Klorgasutsläpp i ett kallvalsverk i en metallindustri.

860311 MARS 1800_003_004

Olyckan inträffade strax före 9.00 i ett lager i den del av ett kallvalsverk där betning (syrabehandling) utförs. En flottörventil som kontrollerade nivån i en tank med natriumhypoklorit hade tillfälligt blockerats av kristaller. Därmed stängdes inte tillflödet av i tid och en okänd mängd natriumhypoklorit rann ut genom skvallerröret. Under skvallerröret befann sig ett kar med vatten, vätefluorid (HF) och salpetersyra (HNO_3). Reaktionen mellan den kraftigt oxiderande natriumhypokloriten och de två syrorna producerade klorgas, och eventuellt också fluorgas. De sex anställda som befann sig i lokalen kände omedelbart lukten av klorgas och skyndade därifrån för att slå larm. Ett räddningslag om fyra personer skickades in för att undersöka om där fanns någon kvar, och för att stänga av tillflödet av natriumhypoklorit. Ungefär klockan 17.00 hade klorgasen skingrats - en koncentration på mindre än 1 ppm uppmättes.

Klorgasen utvecklades till följd av brister i konstruktionen dels av säkerhetssystemet och dels av flöden i fabriken.

Inblandade ämnen och mängder

	CAS Nr.	Mängd
Klor	7782-50-5	Okänt
Natriumhypoklorit	7681-52-9	Okänt
Salpetersyra	7697-37-2	Okänt
Vätefluorid	7664-39-3	Okänt

Skador:

Människor:	10 människor skadades av klorgas. Sex av dem tillbringade en dag på sjukhus, de resterande fyra stannade i upp till fem dagar på sjukhus.
Materiella:	Inga materiella skador rapporterade.
Miljö/ekologi:	Inga skador rapporterade.
Infrastruktur:	Inga effekter rapporterade.

Erfarenheter redovisade (Ja/Nej): Nej

Endast indirekt i form av analys av olyckans orsaker.

Report Profile

Identification of Report:

country: FA **ident key:** 1800_003_04

reported under Seveso I **directive as** major accident **reports:** SHORT+FULL

Date of Major Occurrence: Time of Major Occurrence

start: 11/03/1986 **start:** 09:00:00

finish: 11/03/1986 **finish:**

Establishment:

name:

address:

industry: 2011 metal refining and processing (includes foundries, electrochemical refining, plating, etc.)

Metal

Seveso II status: not applicable: Yes **art. 6 (notification):** No

art. 7 (MAPP): No

art. 9 (safety report): No

Date of Report:

short: full:

Authority Reporting:

name:

address:

Authority Contact:

rep_cont_name:

rep_cont_phone:

rep_cont_fax:

Additional Comments:

a) - not applicable -

b) - not applicable -

c) - not applicable -

d) - not applicable -

e) - not applicable -

Short Report

country: FA **ident key:** 1800_003_04

Accident Types:

release: Yes **explosion:** No

water contamination: No **other:** No

fire: No

description:

SYSTEM ORIGINATING AND OPERATING CONDITIONS:... see Appendix Short Report / description of accident types

Substance(s) Directly Involved:

toxic: Yes **explosive:** Yes

ecotoxic: No **other:** No

flammable: No

description:

- Chlorine (C.A.S. CODE:7782-50-5, E.E.C. CODE: 017-001-00-7): amount involved = not known.... see Appendix Short Report / description of substances involved

Immediate Sources of Accident:

storage: Yes **transfer:** No

process: Yes **other:** No

description:

The accident occurred in the storage area of the second cold rolling mill's pickling section of a metal industry (the location of the second cold rolling mill is shown in Fig. 1 attached to the Original Report). In the pickling section the ... see Appendix Short Report / description of immediate sources

Suspected Causes:

plant or equipment: Yes **environmental:** No

human: No **other:** No

description:

INITIATING EVENT AND CONSEQUENCES:... see Appendix Short Report / description of suspected causes

