

SODIUM HYDROXIDE

50% SOLUTION

E.U. Classification:

C: corrosive



UN N°: 1824

MARPOL classification: D until 31/12/2006

Y from 01/01/2007

SEBC Classification: D (dissolver)



SODIUM HYDROXIDE 50% SOLUTION

PRACTICAL GUIDE

INFORMATION

DECISION-MAKING

RESPONSE

This document was drafted by *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) with financial support and technical guidance from ARKEMA.

The information contained within this guide is a result of *Cedre's* research and experience. *Cedre* cannot be held responsible for the consequences resulting from the use of this information.

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Translated by Sally Ferguson.

Purpose of this guide

As part of the research funded, ARKEMA and *Cedre* (the Centre of Documentation, Research and Experimentation on Accidental Water Pollution) have produced a series of response guides for chemical hazards. They can be used to assist in emergency response in the event of an incident involving a vessel carrying hazardous substances which may cause water pollution.

These guides are updates of the 61 "mini response guides" published by *Cedre* in the early 1990s.

These guides are designed to allow rapid access to the necessary initial information (see chapter entitled "First line emergency data"), in addition to providing relevant bibliographical sources to obtain further information.

They also contain the results of scenarios

relating to incidents in the Channel, the Mediterranean and in ports and rivers. These scenarios are only intended to provide response authorities with indications of what to do in an emergency. Each real incident should be analysed individually and the response authorities should not underestimate the importance of taking in-situ measurements (air, water, sediment and marine fauna) in order to determine exclusion areas.

These guides are intended primarily for specialists who know about the techniques to use in the event of an emergency in addition to the relevant operational response measures. The main concern is to mitigate the consequences of a spill, however we cannot afford to overlook responder safety and human toxicology.

To contact the duty engineer at *Cedre* (24/7)
Please call: + 33 (0)2 98 33 10 10

National toxicology surveillance system in the event of a major toxicological threat.

In France, a hotline is manned around the clock by Division 7 of the General Department of Health (SD7/DGS).

During opening hours please call:

Tel.: + 33 (0)1 40 56 47 95

Fax: + 33 (0)1 40 56 50 56

Outside normal working hours please call the relevant authority.

Poison Control Centres in France

Angers (Centre Hospitalier d'Angers) Tel.: + 33 (0)2 41 48 21 21

Bordeaux (Hôpital Pellegrin-Tripode) Tel.: + 33 (0)5 56 96 40 80

Grenoble (Hôpital Albert Michallon) Tel.: + 33 (0)4 76 76 56 46

Lille (Centre Hospitalier Régional Universitaire) Tel.: + 33 (0)8 25 81 28 22

Lyon (Hôpital Edouard Herriot) Tel.: + 33 (0)4 72 11 69 11

Marseille (Hôpital Salvator) Tel.: + 33 (0)4 91 75 25 25

Nancy (Hôpital Central) Tel.: + 33 (0)3 83 32 36 36

Paris (Hôpital Fernand Widal) Tel.: + 33 (0)1 40 05 48 48

Reims (Hôpital Maison Blanche) Tel.: + 33 (0)3 26 78 48 21

Rennes (Hôpital de Pontchaillou) Tel.: + 33 (0)2 99 59 22 22

Rouen (Hôpital Charles Nicolle) Tel.: + 33 (0)2 35 88 44 00

Strasbourg (Hôpitaux Universitaires) Tel.: + 33 (0)3 88 37 37 37

Toulouse (Hôpital de Purpan) Tel.: + 33 (0)5 61 77 74 47

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What you need to know about sodium hydroxide 50% solution

Definition

Pure sodium hydroxide, or caustic soda, is a white, translucent, highly hygroscopic solid. In solution, it is a highly soluble, colourless liquid, varying in viscosity according to the concentration. At sea, a spill of caustic soda will rapidly be diluted.

Uses

Soda is used in the artificial textile industry, oil refinery, soap making, the metal industry (stainless steel passivation) and in metal construction (glaze removal). It is also used in the manufacture of cellophane and many chemicals.

Risks

- Explosion: caustic soda is stable and non-combustible. However, contact between soda (especially in its anhydrous form) and water generates a major release of heat, enough to ignite flammable substances. Risks of fire and even explosion exist when sodium hydroxide comes into contact with many other products.

- Toxicity: sodium hydroxide solutions are highly corrosive. They attack certain organic materials (leather, fabric) and metals. The risks for humans and for the environment and are therefore due to the corrosive nature of caustic soda when in contact with this chemical (burning of tissue).

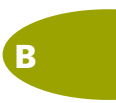
Projections are given off when large quantities of sodium hydroxide come into contact with water (or when water comes into contact with sodium hydroxide in a reservoir for instance).

Behaviour in the environment

When spilt into water, caustic soda completely dissolves and gives off heat. The risk incurred by the environment is due to hydroxyl ions (pH effect). The effect of caustic soda on aquatic organisms therefore depends on the buffering capacity of the ecosystem. This buffering capacity is very marked in the marine environment. A pH greater than 9 is harmful for aquatic life. The release of caustic soda into the aquatic environment produces a white trail making the pollutant visible (precipitation of magnesium hydroxide).

First line emergency data

- First aid information _____ **B1**
- ID card _____ **B2**
- Physical data _____ **B3**
- Flammability data _____ **B4**
- Toxicological data _____ **B5**
- Ecotoxicological data _____ **B6**
- Persistence in the environment _____ **B7**
- Classification _____ **B8**
- Particular risks _____ **B9**
- Transportation, handling, storage _____ **B10**



First aid information (ICSC, 2001)

Immediately remove all soiled or spotted clothes with suitable gloves.

Intoxication by inhalation (vapours)

- Remove the victim from the polluted area and them up into a half-sitting position.
- Apply artificial respiration if the person has stopped breathing and provide oxygen if breathing is difficult.
- Transfer the victim to hospital.

Skin contact

- Rinse the skin with clean water for 20 minutes until the product has been eliminated then apply a neutralising solution.
- Consult a doctor.

Eye contact

- Rinse the eyes with plenty of clean water for at least 30 minutes while keeping the eyelids open then apply a neutralising solution.
- Consult a doctor.

Intoxication by ingestion

- Do not induce vomiting.
- Rinse the mouth and lips with water if the person is conscious, then transfer to hospital urgently.

In the case of ingestion of a very small quantity of diluted solution with a pH of less than 11.5:

- Ensure that the person drinks 1 or 2 glasses of water (only if the person is conscious).
- Consult a doctor.

In the case of ingestion of a diluted solution with a pH greater than 11.5 or unknown:

- Transfer the victim to hospital without giving them anything to drink.
- Do not attempt to induce vomiting or to neutralise with acidic agents (e.g. vinegar or fruit juice).

Sodium hydroxide solution

Gross formula: NaOH

Synonyms

Caustic soda solution, sodium hydrate solution, white caustic solution, lye solution.

E.U. Classification

C: corrosive

R35: causes severe burns.

S26: in case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S37/39: Wear suitable gloves and eye/face protection.

S45: In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).

CAS n°: 1310-73-2

E.C. N° (EINECS): 215-185-5

Index n°: 011-002-00-6

Classification for transportation

UN N°: 1824

Class: 8

¹ Additional data and sources in annex 2

Physical data

Conversion factor in air at 20° C:	1 ppm = 1.63 mg/m ³ 1 mg/m ³ = 0.61 ppm 1 atm = 1.013.10 ⁵ Pa
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B3

Melting point	N/A
Boiling point:	142°C < T < 144°C
Critical temperature:	N/A
Relative density (water = 1)	1.52 at 20°C
Relative vapour density (air = 1)	N/A
Solubility in fresh water	completely soluble at 20°C precipitates as of 52%
Vapour pressure/tension	2 hPa (mbar) at 20°C
pH of a 50 % solution	14
Viscosity at 20°C	78 mPa.s
Freezing point	12°C for a 50% solution
Olfactory threshold in air	unknown
Diffusion coefficient in water	N/A
Diffusion coefficient in air	N/A
Henry's law constant	N/A

Flammability data

Explosive limits

Non-explosive product

Regression speed

Non-flammable product

Flash point

Non-flammable product

Self-ignition point

Non-flammable product

Dangerous products of decomposition (ARKEMA SDS, 2003)

Formation of flammable and explosive hydrogen by corrosion of metals

B4

Toxicological data

Acute human toxicity

(ARKEMA SDS 2003)

The acute toxicity of sodium hydroxide depends on its **physical state** (solid or in solution), on its **concentration** and on the **dose**.

- By ingestion: severe burns to the digestive tract, risk of perforation of the alimentary canal, state of shock.
- By skin contact: very corrosive for the skin, severe burns, severe lesions, scarring (sometimes retractile), dermatitis possible in the case of repeated contact.
- By eye contact: corrosive for the eyes, severe lesions possibly with lasting effects if the eyes are not rinsed immediately, harm to all the eye tissues, risk of sight loss.
- By inhalation: corrosive for respiratory tract.

Chronic human toxicity

(SIDS - OCDE, 2004)

Few studies have been conducted, as low concentrations of sodium hydroxide are neutralised by the acidity of the stomach.

Sodium hydroxide 50% solution however has no sensitising potential or mutagenicity.

B5

Ecotoxicological data (ECB PROJECT, 2005)

Acute ecotoxicity: data expressed in milligrams of pure sodium hydroxide per litre of water

Daphnia (<i>Ceriodaphnia dubia</i>)	LC ₅₀ (48h) = 40 mg/L (fresh water)
Fish (<i>Brachydanio rerio</i>)	55.6 mg/L < LC ₅₀ (96h) < 100 mg/L - pH: 7.9 to 8.1 (fresh water)
Fish (<i>Lucioperca lucioperca</i>)	Toxic concentration > 35 mg/L (fresh water)
Marine invertebrate (<i>Ophryotrocha diadema</i>)	33 mg/L < LC ₅₀ (48h) < 100 mg/L (seawater)

Chronic ecotoxicity: no data available.

PNEC (Predicted No-Effect Concentration): no PNEC was able to be calculated as the buffering capacity, the pH and its fluctuation are very specific to the ecosystem in question. To estimate the effect of a sodium hydroxide spill, the change in pH of the water must be calculated or measured.

Variation by one pH unit could affect flora and fauna (ECB PROJECT, 2005). The average pH of water can vary in seawater from 8 to 8.4 (stable pH) and in fresh water from 6 to 7.5.

Examples of pH in natural waters

Brest's estuary	Fos sur Mer	Fresh water
8	7.95	6 - 7.5

Persistence in the environment

The risk presented by caustic soda for the environment is due to hydroxyl ions (pH effect). The effect of caustic soda on aquatic organisms therefore depends on the buffering capacity of the aquatic or land-based ecosystem. **A pH greater than 9 is harmful for aquatic life.** The effect of these ions is naturally reduced by dilution, absorption of carbon dioxide from the air and, for fresh waters, by the natural variation in the pH of the water throughout the day and according to the season.

Risk for the environment

A high concentration of sodium hydroxide in the water will increase the alkalinity of the water, which can be harmful for aquatic life. In fresh waters, most algae are killed when the pH exceeds 8.5 and fish cannot tolerate a pH of over 8.4.

In seawater, a high pH can cause burns to the skin and gills, and fish die of suffocation.

Breakdown

Sodium hydroxide will be transformed into salts depending on the ions present in the environment.

Bioaccumulation

Sodium hydroxide is an inorganic substance which does not bioaccumulate along the food chain.

B7

Partition coefficient for organic carbon and water (K_{oc}): N/A

Partition coefficient for octanol and water (K_{ow}): N/A

Bioconcentration factor (BCF): N/A

Classification

IBC Code (IMO, 2001):

for a 15% solution and over

- hazards: S (Safety risk)
- ship type: 3
- tank type: 2G (integral gravity tank)
- tank vents: open
- controlled tank environment: no
- electrical equipment:
class I": NF (non-flammable)

- gauging: O (open type)
- vapour detection: no
- fire protection: no
- construction material (N8) : aluminium, zinc, galvanised steel and mercury should not be used for constructing tanks, piping, joints, accessories or other elements likely to come into contact with these products or vapours.

