptied by absorbing in 8 N caustic soda solution or alternatively in soda ash or lime solution.

The presence of chlorine in atmosphere can be detected by the odour at 3-5 ppm. Though 3 ppm may be tolerated for a few minutes the breathing is difficult with 5 ppm. Concentration of 15 ppm causes coughing 40-60 ppm becomes dangerous in about 30 minutes³⁻⁵.

Extensive chlorine concentration in air causes restlessness, coughing and copious salivation. Lung tissues may be attacked resulting in pulmonary odema on prolonged exposure.

Skin and eye should be thoroughly washed with water on contact with liquid or gas and no ointment should be used for 24 hours.

Sodium hypochlorite is more easily handled as an aqueous solution. It is irritating to skin and eye and

is harmful if swallowed. On heating it decomposes giving chlorine and so in case of fire it poses all the hazards of chlorine.

Chlorine dioxide and Sodium chlorite :

Chlorine dioxide is explosive in the pure state and cannot be transported like chlorine in the liquid form. It is prepared at the pulp mill. Sodium chlorite which generates chlorine dioxide under acidic conditions is in a convenient solid form for handling but is much more expensive and less efficient in terms of available chlorine. Their actions are, however, similar.

Chlorine dioxide is an efficient bleaching agent, selective for lignin degradation and with least attack on carbohydrates. But it is a toxic and corrosive gas and requires high temperatures (60–80°C) for bleaching action.

In handling chlorine dioxide the temperatures must be controlled accurately. In presence of water it decomposes giving chloride and chlorate by U.V. irradiation or heat. Live steam should not come into contact with the flow of gas in the pipe line. Closed systems and continuous operations are preferable to batch bleaching. The gas concentration can be measured by U.V. absorption at 436 nm⁶⁻⁸.

Polymeric lining in steel shells though very useful in storage and piping have limitations when temperatures exceed 50°C, for this gas. Stainless steel can be attacked heavily by ClO₂. Titanium and hastelloy have good resistance.

Continuous exposure to gas even in dilute concentration produces headache, stomach trouble and irritation to mucous membrane. Gas concentration of 20% and above by volume, if contaminated by organic impurities like oil or dry wood, may cause violent decomposition. The ClO radical is found to be responsible for such violent reactions.

Oxygen and Hydrogen peroxide :

Fires and explosions are a potential source of trouble in oxygen bleaching. When pulp consistency is very high (40%), pulp can be ignited by a heating filament in an oxygen atmosphere. The reaction products during bleaching particularly carbon mono oxide and turpentine can give explosive mixtures with

oxygen⁷. Reactors for oxygen bleaching should be so designed that any excess build up of pressure or temperature is quickly released. Special lubricants (oil free) should be used in valves and bearings.

Carbon steel is satisfactory with oxygen in alkaline medium but is corroded in acidic medium, S.S.—304 is, however, found satisfactory.

Hazards in the use of hydrogen peroxide increase with its concentration. It is available in concentrations of 60-90% (w/v) as aqueous solutions but concentrations up to 98% are commercially feasible. These are stable when stored in pure aluminium containers below 30°C. Rise in temperature and presence of ions such as zinc, ferric, cupric and chromic cause decomposition⁹⁻¹⁰. It is not flammable but the fires are flared by evolution of oxygen from it.

A concentration of H₂O₂ > 65%, if once ignited will burn rapidly. Most of the dry organic materials such as wood, straw, rags and clothings contain enough catalytic material to cause ignition with 90% H₂O₂. For storage, a temperature below 60°C is recommended.

Concentrated vapours of hydrogen peroxide cause burning of nose, throat and coughing, when inhaled. Prolonged exposure can produce swelling of the respiratory membranes and fluid accumulation in the lungs. Touch with the skin can cause blisters which, however, heal quickly. Ingestion of liquid may cause bleeding and severe distention of stomach¹¹.

Sodium Hydroxide

It is the most common chemical used in various stages of pulping, bleaching and analysis. It is not flammable but can produce flammable gases on contact with metals.

Skin contact of solid caustic or solution causes burns. Inhalation of dust may cause severe damage to body tissues. It destroys living tissues. Ingestion can cause severe and extensive scar formation, corrective surgery may be required to repair the damaged tissues. Even the waste containing alkali should be neutralized before discharge as it diminishes bacterial activity in the streams^{11,12}.

If solutions spill on the skin, the affected areas should be washed with water for 1–2 hours. If 5% NH₄Cl solution is on hand, a wash with it is useful.

Cast iron, steel and stainless steel are good materials to handle caustic solutions. Polyethylene, PVC and epoxy lining can be used for piping. It corrodes aluminium, tin, lead and zinc.

Effluent liquors from bleaching section

The process liquor streams from bleaching section are not mixed up with chemical recovery, particularly for chlorine based chemicals and are separately discharged after neutralization.

Lately, many studies have been done on the toxicity of these effluents. The most toxic stream has been found to be the one after the alkali extraction stage following chlorination. The LC₅₀ value for it has been found to be 0.5mg/L bringing it to the highly toxic group. The chlorination stage discharge ranks next in toxicity. The mixed and diluted liquor are far less toxic than fresh and undiluted ones. Nevertheless the chlorinated phenolic compounds responsible for toxicity in these liquors are slowly absorbed by the soil and organisms, and thus show long term toxic effects. The threshold concentration for these effects has been found to be about 10–20% of the LC₅₀ values for the bleach plant effluents^{13,14}.

It is necessary that these liquors are properly treated to remove coloured and precipitable impurities, neutralised and diluted before discharge to waste streams.

General Safety Considerations

The following measures should be taken as a routine to safeguard against possible hazards in handling these chemicals.

- (1) Periodic check-up and maintenance of the equipment involved in storage and handling. Containers, fittings and valves should be in good condition.
- (2) Plant equipment should be properly designed and appropriate material of construction should be used. Pipelines should be colour coded for identification.
- (3) Use of apron, gloves, goggles and rubber boots when necessary should be insisted upon. Other safety equipments such as gas masks should be readily available in good condition.

- (4) Persons working in the plant should be trained and kept well informed. A chart indicating the method of detecting leaks and simple measures to handle such leaks should be displayed at various points where such chemicals are being handled.
- (5) Hazardous chemicals should be stored separately and as far away as possible from the crowded areas.
- (6) Proper warning system should be installed to inform and clear the persons from the danger areas.
- (7) Environment in the plant should be instrumentally monitored to detect any leak of toxic gases.
- (8) Effluents should be properly treated.

It can be said that a complacent attitude arising out of familiarity and negligence of safety precautions are responsible for human failures. These should be eliminated to make these chemicals safe in handling.

Acknowledgement

Author is grateful to his colleagues for helpful discussions and to the institute authorities to enable him to write this article.

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