Immediate Effects:

material loss: No

human deaths: No

human injuries: Yes **community disruption:** No

other: Yes

ecological harm: No

national heritage loss: No

description:

EFFECTS ON PEOPLE:... see Appendix Short Report / description of immediate effects

Emergency Measures taken:

on-site systems: Yes **decontamination:** No

external services: No **restoration:** No

sheltering: No **other:** No

evacuation: No

description:

INTERNAL TO THE ESTABLISHMENT:... see Appendix Short Report / description of emergency measures taken

Immediate Lessons Learned:

prevention: No **other:** Yes

mitigation: No

description:

not given

A Occurrence Full Report

country: FA **ident key:** 1800_003_04

1 Type of Accident

remarks: In a sodium hypochlorite transfer tank, an unknown quantity of sodium hypochlorite flowed into the overfilling pipe owing to the blockage of the float valve that controlled the level in the tank. The overfilling pipe was connected with a ta... see Appendix Full Report A / type of accident

2 Dangerous Substances

remarks: No data are available about the amount of released sodium hypochlorite and of nitric acid and hydrogen fluoride contained in the transfer tank. Also no data are available about the amount of the chlorine gas formed by the reaction of sodium... see Appendix Full Report A / dangerous substances

3 Source of Accident

illustration: - not applicable -

remarks: The accident involved a sodium hypochlorite transfer tank in the storage area (codes 3201 and 4003) of the second cold rolling mill's pickling section of a metal industry [code 2011] (the location of the second cold rolling mill is shown in... see Appendix Full Report A / source of accident - remarks

4 Meteorological Conditions

precipitation none: fog: rain: hail: snow:

No No No No No

wind speed (m/s):

direction (from):

stability (Pasquill):

ambient temperature (°C):

remarks: - not applicable -

5 Causes of Major Occurrence

main causes

technical / physical 5105 operation: instrument/control/monitoring-device failure

5107 operation: unexpected reaction/phase-transition

- not applicable -

- not applicable -

- not applicable -

human / organizational 5307 organization: process analysis (inadequate, incorrect)

5308 organization: design of plant/equipment/system (inadequate, inappropriate)

- not applicable -

- not applicable -

- not applicable -

remarks: In a sodium hypochlorite transfer tank, an unknown amount of sodium hypochlorite flowed into the overfilling pipe owing to the blockage of the float valve (due to the presence of crystals) that controlled the level in the tank (code 5105). ... see Appendix Full Report A / causes of major occurrence

6 Discussion about the Occurrence

- not applicable -

Type of Accident **country:** FA **ident key:** 1800_003_04

event:

major occurrence 1101 release: gas/vapour/mist/etc release to air

initiating event 1999 other: other

associated event - not applicable -

Dangerous substances

country: FA **ident key:** 1800_003_04

a) total establishment inventory

CAS number: 7697-37-2 **identity:** Nitric Acid

name from Seveso I Directive: - not applicable -

name from Seveso II Directive: - not applicable -

category from Seveso II: - not applicable -

other hazards (1): - not applicable -

other hazards (2): - not applicable -

maximum quantity (tonnes): -1

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: -1 **potential quantity:** -1

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 **indir_pot_quant:** -1

a) total establishment inventory

CAS number: 7664-39-3 **identity:**

name from Seveso I Directive: Hydrogen fluoride

name from Seveso II Directive: - not applicable -

category from Seveso II: very toxic

other hazards (1): - not applicable -

other hazards (2): - not applicable -

maximum quantity (tonnes): -1

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: -1 **potential quantity:** -1

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 **indir_pot_quant:** -1

a) total establishment inventory

CAS number: 7782-50-5 **identity:**

name from Seveso I Directive: Chlorine

name from Seveso II Directive: Chlorine

category from Seveso II: toxic

other hazards (1): - not applicable -

other hazards (2): - not applicable -

maximum quantity (tonnes): -1

use of substance as: ABNORMAL PRODUCT

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: -1 **potential quantity:** -1