B8

SEBC Classification: D (dissolver)

MARPOL classification: D (definition in annex 4) until 31/12/2006
Y (definition in annex 4b) from 01/01/2007

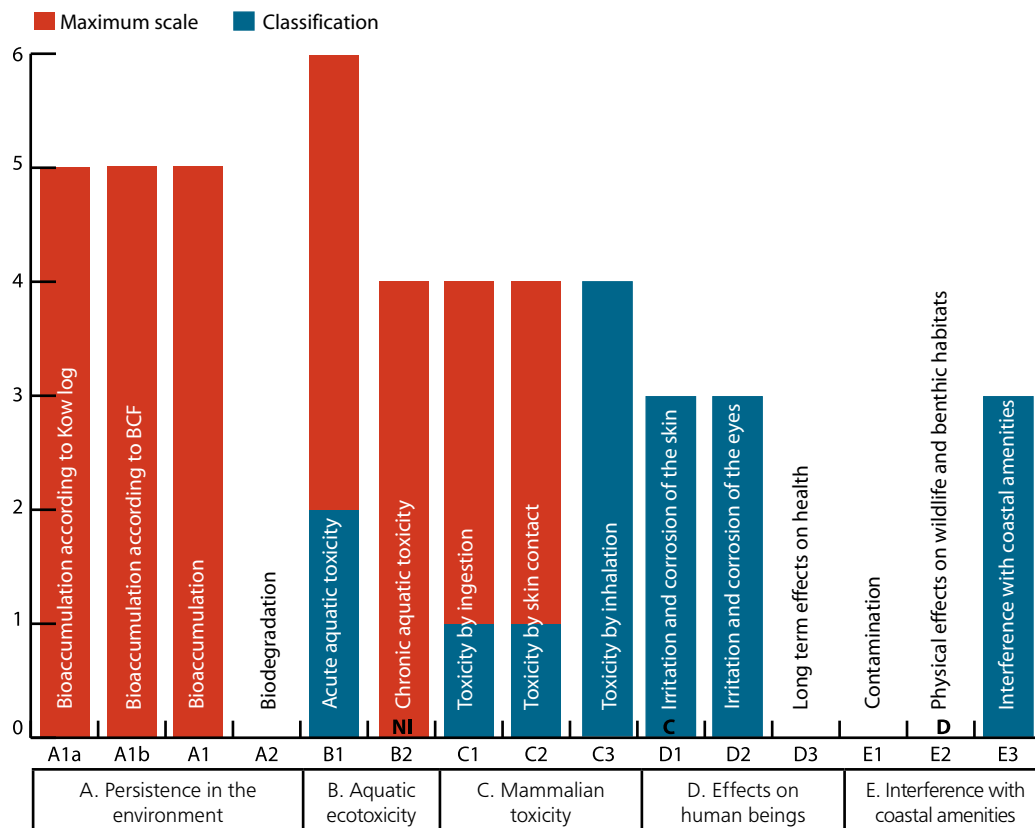
E.U. Classification:



C: corrosive

R35	causes severe burns.
S26	in case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S37/39	wear suitable gloves and eye/face protection.
S45	in case of accident or if you feel unwell, seek medical advice. Show the label where possible.
215-185-5	E.C. N° (EINECS)

GESAMP classification of sodium hydroxide solution:



A1a, A1b: sodium hydroxide is an inorganic product

A1: inorganic, non-bioaccumulable product

A2: inorganic product

B1: slight aquatic toxicity

B2: NI: No Information

C1: slightly toxic when ingested by mammals

C2: slightly toxic by skin contact with mammals

C3: slightly toxic when inhaled by mammals

D1: C: corrosive substance. Complete necrosis of the skin < 3 minutes

D2: severely irritating for eyes leading to irreversible corneal lesions

D3: no long term effects

E1: no contamination

E2: D: Dissolves

E3: highly objectionable, closure of amenity

Particular risks

Polymerisation

N/A

Danger (ERICARDS - CEFIC, 2003)

- heating the recipient can cause an increase in pressure and the recipient may shatter.
- possibility of attacking metals and production of hydrogen which may form an explosive mixture with the air.

Stability and reactivity (ARKEMA SDS, 2003)

- substances to be avoided: water, acid, zinc, aluminium, copper, alkali metals, alkaline earth metals, acetaldehyde, acroleine, acrylonitrile, allyl alcohol, halon, maleic anhydride, bromine, nitroparaffins, nitroaromatics, oleums, tetrahydrofuran.
- hygroscopic product sensitive to the carbon dioxide in the air (carbonation).
- dangerous products of decomposition: by corrosion of metals, formation of flammable and explosive hydrogen.

B9

Behaviour when in contact with other products

A violent reaction occurs with mineral or organic acids and ketones.

Sodium hydroxide solutions are highly corrosive to certain metals and alloys: zinc, aluminium, tin, copper, lead, bronze, brass. Sodium hydroxide also destroys leather, strips paint and attacks certain plastics, rubbers and coatings.

Explosion: sodium hydroxide is a stable product, however certain risks exist in the presence of:	
explosives such as nitrous compounds	reaction producing enough heat to detonate the explosive
vinyl chloride monomer	formation of chloroacetylene
tetrahydrofuran	explosion upon contact
sodium tetrahydroborate	gives off hydrogen with an explosion
pentachlorophenol	explosion and formation of toxic vapours
tetrachlorobenzene	explosion due to an increase in pressure
maleic anhydride	explosive decomposition
Fire: sodium hydroxide is neither flammable nor combustible, but it can be a secondary source of fire. Overheating a container of sodium hydroxide solution will accelerate the corrosion of metal.	
Risk of fire in the presence of:	
metals	formation of hydrogen
Sudden polymerisation caused upon contact with:	
epoxides	
polymerisable compounds such as: acetaldehyde, acrylonitrile, acroleine, allyl alcohol, 1,2-dichloroethane	

Transportation, handling, storage

Transportation (ARKEMA SDS, 2003)

Identification n° (UN): 1824

Land transportation:

RID (rail) /ADR (road)

Hazard classification: 80

Class: 8

Packaging group: II

Classification code: C5

Labels: 8

Transportation via inland waterways:

ADN/ADNR

Hazard classification: 80

Class: 8

Classification code: C5

Labels: 8

Maritime transport: IMDG

Class: 8

Packaging group: II

Marine pollutant: no

Labels: 8

Air freight: IATA

Class: 8

Packaging group: II

Labels: 8

Handling (ARKEMA SDS, 2003)

In high concentration of vapours/clouds:

- Ventilate and evacuate appropriately.
- Provide showers and eye washers.
- Ensure that there is a water source nearby.
- Prevent projections during handling.

Storage (ARKEMA SDS, 2003)

- Store in firmly closed receptacles in a cool and well aerated place.
- Keep above 20°C.
- Provide a retention tank and ensure that the ground is impermeable and resistant to corrosion, with a drainage system sending run-off to a neutralisation tank.

B10

Results of accident scenarios

- Reminder of properties _____ C1
- Accident scenarios _____ C2
- Consumption scenarios _____ C3



Reminder of properties

Transportation

Sodium hydroxide solution is transported in containers (steel barrels) or in bulk (in stainless steel tanks which can be equipped with a heating system).

Vapour density and tension

- Relative density: 1.52 to 20°C
- Vapour density: data unavailable
- Vapour tension: 2 hPa (mbar) at 20°C

Solubility

Sodium hydroxide 50% solution is completely soluble in water at 20°C.

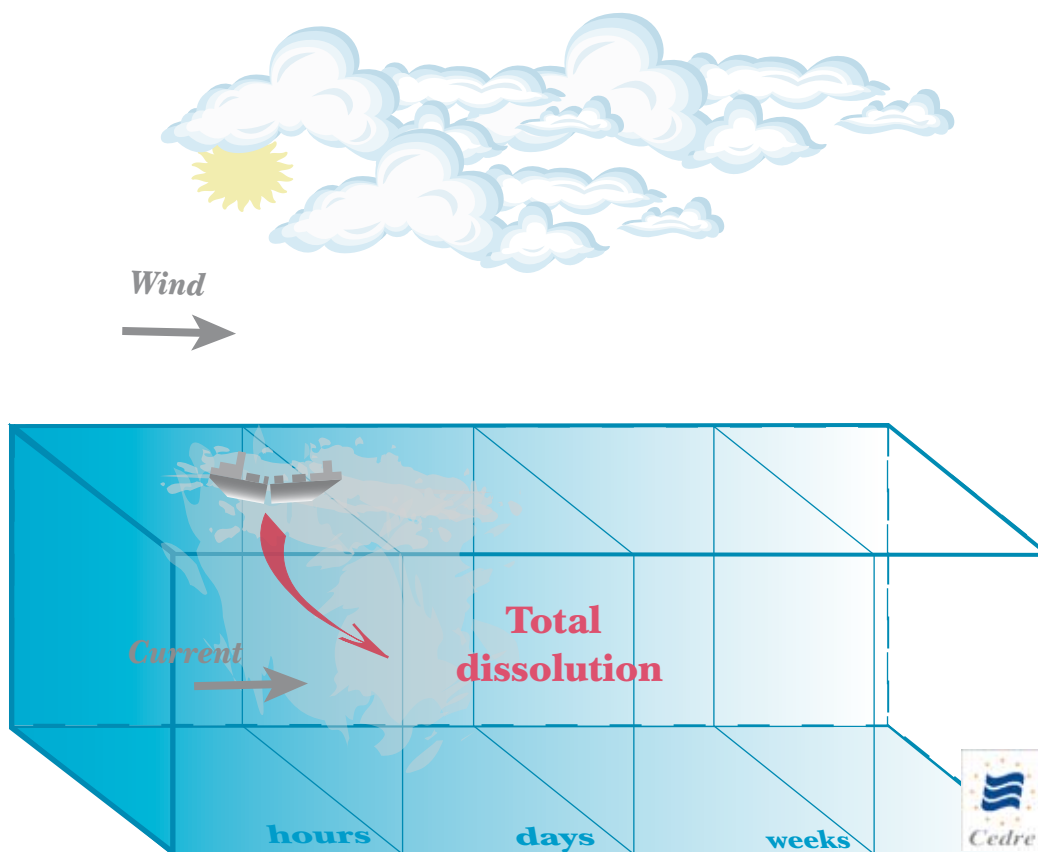
Behaviour in the environment

When spilt into water, sodium hydroxide completely dissolves.

A high concentration of sodium hydroxide in the water will increase the alkalinity of the water, which can be harmful for aquatic life.

A white plume may appear in the water after a spill of sodium hydroxide, due to the formation of magnesium hydroxide, thus making the pollutant visible.

C1



Behaviour of sodium hydroxide spilt at sea

Accident scenarios

The scenarios defined here are simply designed to give an indication of the possible behaviour of sodium hydroxide. In the event of a real spill, the results of simulations will naturally be different from those given here. The CHEMMAP behaviour model, the emergency response model employed by *Cedre*, was used for these simulations. Other more sophisticated models exist, but require response times which are incompatible with emergency situations.

Three sodium hydroxide solution spill scenarios were presented with different quantities of this product:

- a high sea scenario (Channel): 500 tonnes of sodium hydroxide spilt instantaneously
- a port scenario (Cherbourg): 100 tonnes of sodium hydroxide spilt instantaneously
- a river scenario: 20 tonnes of sodium hydroxide spilt gradually.

The scenarios

Channel scenario

- Location 50°N, 3°W
- Air and water temperature: 10°C
- Two wind speeds: 3 and 10 m/s (NW)
- Spill depth: 1 m
- Model time step: 15 min

Port scenario

- Depth of the port basin: 15 m
- Air and water temperature: 10°C
- Slow current
- No wind
- Model time step: 15 min

River scenario

- Depth of river: maximum 10 m
- Width of river: average 300 m
- Spill depth: 1 m
- Air and water temperature: 10°C
- Two current speeds: fast and slow
- Wind speed: 6 m/s
- Duration of spill: 5 hours
- Model time step: 15 min

The pH values for the different concentrations of sodium hydroxide 50% solution are given in table 1 on the following page and in annex 1.

Modelling

CHEMMAP software was used to model hypothetical spillages of sodium hydroxide 50% solution in the aquatic environment.

This chemical spill model was designed by ASA (Applied Science Associates, Inc. - USA) and predicts the movement and fate of spilt

products in fresh and sea water.

This model indicates both the movement of the product on the water surface and its distribution in the environment (evaporation, dissolution in the water column...).

Results obtained after a spill of 100 tonnes of sodium hydroxide 50% solution in the Channel, with a wind of 3 m/s.





Figure 1

Location of the hypothetical spill in the Channel



















Figure 2

View of the dissolved part

-  Spill location
-  Sampling location

The CHEMMAP model does not take into account the buffering capacity of seawater. Graphs therefore had to be drawn up in order to obtain the pH values in the aquatic environment according to the concentration of sodium hydroxide spilt in this environment. These graphs (established for fresh water and seawater) are given in annex 1.

Concentrations of dissolved sodium hydroxide with the corresponding pH ranges

mg/m ³	seawater	fresh water	g/L	pH
1 to 10			10 ⁻⁶ to 10 ⁻⁵	close to initial pH
10 to 100			10 ⁻⁵ to 10 ⁻⁴	close to initial pH
100 to 1,000			10 ⁻⁴ to 0.001	8
1,000 to 10,000			0.001 to 0.01	8 < pH < 10
10,00 to 100,000			0.01 to 0.1	10
100,000 to 1,000,000			0.1 to 1	10 - 13
1,000,000 to 10,000,000			1 to 10	> 13
10,000,000 to 100,000,000			10 to 100	> 13

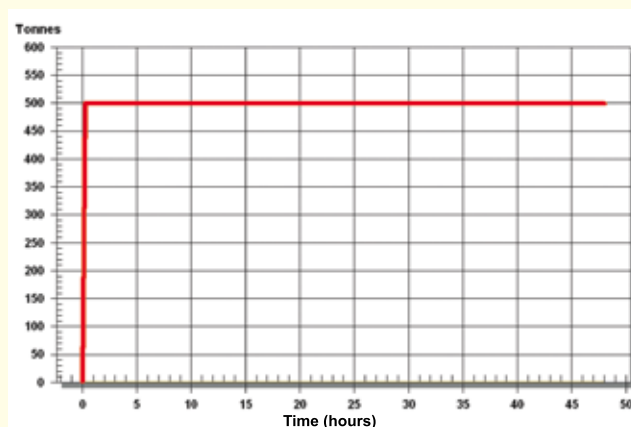
acceptable
up to pH 9



Table 1

Results of the Channel scenario

Instantaneous spill of 500 tonnes of sodium hydroxide 50% solution with a wind of 3 m/s



Graph 1

— Quantity evaporated — Quantity dissolved — Quantity on the surface

The sodium hydroxide dissolves in the water column almost immediately, whatever the quantity (20, 100 or 500 tonnes).

- Concentrations obtained **2 hours** after the spill

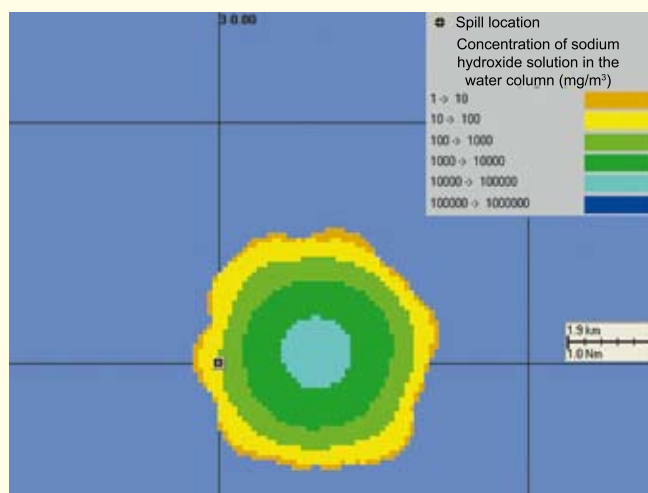


Figure 3

2 hours after the spill, the area affected extends to 2.8 nautical miles around the spill location.

• **2 hours** after the spill

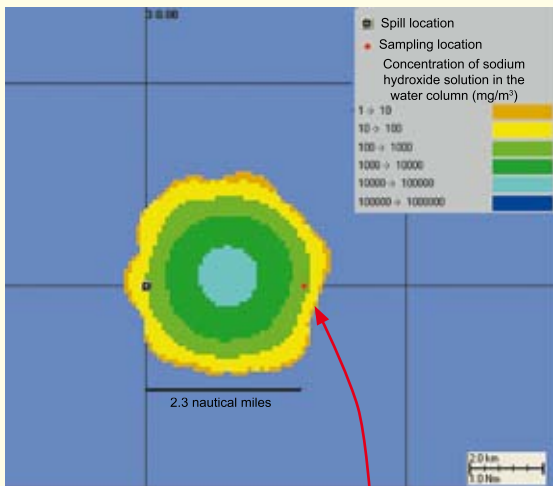
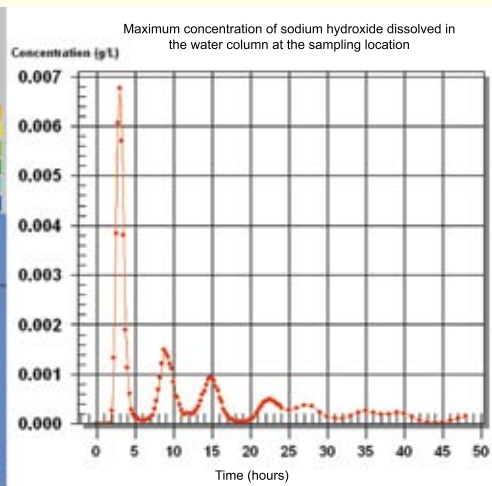


Figure 4

Location of sampling point

The concentration of sodium hydroxide reaches 0.007g/L at the sampling point, 3 hours after the spill. This corresponds to an expected pH of 8.



Graph 2

• **24 hours** after the spill

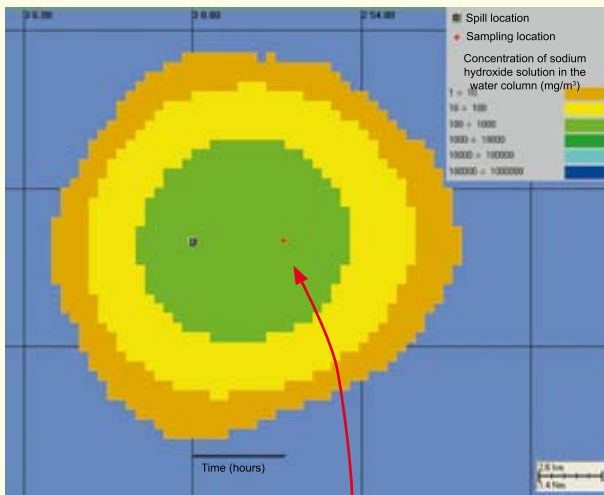
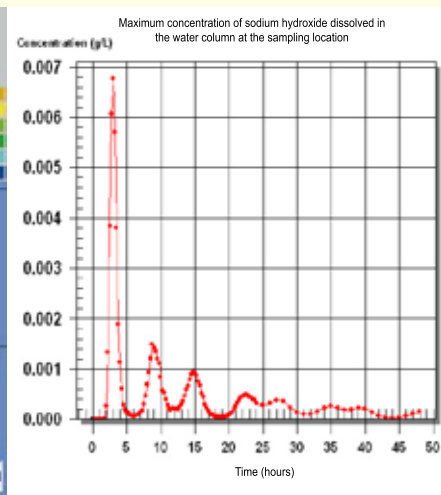


Figure 5

Location of sampling point

The concentration of sodium hydroxide reaches 0.0005 g/L at the sampling point, 24 hours after the spill. This corresponds to an expected pH of less than 8.



Graph 3

Results of the port scenario

Instantaneous spill of 100 tonnes of sodium hydroxide 50% solution, with no wind and a slow current in waters 15 m deep.

- Concentrations obtained **15 minutes** after the spill

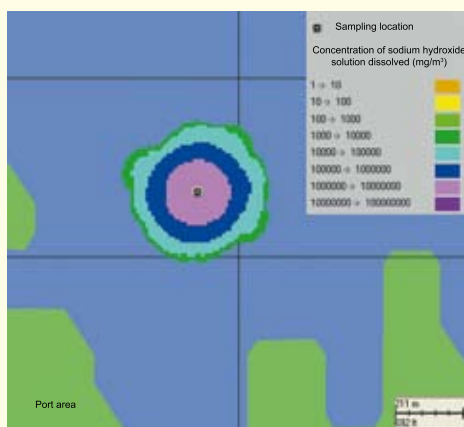


Figure 6

The highest concentration at the spill location **15 minutes** after the spill is 7.4 g/L.
The expected pH is around **13**.

- Concentrations obtained **2 hours** after the spill

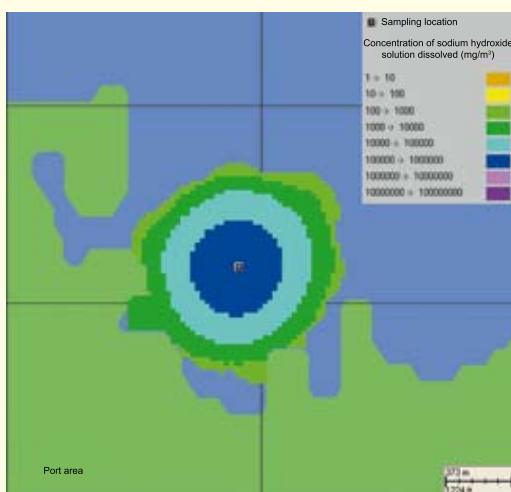
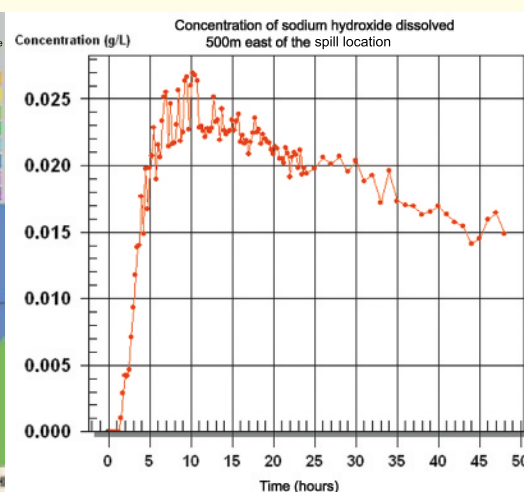


Figure 7

The highest concentration at the **spill location** 2 hours after the spill is 4.5 g/L.
The expected pH is **12**.



Graph 4

At a point located **500 m east of the spill location**, the concentration reaches 0.025 g/L after 10 hours, which corresponds to an expected pH of **8.7**. This concentration evolves as shown in graph 4.

Results of the river scenario

Continuous spill over 5 hours of 20 tonnes of sodium hydroxide 50% solution, with a current speed of 0.12 m/s.