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 **indir_pot_quant:** -1

a) total establishment inventory

CAS number: 7681-52-9 **identity:** Sodium Hypochlorite

name from Seveso I Directive: - not applicable -

name from Seveso II Directive: - not applicable -

category from Seveso II: - not applicable -

other hazards (1): - not applicable -

other hazards (2): - not applicable -

maximum quantity (tonnes): -1

use of substance as: STARTING MATERIAL

b) substance belongs to relevant inventory directly involved: Yes

actual quantity: -1 **potential quantity:** -1

c) substance belongs to relevant inventory indirectly involved: No

actual quantity: -1 **indir_pot_quant:** -1

Source of Accident - Situation **country:** FA **ident key:** 1800_003_04

situation

industry

inititating event 2011 metal refining and processing (includes foundries, electrochemical refining, plating, etc.)

associated event - not applicable -

activity/unit

major occurrence 3201 storage: process-associated (stockholding, etc. on-site of manufacture)

inititating event 3201 storage: process-associated (stockholding, etc. on-site of manufacture)

associated event - not applicable -

component

major occurrence 4003 container; non-pressurised (hopper, tank, drum, bag, etc.)

inititating event 4003 container; non-pressurised (hopper, tank, drum, bag, etc.)

associated event - not applicable -

B Consequences Full Report

country: FA **ident key:** 1800_003_04

1 Area concerned

affected

extent of effects installation: Yes

establishment: Yes

off-site; local: No

off-site; regional: No

off-site; transboundary: No

illustration of effects - not applicable -

remarks In the Original Report there is no evidence of significant effects outside the b... see Appendix Full Report B / area concerned - remarks

2 People

establishment popul. emergency personnel off-site population

total at risk -1 -1 -1

immediate fatalities 0 0 0

subsequent fatalities 0 0 0

hospitalizing injuries 10 0 0

other serious injuries 0 0 0

health monitoring 0 0 0

remarks 10 people were injured by the chlorine release. The six workers of ALZ were take... see Appendix Full Report B / people

3 Ecological Harm

pollution/contamination/damage of:

- residential area (covered by toxic cloud) Suspected

- common wild flora/fauna (death or elimination) Suspected

- rare or protected flora/fauna (death or elimination) Suspected

- water catchment areas and supplies for consumption or recreation Suspected

- land (with known potential for long term ecological harm or Suspected

preventing human access or activities)

- marine or fresh water habitat Suspected

- areas of high conservation value or given special protection Suspected

remarks In the Original Report there is no evidence of significant ecological harms.... see Appendix Full Report B / ecological harm

4 National Heritage Loss

effects on:

- historical sites not applicable **- historic monuments** not applicable

- historic buildings not applicable **- art treasures** not applicable

remarks No data available.

5 Material Loss

establishment losses off site losses

costs (direct costs to operator) (social costs)

in ECU BFr ECU BFr

material losses -1 -1 -1 -1

response, clean up, restoration -1 -1 -1 -1

remarks No material losses occurred except the lost substances.... see Appendix Full Report B / material loss

6 Disruption of Community Life

establishment/plant evacuated disabled/unoccupiable destroyed

- nearby residences/hotels No No No

- nearby factories/offices/small shops No No No

- schools, hospitals, institutions No No No

- other places of public assembly No No No

interruption of utilities etc. no / yes duration

- gas No

- electricity No

- water No

- sewage treatment works No

- telecommunications No

- main roads No

- railways No

- waterways No

- air transport No

significant public concern none local level national level

- off site populations Yes No No

- media interest No No No

- political interest No No No

remarks In the Original Report there is no evidence of significant effects outside the b... see Appendix