- Concentrations obtained **1 hour** after the spill

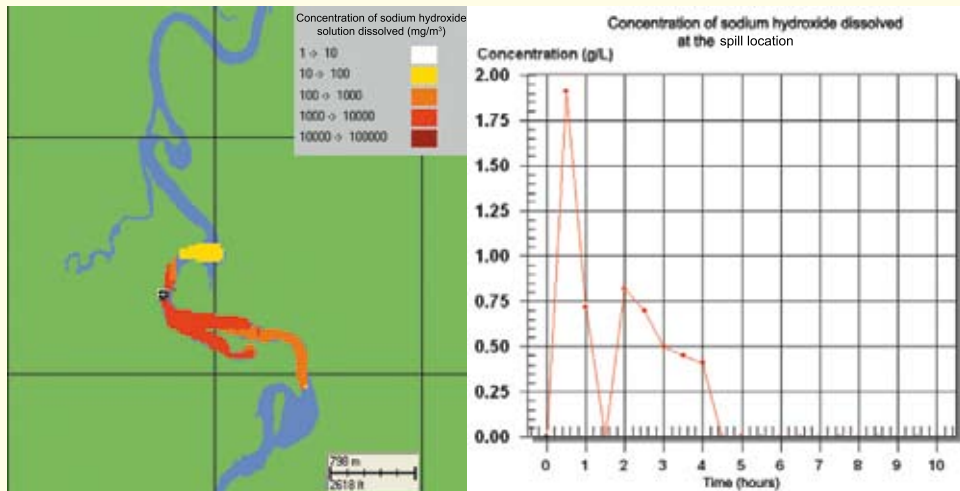


Figure 8

Graph 5

The highest concentration at the **spill location** after the spill is 2 g/L.
The expected pH is around 12.

- Concentrations obtained **48 hours** after the spill

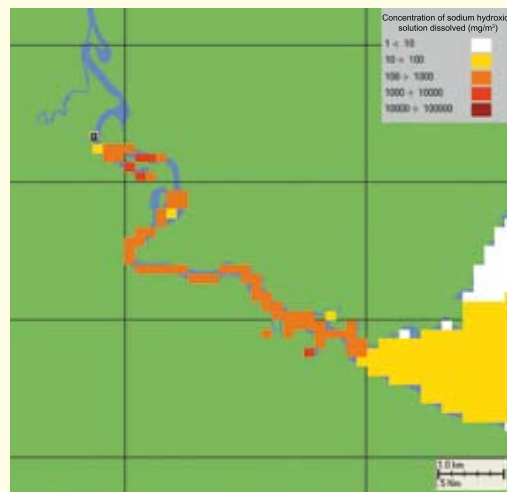


Figure 9

Evolution of the concentration of sodium hydroxide **48 hours** after the spill, **6 km downstream** (as the crow flies) from the spill location.

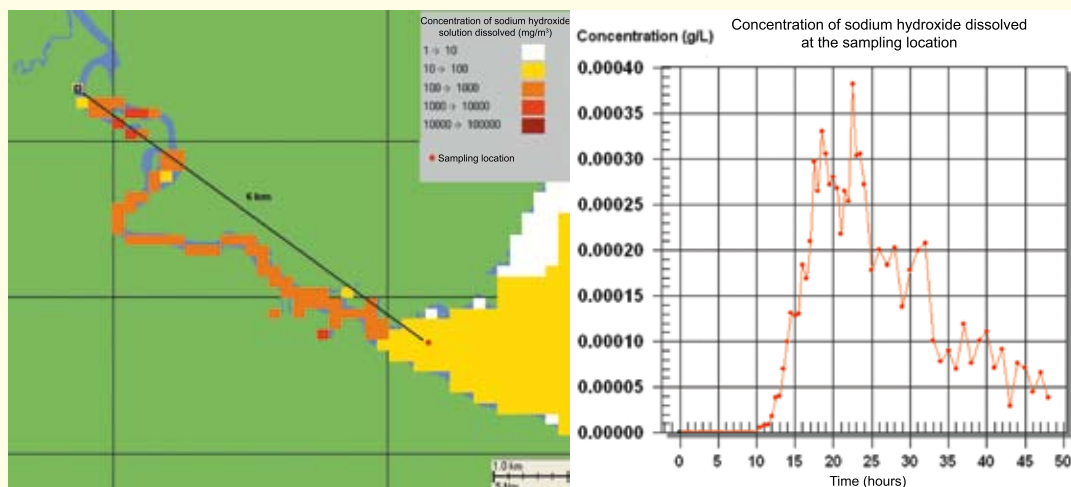


Figure 10

Graph 6

The highest concentration at this point (0.0004 g/L) is reached 22 hours after the spill and corresponds to an expected pH around 7.

Continuous spill over 5 hours of 20 tonnes of sodium hydroxide 50% solution, with a current speed of 0.74 m/s.

- **1 hour** after the spill, the highest concentration reached at the **spill location** is 0.7 g/L, corresponding to an expected pH of **around 12**.
- **48 hours** after the spill, the highest concentration reached **6 km downstream** of the spill location is 0.0001 g/L, corresponding to an expected pH **close to the initial pH**.

Consumption scenarios

As sodium hydroxide 50% solution does not bioaccumulate along the food chain, it will therefore not be found in aquatic organisms in high enough concentrations to have an impact on consumers of exposed sea produce.

Response

- Example of a sodium hydroxide solution spill _____ **D1**
- Response recommendations _____ **D2**
- Response techniques _____ **D3**
- Choosing personal protective equipment (PPE) _____ **D4**
- Measuring devices and waste treatment _____ **D5**

Examples of sodium hydroxide solution spills

Barge *Cynthia M* (NOAA, 2003)

On 15 March 1994, the barge *Cynthia M* was listing 70 degrees when she was moored to the landing stage at the Kuehne chemical plant south of Kearny, New Jersey (USA).

The barge, with a capacity of 1,300 m³, was carrying **1,200 m³ of caustic soda 30% solution**. On 16 March, around 570 m³ of the sodium hydroxide solution were spilt in Hackensack River and Newark Bay.

At 12:35 pm, the pH around the barge was 12, but by 3:35 pm it had lowered to 9. Only the area immediately surrounding the barge was affected by the pollution.

According to final estimations, the barge lost her entire cargo of sodium hydroxide. Recovery was impossible as the chemical immediately dissolved in the water.

The spill affected **birds**, caused the death of **fish** and destroyed the surrounding **marshlands**.

The possibility of adding weak acid to neutralise the alkali solution was studied, but NOAA recommended the **use of fire hoses** to increase dilution and to encourage the dissolution of the substance in the water column.

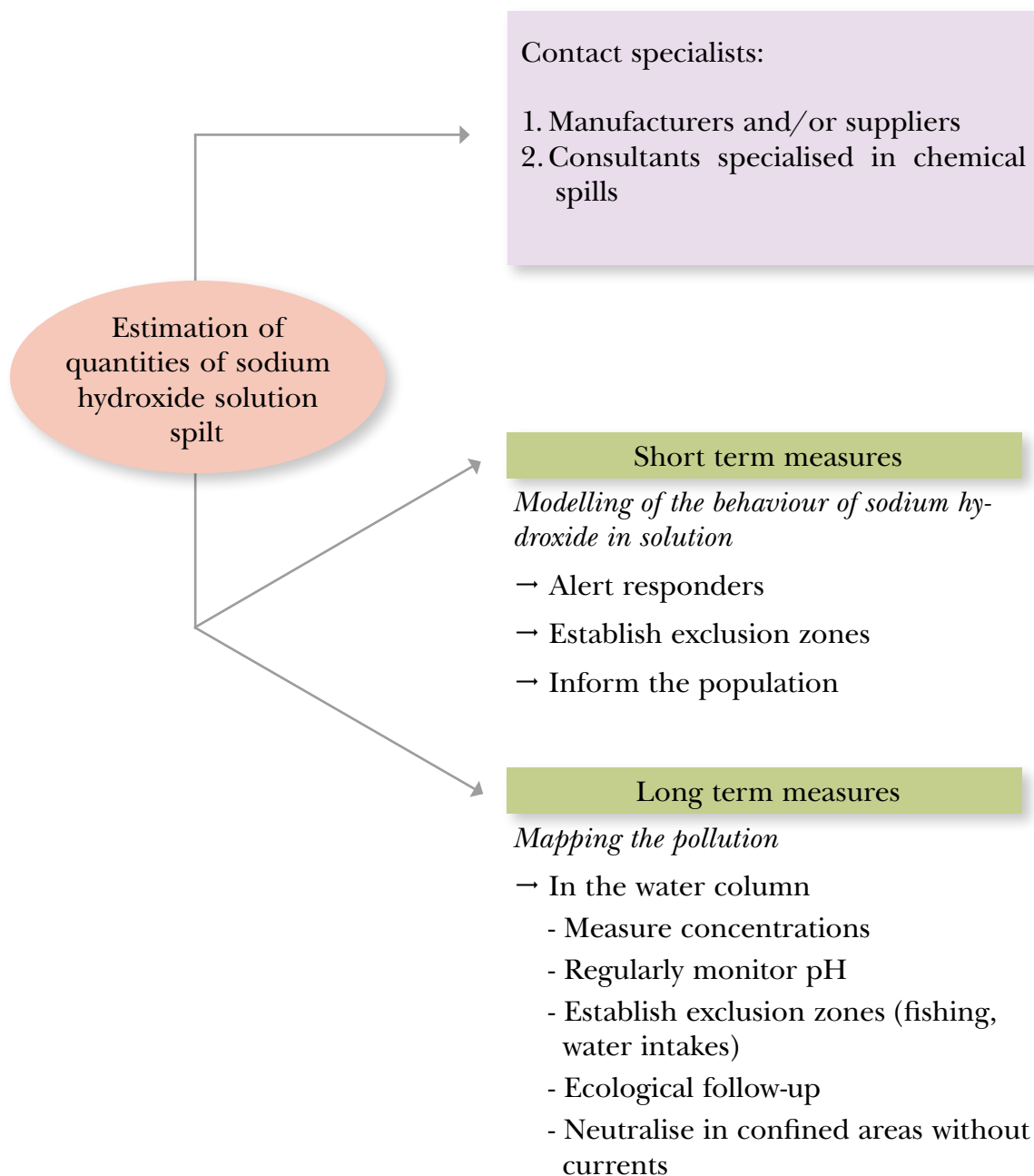
Le *Puerto Rican* (TROCS, 2004)

The tanker the *Puerto Rican* was devastated in November 1984 by **several explosions and fires** in one of her empty central tanks and in the adjacent lateral tanks. Caustic soda infiltrated into an empty adjacent tank through a small hole in one of the tank walls.

The caustic soda reacted with the epoxy coating, rich in zinc, on the tank walls and the structure of the empty tank, releasing hydrogen. This gas ignited, due to contact between metals or an electrostatic discharge. Four days after the explosion, the vessel's stern broke off and sank.

Response recommendations

Diagram showing response actions in the event of a soluble product being spilt into water



D2

Is response possible?

As sodium hydroxide is stable, non-combustible and non-volatile, **response** to an incident involving a damaged vessel is **possible** if the following precautions are taken.

- Approach the accident area from upwind (wind behind you), equipped with the personal protective equipment (PPE) described in the "Personal Protective Equipment" chapter.
- The possibility of **incompatibility with other chemicals** transported by the vessel, as well as storage materials must be taken into account (example of the *Puerto Rican* in 1984 in which the sodium hydroxide reacted with the epoxy coating rich in zinc of another empty tank, thus releasing oxygen) (TROCS, 2004).

The engine cooling systems of vessels near to the spill location may also be damaged by contamination of their water intake.

- In theory, the **action of sodium hydroxide could be neutralised** in shallow waters with a limited volume.

However, no example of this type of in situ application is available. Neutralisation currently continues to be studied in laboratory conditions and applied with precaution.

In confined shallow waters with no current, polluted waters can be **pumped off and stored** for subsequent neutralisation. The part which cannot be pumped will remain in the environment and be diluted. In rivers, if conditions allow:

- stop the arrival of water upstream by digging a reach (diversion channel)
- build a dyke upstream
- pump, store and treat as much polluted water as possible.

Emergency response in the event of fire

- Remove containers of sodium hydroxide from the area on fire if this is not dangerous.
- Otherwise, cool the containers by spraying with water to prevent them from bursting or corroding and continue this operation for a long time after the fire has been extinguished.
- Ensure that no water leaks into the containers of sodium hydroxide.
- The fire extinguishers which can be used will depend on the products on fire. Use foam, chemical powder or carbon dioxide for preference over water, although water can be used to flood the area if necessary.
- Contain run-off which could be a source of pollution.

Emergency measures in the event of a leak or spill

- Ban access to the spill site and prohibit the use of polluted waters.
- Stop or reduce water flow if doing so is not dangerous.
- Avoid inhaling vapours and prevent contact with the skin.

Response techniques

Response

(POLLUTION RESPONSE REFLEX DATASHEET "PRODUCTS IN THE WATER COLUMN AND ON THE BOTTOM: SOLUBLE AND SINKING LIQUIDS", GUIDE DATASHEET N°3: "RESPONSE IN THE AQUATIC ENVIRONMENT", STRATEGY AND MEANS DATASHEETS N°4, 5, 8, 9, 13, CEDRE-ARKEMA 2004.)

On land

It is essential to intervene as rapidly as possible in order to **prevent any polluted water from reaching the sewer system or a waterway, by containing the spill** with dams made of earth, sand or other materials or by deflecting it towards an impermeable surface.

Inland waters

As sodium hydroxide is highly soluble in water, it is difficult to respond to a spill in water. Where possible, isolate and **deflect** polluted waters immediately after the spill. If the polluted water cannot be deflected for subsequent storage or treatment, a possible response option is to **promote dilution**. Accelerated dilution may occur naturally (for instance in the case of a small stream flowing into a larger river with a faster flow). The **pH** of the aquatic environment must be **monitored** in the case of a spill of a strong base.

Calm, shallow waters

Water intakes must be closed off and the **pH regularly monitored**. The polluted water mass may be pumped off for **treatment** in an appropriate treatment plant.

At sea

It is important to **stop** the leak and the flow into the aquatic environment if this is possible without being dangerous. The role of natural dilution must be taken into account in the case of a spill at sea, as well as the buffering capacity of the seawater in the event of a spill of a base.

The environment must be monitored by **regularly measuring the pH**.

Be careful of sodium hydroxide spray due to wave and wind action.

Except in a few rare cases (e.g. harbour basins with no current), it is impossible to recover the polluted water.

However, if the polluted water is even partially pumped, it may be **neutralised**. This involves bringing the pH of the polluted water mass back as close as possible to its usual value. This can be carried out using two different methods: either by natural dilution in a large water mass (spill at sea) or by adding a neutralising agent such as monosodium phosphate (NaH_2PO_4). This second possibility can only be conducted for small or moderate volumes of pollution due to the necessary quantity of the agent (2 to 3 times the mass of the product spilt). The agent is added using a fire hose or by directly applying it from the container.

Finally, it is useful for responders to understand the behaviour of sodium hydroxide in the water column. This behaviour is modelled using the CHEMMAP model for the simulation of chemical spills (see the "Accident scenarios" chapter).

Choosing personal protective equipment (PPE)

Ensure maximum protection in the case of high concentrations of the product

Choosing breathing apparatus

(FINGAS, 2000)

According to maximum use concentrations (MUC)¹:

- gas mask for up to 6 ppm
- self contained breathing apparatus (SCBA): no concentration limit.

Wear a hazmat suit if vapour concentrations are likely to be high.

Selecting protective clothing

(CCHST, 2003)

In most cases, a splash suit should be worn, as well as facial protection such as safety goggles and a face mask. Protective gloves are also recommended (neoprene or nitrile, see the table on p. 35).

After response, promptly remove all contaminated clothing and place it in containers provided for this purpose. Protective clothing should then be disposed of or be washed before being reused. Inform personnel in charge of cleaning the clothing of the dangers of the pollutant.

- An air purifying respirator can be used in stable situations.
- Warning: certain facial characteristics such as scars, a narrow face shape or facial hair may lead to poor adjustment of the mask and impair the level of protection.
- In warm weather: excessive perspiration reduces the effectiveness of the seal between the mask and the skin.
- In cold weather: ice may form on the regulator and the mask may steam up.
- Warning: ordinary glasses cannot be worn under the mask (special frames exist). Contact lenses are permitted with new models of masks which allow gas exchange as the lenses therefore do not dry out or stick to the eye.
Mask adjustment tests are recommended for new users and regular tests for other users.

Recommendations for use in the event of a spill (FINGAS, 2000)

- Pressure demand open-circuit SCBAs give the best safety protection. Their protection factor is around 10,000 (e.g. ELV = 20 ppm, protection up to 200,000 ppm of product in ambient air temperatures).
- Use SCBA to face unknown situations or to enter an area with unknown or high concentrations of a toxic substance or areas where there may be a lack of oxygen (enclosed spaces).

¹ Maximum use concentrations can vary according to the make and model. Contact the manufacturer for more information.

Measures to take after using PPE in a spill situation

- Decontaminate boots after use. A foot bath and mild detergent can be used. Do not forget to treat the contaminated water.
- Decontaminate gloves separately from boots in a bucket with a mild detergent.

Permeation times through different materials (FORSBERG & KEITH, 1995 IN FINGAS, 2000)

BETEX (butyl/neoprene): > 360 min
 Butyl: > 360 min
 Natural rubber: 360 min
 Neoprene: 360 min
 Nitrile: 360 min
 Polyvinyl chloride: 360 min
 Polytetrafluoroethylene: no data available
 Viton: no data available

Chemical resistance

Material	Breakdown	Permeation	Use
Nitrile	very minimal	0 to 0.5 drops per hour pass through the glove	appropriate
Neoprene	very minimal	0 to 0.5 drops per hour pass through the glove	appropriate
Polyvinyl alcohol (PVA)			not recommended
Polyvinyl chloride (PVC)		6 to 50 drops per hour pass through the glove	appropriate
Natural rubber		0 to 0.5 drops per hour pass through the glove	appropriate
Linear Low Density PolyEthylene (LLDPE)	no breakdown tests have been carried out but should be good or excellent as the passage time is > 8 hours	permeation time: > 480 min	appropriate

Note: this chemical resistance table is intended simply to give an indication of relative values. An assessment in the real conditions of usage should be carried out.

Measuring devices and waste treatment

Measuring devices

pH meter

Addresses of special industrial waste treatment plants in France




The organisations able to treat this type of waste are listed at the following address:
<http://www.observatoire-dechets-bretagne.org> (French only).

European manufacturers of sodium hydroxide

(EUROPEAN CHEMICAL BUREAU, 2005)

Arkema, Solvay, Albemarle, ChlorAlp, BASF.

Further information

- Glossary  E1
- Acronyms  E2
- Useful websites  E3
- Bibliography  E4



Glossary

Acceptable Daily Dose (ADD)

For humans this dose is the quantity of a substance that can be ingested by an organism per day for its entire lifetime without presenting a health hazard for the organism in question.

Acute Exposure Guideline Levels (AEGs)

Defined by the National Research Council's Committee on Toxicology (USA), AEGs are three levels above which the general population may experience certain effects. These three AEGs are given for five exposure times: 10, 30 min, 1, 4 and 8 hours.

AEGL 1: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non sensory effects. However, the effects are transient and reversible when exposure ceases.

AEGL 2: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL 3: the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

Adsorption

Elevation of the concentration of a substance dissolved at the interface of a condensed phase and a liquid phase under the influence of surface forces. Adsorption can also occur at the interface of a condensed phase and a gas phase.

Bioaccumulation

Continued retention of a substance in the tissue of an organism throughout the course of its existence (the bioaccumulation factor increases all the time).

Bioamplification

Retention of a substance in the tissue at increasingly higher concentrations the higher one goes in the food chain.

Bioconcentration

Retention of a substance in the tissue of an organism to the extent that the content of the substance in the tissue exceeds that found in nature at one point in the lifetime of the organism.

Bioconcentration factor (BCF)

Ratio of the chemical concentration in the exposed organism (minus the concentration in a control organism) to that in surrounding water.

Biotransformation

Biological transformation of substances in a living organism via enzymatic processes.

Boiling Liquid Expanding Vapour Explosion (BLEVE)

A violent vapour explosion of a liquid that is significantly above its usual boiling point at atmospheric pressure after a tank has burst.

Boiling point (measured at a pressure of 1 atmosphere)

Temperature at which a liquid begins to boil. More specifically, when the temperature at which saturating vapour pressure of a liquid is equal to standard atmospheric pressure (1,013.25 hPa). The boiling point measured depends on atmospheric pressure.

Buffering capacity

Capacity of a solution to absorb a certain quantity of acid or base without causing a significant variation in pH. In the marine environment, the buffering capacity is due to the dihydrogenocarbonate/carbonate balance.

Critical point

Point at which the temperature and pressure at which the intensive properties of a liquid and vapour (density, calorific value...) are equal. It represents the highest temperature (critical temperature) and pressure (critical pressure) at which a gas phase and a liquid phase of a given compound can coexist.

Critical pressure

Maximum pressure for which the distinction can be made between a gas and a liquid.

Critical temperature

Temperature at which, when boiling, there is no longer any clear cut transition between the liquid and the gas state.

Daily exposure dose

Dose (internal or external) of a substance in an organism compared to the weight of the individual and the number of days of exposure (in the case of a non carcinogenic substance) and the number of days lived by the organism (for a carcinogenic substance).

Decomposition products

Products stemming from chemical or thermal disintegration of a substance.

Diffusion coefficient in air (and in water)

A constant that describes the movement of a substance in the gas phase (or liquid phase) in response to a concentration differential in the gas phase (or liquid phase).

Effective concentration 50 (EC₅₀)

Concentration causing a given effect (mortality, growth inhibition...) for 50% of the population under consideration during a given period of time.

Emergency Response Planning Guidelines (ERPG)

The American International Health Alliance (AIHA) set three maximum concentrations in 1988 below which a category of effects is not expected for an exposure duration of one hour, in a bid to protect the general public.

ERPG1: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing other than mild transient adverse health effects or perceiving a clearly identifiable odour.

ERPG2: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair their abilities to protect themselves.

ERPG3: is the maximum airborne concentration below which nearly all individuals could be exposed for up to 1 hour without experiencing or developing life-threatening health effects.

Exposure limit value (ELV)

Ceiling exposure value measured for a maximum duration of 15 minutes.

Flash point

The lowest temperature at which a substance generates vapours that ignite or burn immediately when in contact with a flame.

Foam

The foam layer absorbs most of the vapours, physically eliminates vapours and isolates the chemical from sunlight and ambient air which reduces the amount of heat and subsequent vaporisation.

Henry's law constant

Value indicating a substance's volatility (see graph on p. 41)

Immediately Dangerous to Life or Health (IDLH)

Level below which a worker can escape to safety in thirty minutes in the event of sudden exposure to a dangerous atmosphere, without respiratory protection and without impairing his ability to escape.

Irreversible effect threshold (IET)

Concentration, for a stated exposure duration, above which irreversible effects can occur in the exposed population.

Lethal effect threshold (LET)

Concentration, for a stated exposure duration, above which mortality can be observed in the exposed population.

Lower Explosive Limit (LEL)

Minimum airborne concentration above which vapours ignite.

Lowest Observed Effect Concentration (LOEC)

Lowest concentration at which an effect is observed.

Marine pollutant

Substance, object or matter likely to cause serious damage to the marine environment when spilled.

Maximum Allowable Relief Valve Setting (MARVS)

Indicates the maximum admissible calibration of pressure relief valves of a cargo tank.

Mean exposure value (MEV)

Value that has been measured or estimated for a work station lasting 8 hours and is intended to protect workers from long term effects. MEV can be exceeded for very short periods providing the ELV value (should there be one) is not exceeded.

Median lethal concentration (LC₅₀)

Concentration of a substance deduced statistically that should, during or after exposure and for a given period of time, cause the death of 50% of the animals exposed during a given time period.

Melting point

Temperature at which solid and liquid state coexist. The melting point is a constant for a pure substance and is usually calculated at standard atmospheric pressure (one atmosphere).