7 Discussion of Consequences

Ecological Components involved

country: FA **ident key:** 1800_003_04

type: - not applicable -

threatened: not applicable **affected:** not applicable

C Response Full Report

country: FA **ident key:** 1800_003_04

1 Emergency Measures

taken - on site - not applicable - - not applicable -

- not applicable - - not applicable -

- not applicable - - not applicable -

- off site - not applicable - - not applicable -

- not applicable - - not applicable -

- not applicable - - not applicable -

still - on site - not applicable - - not applicable -

required

- not applicable - - not applicable -

- not applicable - - not applicable -

- off site - not applicable - - not applicable -

- not applicable - - not applicable -

- not applicable - - not applicable -

continuing contamination or danger

-on site not applicable

-off site not applicable

remarks - not applicable -

2 Seveso II Duties

pre-accident evaluation

Article item not due yet not done done/submitted evaluated

6 notification No No No No

7 policy (MAPP) No No No No

9 safety report No No No No

9, 10, 11 update No No No No

11 internal plan No No No No

11 external plan No No No No

13 informing public No No No No

9, 12 siting policy No No No No

post-accident evaluation

Seveso II duty was actual were actual compared with actual

contingency consequences consequences, the

addressed? addressed? predicted extent was?

Article item

7 policy (MAPP) not applicable not applicable not applicable

9 current safety report not applicable not applicable not applicable

11 internal plan not applicable not applicable not applicable

11 external plan not applicable not applicable not applicable

13 informing public not applicable not applicable not applicable

9, 12 siting policy not applicable not applicable not applicable

evaluation of safety organisation

organisational element element existed **did element relate to actual circumstances of**

yes / no no / partly / yes adequate?

- written policy objectives No

- specified management No

structure

- specified responsibilities No

- specified working procedures No

- specified procedures for No

assessment/auditing of

management system

- specified procedures for No

review and update of

management policy

- specified general training No

procedures

- specified emergency No

training procedures

evaluation of ecological impact control

organisational element element existed **did element relate to actual circumstances of**

yes / no no / partly / yes adequate?

- ecological status review No

before incident

- potential ecological No

consequences assessment

- ecological impact review No

after incident

- ecological restoration No

procedures

- subsequent review of No

restoration success

remarks - not applicable -

3 Official Action Taken

legal action

- not applicable -

other official action

- not applicable -

4 Lessons Learned

measures to prevent recurrence

not given

measures to mitigate consequences:

not given

useful references:

not given

5 Discussion about Response

- not applicable -

Appendices for the FA / 1800_003_04 report

Appendix Short Report / description of accident types:

SYSTEM ORIGINATING AND OPERATING CONDITIONS:

Storage area of the second cold rolling mill's pickling section.

ACCIDENT CASE HISTORY DESCRIPTION:

In a sodium hypochlorite transfer tank, an unknown amount of sodium hypochlorite flowed into the overfilling pipe owing to the blockage of the float valve (due to the presence of crystals) that controlled the level in the tank. Therefore, when the level reached the maximum value, the valve did not stop the pump. The overfilling pipe was connected with a tank installed below, covered with a metal grid, which was containing water, nitric acid and hydrogen fluoride. The reaction of the sodium hypochlorite with the two acids produced chlorine gas and probably fluoride gas. The release occurred at 08:45 am. In the area there were 6 employees and each of them noticed a strong smell of chlorine and left the building as soon as possible. The security department was immediately alerted which in turn alerted the medical service and the management. A 4 men rescue team was formed and instructed to enter the pickling section to check if someone was still there. They were also instructed to switch-off the equipment. The rescue team found that the sodium hydroxide transfer tank had overflowed and the liquid had run into the tank below containing water, nitric acid and hydrogen fluoride. The pump which was transferring the sodium hypochloryte from the storage tank to the transfer tank had already stopped. Since chlorine gas is heavier than air, it was expected that it would take some time for the chlorine vapours to disperse from the building. At about 17:00 hours the production was started up again since no more than 1ppm concentration of chlorine could be detected in the production hall by means of Draeger tubes.

Appendix Short Report / description of substances involved:

- Chlorine (C.A.S. CODE:7782-50-5, E.E.C. CODE: 017-001-00-7): amount involved = not known.