Minimum Risk Level (MRL)

This level is an estimate of daily human exposure to a chemical which probably has no appreciable risk of non-carcinogenic noxious effect on health for a specific exposure duration.

Miscible

Matter that mixes readily with water

N-octanol/water partition coefficient (K_{ow})

Ratio of the equilibrium concentrations of a substance dissolved in a two phase system made up of two solvents that virtually do not mix.

No Observed Effect Concentration (NOEC)

Concentration of a substance measured during chronic toxicity tests for which no effect is observed, meaning that the substance presents no chronic toxicity below this concentration.

No Observed Effect Level (NOEL)

The highest dose of a substance that causes no distinct changes as compared with those observed in control animals.

Olfactory threshold

Minimum air or waterborne concentration to which the human nose is sensitive.

Partition coefficient for organic carbon and water (K_{oc}) (for organic substances)

Ratio of the amount of compound absorbed per unit mass of organic carbon in the soil or in a sediment and the concentration of the same compound in a water solution in a state of equilibrium.

Photo-oxidation

Oxidation of a chemical compound caused by exposure to light energy.

Polymerisation

This term describes the chemical reaction generally associated with the production of plastics. Fundamentally, the individual molecules of a chemical (liquid or gas) react together to form a long chain. These chains can be used for many applications.

Protective equipment

This refers to the respiratory or physical protection of a human being. Protection levels have been defined, including both protective clothing and breathing apparatus as accepted by response authorities such as the USCG, NIOSH and the EPA (US).

Level A: an SCBA (self contained breathing apparatus/respirator) and fully air and chemical-tight suit (that resists permeation).

Level B: an SCBA and a suit that protects against liquid spray (splash proof).

Level C: a full face mask or goggles and a suit that protects responders against chemicals (splash proof).

Level D: overalls without a respirator.

Rate of evaporation or volatility (ether = 1)

The rate of evaporation expresses the number of times that a product takes to evaporate as compared with a control substance of an equal volume (ether for instance). This rate varies with the nature of the product and the temperature.

Regression speed

Speed at which a burning liquid slick reduces in thickness. For a given liquid, this speed is constant regardless of the slick surface (slick diameter greater than 2 metres). Regression speed allows the total duration of a fire to be estimated if no attempt is made to extinguish it.

e.g. a 1,000 mm thick slick, where the regression speed is 10 mm/minute
duration of fire = 1000/10 = 100 minutes.

Relative density

Ratio of the mass of a substance to that of water for a liquid or to that of air for a gas.

Relative vapour density

Weight of a volume of vapour or pure gas (without air) compared to that of an equal volume of dry air at the same temperature and pressure.

A vapour density lower than 1 indicates that the vapour is lighter than air and will have a tendency to rise. When the vapour density is higher than 1, vapour is heavier than air and will tend to stay near ground level and spread.

Self-ignition temperature

Minimal temperature at which vapours ignite spontaneously.

Solubility

Quantity of a substance dissolved in water. It will depend on salinity and temperature.

Source of ignition

Examples of sources of ignition: heat, sparks, flame, static electricity and friction. Sources of ignition should always be eliminated when handling flammable products or responding to an emergency in risky areas (use explosion proof pumps and VHF walky-talkies).

Surface roughness

Length of a transfer area between the atmospheric layer and a contact surface. This will depend on the average size of the roughness of the contact and atmospheric parameters near the water surface. When the sea is calm it is of the order of 0.02 to 0.06 cm.

Surface tension

A constant that expresses the force owing to molecular interaction exerted at the surface of a liquid when it comes into contact with another surface (liquid or solid) and that affects surface dispersion.

Temporary Emergency Exposure Limits (TEEL)

Exposure times when there is no ERPG.

TEEL 0 is the threshold concentration below which a large part of the population will experience no

effect on health. TEEL 1 is equivalent to ERPG1, TEEL 2 is equivalent to ERPG2 and TEEL 3 is equivalent to ERPG3.

Threshold Limit Value (TLV)

Average limit value (weighted as a function of time) that people can be exposed to regularly at work 8 hours a day, 5 days a week without experiencing noxious effects. This value was defined and determined by ACGIH.

TLV-STEL: Mean weighted 15 minutes concentration that must never be exceeded at any time during the day.

TLV-TWA: Mean weighted values for an 8 hour period per day and 40 hours a week.

TLV-ceiling Ceiling values never to be exceeded not even for an instant.

Unconfined Vapour Cloud Explosion (UVCE)

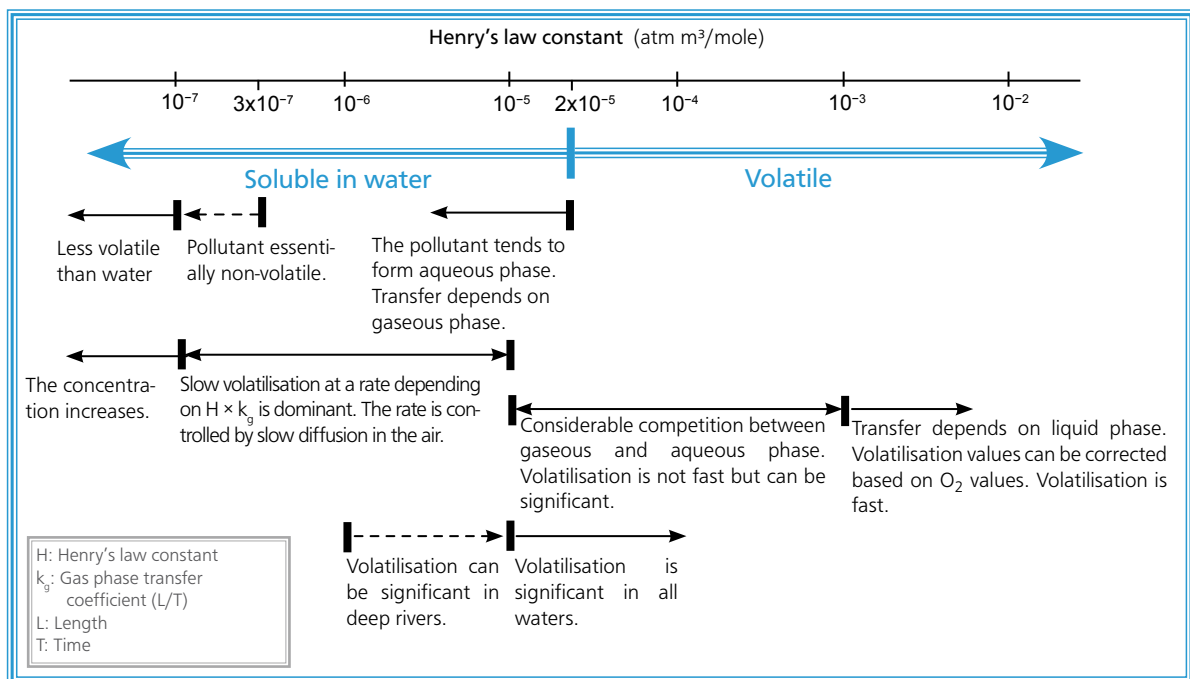
Explosion of a gas cloud or slick of combustible vapours in an unconfined environment.

Upper Explosive Limit (UEL)

Maximum airborne concentration of a compound above which vapours will not ignite for lack of oxygen.

Vapour pressure or tension

Partial pressure of gas molecules in a state of equilibrium with the liquid phase for a given temperature.



Characteristics of volatilisation associated with different Henry's law constant values (Lyman et al., 1990).

Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
ADD	Acceptable Daily Dose
ADNR	European Agreement concerning International Carriage of Dangerous Goods on the Rhine river
ADR	European Agreement concerning the International Carriage of Dangerous Goods by Road
AEGLs	Acute Exposure Guideline Levels
AFFF	Aqueous Film-Forming Foam
AFSSA	French National Agency for Food Safety
AIHA	American International Health Alliance
ALOHA	Areal Locations of Hazardous Atmospheres
ATSDR	Agency for Toxic Substances and Disease Registry
AUV	Autonomous Underwater Vehicle
BCF	Bio Concentration Factor
BLEVE	Boiling Liquid Expanding Vapour Explosion
CAS	Chemical Abstracts Service
CEA	French Atomic Energy Commission
CEDRE	Centre of Documentation, Research and Experimentation on Accidental Water Pollution
CEFIC	European Chemical Industry Council
CHRIS	Chemical Hazards Response Information System
CSST	French Occupational Health and Safety Commission
CSTEE	French Scientific Committee on Toxicity, Ecotoxicity and the Environment
DDASS	French Departmental Health and Social Action Directorate
DDE	French Departmental Equipment Directorate
DRASS	French Regional Department of Health and Social Affairs
DRIRE	French Regional Directorates for Industry, Research and Environment
EC	Effective Concentration
ECB	European Chemicals Bureau
EINECS	European Inventory of Existing Chemical Substances
ELV	Exposure Limit Value
EPA	Environmental Protection Agency
ERPG	Emergency Response Planning Guidelines
ETC	Environmental Technology Centre
HSDB	Hazardous Substances Data Bank
IATA	International Air Transport Association
IBC	International Bulk chemical Code
ICSC	International Chemical Safety Cards
IDLH	Immediately Dangerous to Life or Health
IFREMER	French Research Institute for Exploitation of the Sea
IGC	International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
IMDG	International Maritime Dangerous Goods
IMO	International Maritime Organization
INCHEM	International Chemical industries, Inc.
INERIS	French National Institute for Industrial Environment and Risks
INRS	French National Research and Safety Institute for occupational risk prevention
IPCS	International Programme on Chemical Safety
IPSN	French Institute for Nuclear Safety and Protection
IUCLID	International Uniform Chemical Information Database
LC	Lethal Concentration

LEL	Lower Explosive Limit
LET	Lethal Effect Threshold
LLDPE	Linear Low Density PolyEthylene
LOEC	Lowest Observed Effect Concentration
MARPOL	Marine Pollution
MARVS	Maximum Allowable Relief Valve Setting
MCA	Maritime and Coastguard Agency
MEV	Mean Exposure Value
MP	Marine Pollutant
MRL	Minimum Risk Level
MUC	Maximum Use Concentrations
NIOSH	National Institute for Occupational Safety and Health
NOAA	National Oceanic and Atmospheric Administration
NOEC	No Observed Effect Concentration
OECD	Organisation for Economic Co-operation and Development
PEC	Predicted Effect Concentration
PID	Photo Ionisation Detector
PNEC	Predicted No-Effect Concentration
PPE	Personal Protective Equipment
ppm	Parts per million
PTBC	Para-tertiary-butylcatechol
PVC	Polyvinyl chloride
PVDC	Polyvinylidene chloride
PVDF	Polyvinylidene fluoride
REMPEC	Regional Marine Pollution Emergency Response Centre for the Mediterranean Sea
ROV	Remoted Operated Vehicle
SCBA	Self-Contained Breathing Apparatus
SDS	Safety Data Sheet
SEBC	Standard European Behaviour Classification system of chemicals spilled into the sea
SIDS	Screening Information Data Set
SIW	Special Industrial Waste
TEEL	Temporary Exposure Limits
TGD	Technical Guidance Document
TLV-ceiling	Threshold Limit Values – Ceiling
TLV-STEL	Threshold Limit Values - Short Term Exposure Limit
TLV-TWA	Threshold Limit Values - Time Weighted Average
TNO	Netherlands Organisation for Applied Scientific Research
TRANSAID	Agreement between UIC (French Chemical Industry Association) & the French Government
TROCS	Transport of Chemical Substances - database created by REMPEC
UEL	Upper Explosive Limit
UIISC	French Unit of Instruction and Intervention on Civil Security
US EPA	United States Environmental Protection Agency
UVCE	Unconfined Vapour Cloud Explosion
VCM	Vinyl chloride monomer
VHF	Very High Frequency
v/v	Volume to volume
WHO	World Health Organisation

Useful websites

Bonn Agreement, European Classification System

http://www.bonnagreement.org/eng/html/counter-pollution_manual/chapter26_hazardous_materials.htm

AFSSA (French National Agency for Food Safety) (French only)

<http://www.afssa.fr>

ARKEMA

<http://www.arkemagroup.com>

ATSDR (Agency for Toxic Substances and Disease Registry)

<http://www.atsdr.cdc.gov/>

Cedre (Centre of Documentation, Research and Experimentation on Accidental Water Pollution)

<http://www.cedre.fr>

CEFIC (European Chemical Industry Council)

<http://www.ericards.net>

Chemfinder

<http://chemfinder.cambridgesoft.com>

CHRIS (Chemical Hazards Response Information System)

<http://www.chrismanual.com>

CSST (Occupational Health and Safety Commission)

<http://www.reptox.csst.qc.ca>

CSTEE (Scientific Committee on Toxicity, Ecotoxicity and the Environment)

http://ec.europa.eu/food/index_en.htm

CTE (Environmental Technology Centre, Canada)

http://www.etc-cte.ec.gc.ca/etchome_e.html

European Chemicals Bureau, Risk Assessment

<http://ecb.jrc.it/existing-chemicals>

ICSC (International Chemical Safety Cards)

<http://www.cdc.gov/niosh/ipcs/ipcard.html>

IDLH Documentation for Immediately Dangerous to Life or Health concentrations, List of 387 products (original and amended)

<http://www.cdc.gov/niosh/idlh/intridl4.html>

INCHEM (INternational CHEMical Industries, Inc.)

<http://www.inchem.org> (list of ERPGs)

INERIS (French National Institute for Industrial Environment and Risks)

<http://www.ineris.fr>

INRS (French National Research and Safety Institute for Occupational Risk Prevention)

<http://en.inrs.fr/>

IPCS (International Programme on Chemical Safety)

<http://www.who.int/ipcs/en>

NIOSH (US National Institute for Occupational Safety and Health)

<http://www.cdc.gov/niosh/>

NOAA (US National Oceanic and Atmospheric Administration), historical incident search page

<http://www.incidentnews.gov/>

OECD (Organisation for Economic Co-operation and Development)

http://www.oecd.org/document/55/0,2340,en_2649_34379_31743223_1_1_1_1,00.html

SHELL, Material Safety Data Sheets (MSDS)

<http://www.euapps.shell.com/MSDS/GotoMsds>

UIC (French Chemical Industry Association)

<http://www.uic.fr/index-us.htm>

US Department of Energy, Chemical Safety Program, list of ERPGs

http://tis.eh.doe.gov/web/chem_safety/teel.html

US EPA (Environmental Protection Agency)

<http://www.epa.gov> (list of AEGLs)

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ANNEXES

Annex 1: pH graphs

Annex 2: summary and additional physical and toxicological data

Annex 3: fax format data card

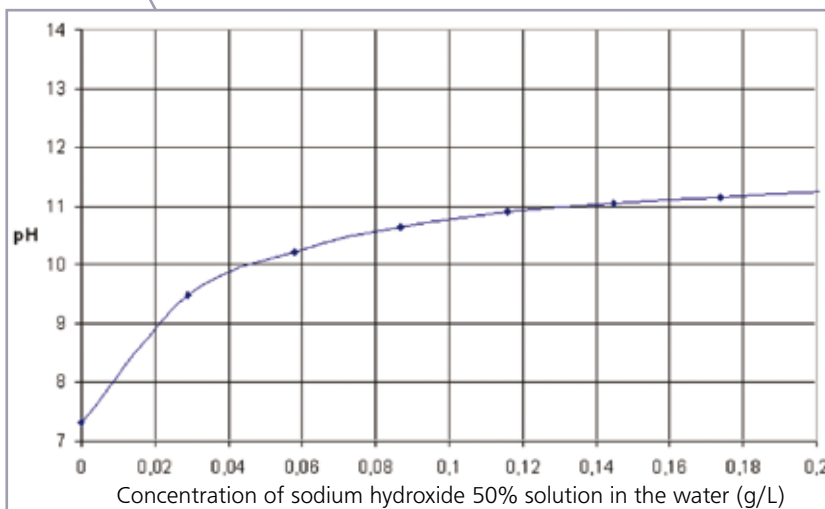
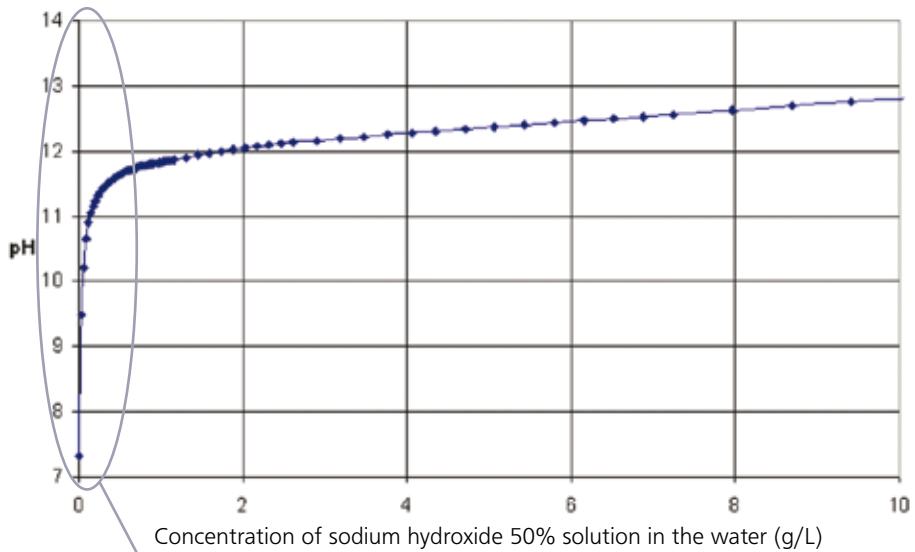
Annex 4: classification of noxious liquid substances

Annex 4b: new classification of noxious liquid substances

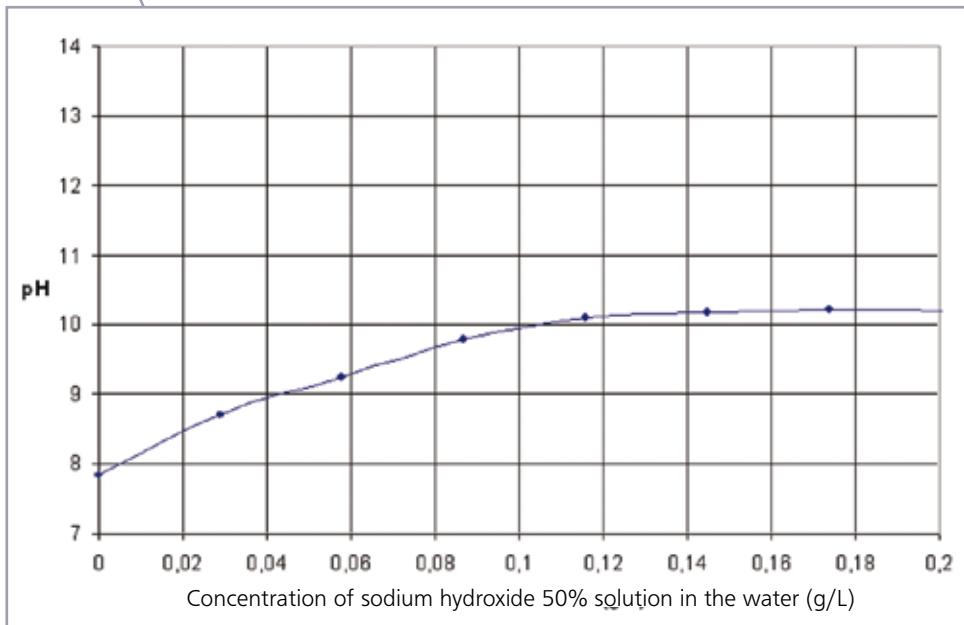
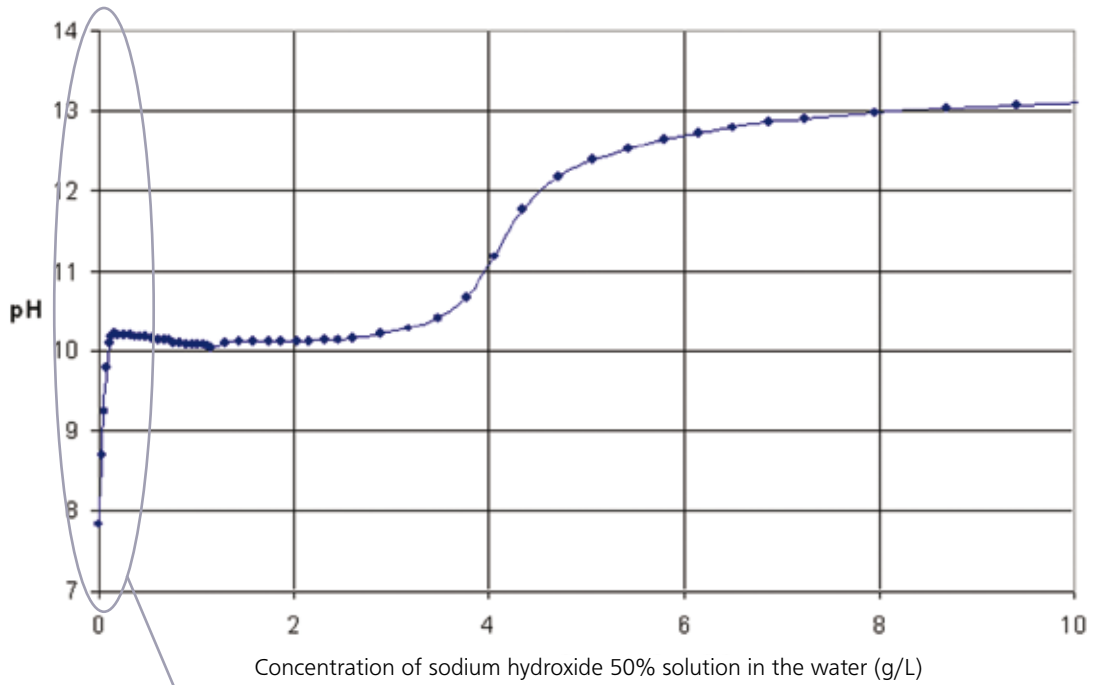
ANNEX 1: pH GRAPHS

The following graphs show the pH values in the aquatic environment according to the concentration in the water of sodium hydroxide 50% solution.

- Fresh water



• Seawater



ANNEX 2: SUMMARY AND ADDITIONAL PHYSICAL AND TOXICOLOGICAL DATA

Classification

(CHRIS, 1999; INRS, 1997)

CAS n°: 1310-73-2
EC n° (EINECS): 215-185-5
UN n°: 1824
Index n°: 011-002-00-6
Class: 8

Physical data

Molar mass: 40.01 g/mol

INRS, 1997

Physical state at 20°C

Appearance: cloudy liquid

Colour: colourless

Odour: none

Solubility

ARKEMA SDS, 2003

In fresh water: completely soluble at 20°C
(precipitates at 52%)

SIDS - OECD, 2004

In other compounds: soluble in glycerine, methanol and ethanol but insoluble in diethyl ether.

ARKEMA SDS, 2003

	50%	30.5%	20%	12%
Liquid volumic mass (20°C)	1,520 kg/m ³	1,330 kg/m ³	1,219 mg/m ³	1,131 mg/m ³
Liquid density (20°C)	1.52	1.330	1.219	1.131
Vapour tension (20°C)	2 hPa (mbar)	11 hPa (mbar)	17.6 hPa (mbar)	
Boiling point	142°C < T < 144°C	119°C	110°C	105°C
Viscosity at 20°C	78 mPa.s	14 mPa.s	4.5 mPa.s	
Freezing point	12°C	3°C	-27°C	

pH of a 50 % solution: 14

ARKEMA SDS, 2003

Important temperatures

ENVIRONMENT CANADA, 1984

Flash point (in closed capsule): N/A

Self-ignition point: N/A

Critical temperature: N/A

Polymerisation heat: N/A

Other properties

Henry's law constant: N/A

Diffusion coefficient in air: N/A

Diffusion coefficient in water: N/A

Critical pressure: N/A

Surface tension: data unavailable

Interface tension/liquid water: data unavailable

Evaporation rate (diethyl ether = 1): N/A

Olfactory threshold: unknown

General toxicity

Acute human toxicity

ARKEMA SDS, 2003

The acute toxicity of sodium hydroxide depends on its physical state (solid or in solution), on its concentration and on the dose.