- Sodium Hypochlorite (C.A.S. CODE: 7681-52-9): amount involved = not known.

- Nitric Acid (C.A.S. CODE: 7697-37-2): amount involved = not known.

- Hydrogen Fluoride (C.A.S. CODE: 7664-39-3): amount involved = not known.

Appendix Short Report / description of immediate sources:

The accident occurred in the storage area of the second cold rolling mill's pickling section of a metal industry (the location of the second cold rolling mill is shown in Fig. 1 attached to the Original Report). In the pickling section the oxide layer (formed during hot rolling and annealing) was removed from the surface of the metal. Pickling was performed in baths (10m long, 40m3 capacity) with water containing HF(1%ö3%) and HNO3 (4%ö6%) at 50øCö60øC. During the oxides dissolution, the fumes produced (containing HNO3, HF, NO2 and NO) were aspirated by means of ventilators and scrubbed in two stages (the system block diagram is shown in Fig. 3 attached to the Original Report). Nitric acid was neutralized in the first absorption tower with sodium hydroxide. Nitrogen oxide was oxidized whilst nitrogen dioxide was reduced with an alkaline solution of KMnO4. The waste waters from the absorption towers, containing nitrites and nitrates, were neutralized with sodium hypochlorite added from a 2 m3 transfer tank automatically filled by means of a pump. This pump automatically started when the minimum level in the transfer tank was reached and stopped when the maximum level was reached. The tanks containing the liquids used in the pickling section were located in the storage area, as shown in Fig. 2 attached to the Original Report. The following storage tanks are important for the accident: sodium hydroxide A, sodium hypochlorite B, sodium trisulphate C, sodium hypochlorite D, the 150 m3 tank where water and acids were sometimes present (it was located under the sodium hypochlorite transfer tank E). When the accident occurred in the storage area there were 6 employees: two people from Democo company painting the sodium hydroxide A and the sodium hypochlorite B storage tanks; two people of Decometa company fitting a heat exchanger to the sodium trisulphate storage tank C; two people of ALZ who were responsible for checking the operations.

Appendix Short Report / description of suspected causes:

INITIATING EVENT AND CONSEQUENCES:

In a sodium hypochlorite transfer tank, an unknown amount of sodium hypochlorite flowed into the overfilling pipe owing to the blockage of the float valve (due to the presence of crystals) that controlled the level in the tank. The overfilling pipe was connected with a tank installed below, covered with a metal grid, which was containing water, nitric acid and hydrogen

fluoride. The reaction of the sodium hypochlorite (a very strong oxidizing agent) with the two acids produced chlorine gas (by oxidation of chlorides) and probably fluoride gas (by oxidation of fluorides) but there is no evidence of it.

CAUSES:

In a sodium hypochlorite transfer tank, an unknown amount of sodium hypochlorite flowed into the overfilling pipe owing to the blockage of the float valve (due to the presence of crystals) that controlled the level in the tank. Therefore, when the level reached the maximum value, the valve did not stop the pump (the control had only temporarely jammed since the rescue team found that the pump had automatically stopped). The overfilling pipe was connected with a tank installed below, covered with a metal grid, which was containing water, nitric acid and hydrogen fluoride. The reaction of the sodium hypochlorite (a very strong oxidizing agent) with the two acids produced chlorine gas (by oxidation of chlorides) and probably fluoride gas (by oxidation of fluorides) but there is no evidence of it.

Besides, the emergency level (i.e. the level at which the stop signal was given to the transfer pump) was too close to the overfilling pipe. This, together with the excessive length (about 75 metres) of the piping between the pump and the transfer tank, may cause the tank overfilling even if the pump stops when the liquid reaches the emergency level.

Finally, the overfilling pipe from the transfer tank was erroneously connected (due to inadequate process analysis and plant design) with the tank below which may contain acids.

Appendix Short Report / description of immediate effects:

EFFECTS ON PEOPLE:

10 people were injured by the chlorine release. The six workers of ALZ were taken to the St. Jansziekenhuis hospital in Genk (they were hospitalized for 1 day). Two people of Democo company and two people of Decometa company were hospitalized from number of days ranging between one and five.