- By ingestion: severe burns to the digestive tract, risk of perforation of the alimentary canal, state of shock.
- By skin contact: very corrosive for the skin, severe burns, severe lesions, scarring, dermatitis possible in the case of repeated contact.
- By eye contact: corrosive for the eyes, severe lesions possibly with lasting effects if the eyes are not rinsed immediately, harm to all the eye tissues, risk of sight loss.
- By inhalation: corrosive for respiratory tract.

Chronic human toxicity

SIDS - OECD, 2004

Few studies have been conducted, as low concentrations of sodium hydroxide are neutralised by the acidity of the stomach.

Sodium hydroxide 50% solution however has no sensitising potential or mutagenicity.

Ecotoxicological data

Acute ecotoxicity

ECB PROJECT, 2005

Daphnia (<i>Ceriodaphnia dubia</i>)	LC ₅₀ (48h) = 40 mg/L (fresh water)
Fish (<i>Brachydanio rerio</i>)	55.6 mg/L < LC ₅₀ (96h) < 100 mg/L pH: 7.9 to 8.1 (fresh water)
Fish (<i>Lucioperca lucioperca</i>)	toxic concentration > 35 mg/L (fresh water)
Marine invertebrate (<i>Ophryotrocha diadema</i>)	33 mg/L < LC ₅₀ (48h) < 100 mg/L (seawater)

Chronic ecotoxicity

No data available

PNEC (Predicted No-Effect Concentration): no PNEC was able to be calculated as the buffering capacity, the pH and its fluctuation are very specific to the ecosystem in question. To estimate the effect of a sodium hydroxide spill, the change in pH of the water must be calculated or measured.

Variation by one pH unit could affect flora and fauna (ECB PROJECT, 2005). The average pH of water can vary in seawater from 8 to 8.4 (stable pH) and in fresh water from 6 to 7.5.

ANNEX 3: FAX FORMAT DATA CARD

Sodium hydroxide Caustic soda solution, sodium hydrate solution, white caustic solution, lye solution.	NaOH	CAS n°: 1310-73-2 EC N° (EINECS): 215-185-5 Index n°: 011-002-00-6 UN N°: 1824 Class: 8
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First aid information

Intoxication by inhalation: Remove the victim from the polluted area and prop the person up to a half-sitting position. Apply artificial respiration if the person has stopped breathing and provide oxygen if breathing is difficult. Transfer the victim to hospital.

Skin contact: Rinse the skin with clean water for 20 minutes until the product has been eliminated then apply a neutralising solution. Consult a doctor.

Eye contact: Rinse the eyes with plenty of clean water for at least 30 minutes while keeping the eyelids open then apply a neutralising solution. Consult a doctor.

Intoxication by ingestion: Do not induce vomiting. Rinse the mouth and lips with water if the person is conscious, then transfer to hospital urgently.

In the case of ingestion of a very small quantity of diluted solution with a pH of less than 11.5: ensure that the person drinks 1 or 2 glasses of water (only if the person is conscious). Consult a doctor.

In the case of ingestion of a diluted solution with a pH greater than 11.5 or unknown: transfer the victim to hospital without making them drink.

Do not attempt to induce vomiting or to neutralise with acidic agents (vinegar or fruit juice).

Physical data (50% solution)

Relative density (water = 1): 1.52 to 20°C

Relative vapour density (air = 1): N/A

Solubility in fresh water: completely soluble at 20°C (precipitates as of 52%)

Vapour pressure/tension: 2 hPa (mbar) at 20°C

pH of the solution: 14

Viscosity: 78 mPa.s

Freezing point: 12°C for a 50% solution

Olfactory threshold in air: unknown

Diffusion coefficient in water: N/A

Diffusion coefficient in air: N/A

Henry's law constant: N/A

Flash point: N/A

Melting point: N/A

Boiling point: 142 < T < 144°C



C: Corrosive

R35: causes severe burns.

S26: in case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S37/39: wear suitable gloves and eye/face protection.

S45: In case of accident or if you feel unwell, seek medical advice.

215-185-5: EC labelling.

Ecotoxicological data

• **Acute ecotoxicity:**

Daphnia (*Ceriodaphnia dubia*)

LC₅₀ (48H) = 40 mg/L (fresh water)

Fish (*Brachydanio rerio*)

55.6 mg/L < LC₅₀ (96h) < 100 mg/L - pH: 7.9 to 8.1 (fresh water)

Fish (*Lucioperca lucioperca*)

Toxic concentration > 35 mg/L (fresh water)

Marine invertebrate (*Ophryotrocha diadema*)

33 mg/L < LC₅₀ (48H) < 100 mg/L (seawater)

• **Chronic ecotoxicity:** no data available

• **PNEC:** no PNEC was able to be calculated as the buffering capacity, the pH and its fluctuation are very specific to the ecosystem in question. To estimate the effect of a sodium hydroxide spill, the change in pH of the water must be calculated or measured. **Variation by one pH unit could affect flora and fauna** (DRAFT, ECB, 2005). The average pH of water can vary in seawater from 8 to 8.4 (stable pH) and in fresh water from 6 to 7.5.

Toxicological data

Acute human toxicity

The acute toxicity of sodium hydroxide depends on its physical state (solid or in solution), on its concentration and on the dose.

- **By ingestion:** severe burns to the digestive tract, risk of perforation of the alimentary canal, state of shock.
- **By skin contact:** very corrosive for the skin, severe burns, severe lesions, scarring, dermatitis possible in the case of repeated contact.
- **By eye contact:** corrosive for the eyes, severe lesions possibly with lasting effects if the eyes are not rinsed immediately, harm to all the eye tissues, risk of sight loss.
- **By inhalation:** corrosive for respiratory tract.

Chronic human toxicity

Few studies have been conducted, as low concentrations of sodium hydroxide are neutralised by the acidity of the stomach.

Sodium hydroxide 50% solution however has no sensitising potential or mutagenicity.

Persistence in the environment

The risk presented by caustic soda for the environment is due to hydroxyl ions (pH effect). The effect of caustic soda on aquatic organisms therefore depends on the buffering capacity of the aquatic or land-based ecosystem (OECD, 2002).

A pH greater than 9 is harmful for aquatic life. The effect of this ion is naturally reduced by dilution, absorption of carbon dioxide from the air and, for fresh waters, by the natural variation in the pH of the water throughout the day and according to the season.

• Risk for the environment

A high concentration of sodium hydroxide in the water will increase the alkalinity of the water, which can be harmful for aquatic life.

In fresh waters, most algae are killed when the pH exceeds

8.5 and fish cannot tolerate a pH of over 8.4. In seawater, a high pH can cause burns to the scales and gills, and fish die of suffocation.

- **Breakdown:** sodium hydroxide will be transformed into salts depending on the ions present in the environment.
- **Bioaccumulation:** sodium hydroxide is an inorganic substance which does not bioaccumulate along the food chain.
- **MARPOL classification:** D until 31/12/2006
Y from 01/01/2007
- **SEBC classification:** D
- **Octanol/water partition coefficient:** N/A
- **Organic carbon/water partition coefficient:** N/A

Particular risks

- **Polymerisation:** N/A

Danger:

- heating the recipient can cause an increase in pressure and the recipient may shatter.
- possibility of attacking metals and production of hydrogen which may form an explosive mixture with the air.

• Stability and reactivity

- Substances to be avoided: water, acid, zinc, aluminium, copper, alkali metals, alkaline earth metals, acetaldehyde, acroleine, acrylonitrile, allyl alcohol, halon, maleic anhydride, bromine, nitroparaffins, nitroaromatics, oleums, tetrahydrofuran.
- Hygroscopic product sensitive to the carbon dioxide in the air (carbonation).
- Dangerous products of decomposition: at high temperatures, by corrosion of metals, formation of flammable and explosive hydrogen.

Transportation

General data: Class: 8
Corrosive liquid
Labels: 8

Land transportation: RID (rail) /ADR (road)

Hazard classification: 80

Packaging group: II

Classification code: C5

ADN/ADNR

Identification n° (UN): 1824

Hazard classification: 80

Classification code: C5

Maritime and air transportation IMDG/IATA

Packaging group: II

Handling

In high concentration of vapours/clouds:

- Ventilate and evacuate appropriately.
- Provide showers and eye washers.
- Ensure that there is a water source nearby.
- Prevent projections during handling.

Storage

- Store in firmly closed receptacles in a cool and well aerated place.
- Store in a dry environment.
- Keep above 20°C.
- Provide a retention tank and ensure that the ground is impermeable and resistant to corrosion, with a drainage system sending run-off to a neutralisation tank.

ANNEX 4: CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

Dangerous goods (IMO, 2002)

Regulations governing the carriage in bulk of hazardous liquid substances (MARPOL Annex II) provide valuable indications on the hazards that such substances can produce during transportation.

Noxious liquid substances are divided into 4 categories (A, B, C and D) starting with the most dangerous substances (MARPOL A) and ending with the least dangerous ones (MARPOL D).

The MARPOL classification system is based on risk assessment profiles for chemicals transported in bulk by sea, as defined by a GESAMP working group (Group of Experts on the Scientific Aspects of Marine Pollution).

Category A - Noxious liquid substances which, if discharged into the sea from tank washing or deballasting operations, are deemed to present a major hazard to marine resources or human health or can cause serious harm to amenities or other legitimate uses of the sea and therefore justify the implementation of strict pollution response measures.

Category B - Noxious liquid substances which, if discharged into the sea during tank washing or deballasting operations, are deemed to present a hazard to marine resources or human health and can harm amenities or other legitimate uses of the sea and therefore justify the implementation of special pollution response measures.

Category C - Noxious liquid substances which, if discharged into the sea during tank washing or deballasting operations, are deemed to be a minor risk for marine resources or human health or cause, to some extent, harm to amenities or other legitimate uses of the sea and therefore require special operating conditions.

Category D - Noxious liquid substances which, if discharged into the sea during tank washing or deballasting operations, are deemed to be a noticeable risk for marine resources or human health or have a very slight effect on amenities or other legitimate uses of the sea and therefore require certain precautions concerning operating conditions.

ANNEXE 4b: NEW CLASSIFICATION OF NOXIOUS LIQUID SUBSTANCES

Revised MARPOL Annex II (IMO, 2005)

The revised Annex II Regulations for the control of pollution by noxious liquid substances in bulk was adopted in October 2004. It includes a new four-category categorization system for noxious and liquid substances. The revised annex entered into force on 1 January 2007.

The new categories are:

Category X: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a major hazard to either marine resources or human health and, therefore, justify the prohibition of the discharge into the marine environment;

Category Y: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a hazard to either marine resources or human health or cause harm to amenities or other legitimate uses of the sea and therefore justify a limitation on the quality and quantity of the discharge into the marine environment;

Category Z: Noxious Liquid Substances which, if discharged into the sea from tank cleaning or deballasting operations, are deemed to present a minor hazard to either marine resources or human health and therefore justify less stringent restrictions on the quality and quantity of the discharge into the marine environment; and

Other Substances: substances which have been evaluated and found to fall outside Category X, Y or Z because they are considered to present no harm to marine resources, human health, amenities or other legitimate uses of the sea when discharged into the sea from tank cleaning or deballasting operations. The discharge of bilge or ballast water or other residues or mixtures containing these substances are not subject to any requirements of MARPOL Annex II.