OTHER:

No material losses occurred except the lost substances.

Appendix Short Report / description of emergency measures taken:

INTERNAL TO THE ESTABLISHMENT:

When the release occurred, 6 employees were present and each of them noticed a strong smell of chlorine (there is no evidence that fluoride gas was present) and left the building as soon as possible. A chlorine detector, located 3 metres away from the sodium hypochlorite transfer tank, activated an alarm (it was set to operate at a chlorine concentration in air of 1 ppm). The security department was immediately alerted which in turn alerted the medical service and the management. A 4 men rescue team was formed and instructed to enter the pickling section to check if someone was still there. They were also instructed to switch-off the equipment. The rescue team found that the sodium hydroxide transfer tank had overflowed and the liquid had run into the tank below containing water, nitric acid and hydrogen fluoride. The pump which was transferring the sodium hypochloryte from the storage tank to the transfer tank had stopped. No measurements were carried out immediately after the accident to estimate the chlorine and fluoride contents in the air. Since chlorine gas is heavier than air, it was expected that it would take some time for the chlorine vapours to disperse from the building. ALZ's security service carried out measurements later with Draeger tubes to detect the presence of chlorine gas in the building. At about 17:00 hours the production was started up again since no more than 1ppm concentration of chlorine could be detected in the production hall by means of Draeger tubes.

Appendix Full Report A / type of accident:

In a sodium hypochlorite transfer tank, an unknown quantity of sodium hypochlorite flowed into the overfilling pipe owing to the blockage of the float valve that controlled the level in the tank. The overfilling pipe was connected with a tank installed below, covered with a metal grid, which was containing water, nitric acid and hydrogen fluoride (code 1999). The reaction of the sodium hypochlorite with the two acids produced chlorine gas and probably fluoride gas (code 1101).

Appendix Full Report A / dangerous substances:

No data are available about the amount of released sodium hypochlorite and of nitric acid and hydrogen fluoride contained in the transfer tank. Also no data are available about the amount of the chlorine gas formed by the reaction of sodium hypochlorite with nitric acid and hydrogen fluoride.

Appendix Full Report A / source of accident - remarks:

The accident involved a sodium hypochlorite transfer tank in the storage area (codes 3201 and 4003) of the second cold rolling mill's pickling section of a metal industry [code 2011] (the location of the second cold rolling mill is shown in Fig. 1 attached to the Original Report). In the pickling section the oxide layer (formed during hot rolling and annealing) was removed from the surface of the metal. Pickling was performed in baths with water containing HF(1%ö3%) and HNO3 (4%ö6%) at 50ö60øC.

Appendix Full Report A / causes of major occurrence:

In a sodium hypochlorite transfer tank, an unknown amount of sodium hypochlorite flowed into the overfilling pipe owing to the blockage of the float valve (due to the presence of crystals) that controlled the level in the tank (code 5105). The overfilling pipe was erroneously connected (codes 5307 and 5308) with a tank containing water, nitric acid and hydrogen fluoride. The reaction of the sodium hypochlorite (a very strong oxidizing agent) with the acids produced chlorine gas (code 5107).

Appendix Full Report B / area concerned - remarks:

In the Original Report there is no evidence of significant effects outside the building where the chlorine release occurred.

Appendix Full Report B / people:

10 people were injured by the chlorine release. The six workers of ALZ were taken to the St. Jansziekenhuis hospital in Genk (they were hospitalized for 1 day). Two people of Democo company and two people of Decometa company were hospitalized from number of days ranging between one and five.

Appendix Full Report B / ecological harm:

In the Original Report there is no evidence of significant ecological harms.

Appendix Full Report B / material loss:

No material losses occurred except the lost substances.

Appendix Full Report B / disruption of community life:

In the Original Report there is no evidence of significant effects outside the building where the chlorine release occurred.