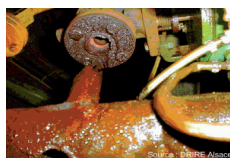




## ACCIDENTOLOGY INVOLVING HYDROGEN







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Hydrogen ( $H_2$ ), often presented as the future source of energy due to its high energy potential and clean combustion, evokes both hope and fear.

In the minds of people, hydrogen is often synonymous with danger especially since the Hindenburg disaster on 6 May 1937. On that day, the Zeppelin inflated with 200,000 m<sup>3</sup> of  $H_2$  ignited in less than a minute resulting in the death of 35 out of the 97 passengers who jumped out of the airship out of panic. Even though the origin of the ignition is unknown, the combined combustion of hydrogen and the coating of the shell (butyrate, iron and aluminium oxide) is the cause. This caused such a fear of hydrogen called the "Hindenburg syndrome" that ever since the gas supply to the town from coking plant made up of 96 %  $H_2$  was called "water gas" to avoid any commercial repercussions !

The best way to calm the fears is to carry out an objective analysis of risks related to hydrogen in order to define and implement preventive and protective measures to avoid such accidents from reoccurring or at least keep the consequences to a strict minimum.

This abstract, based on the analysis of 215<sup>1</sup> accidents recorded in the ARIA database involving hydrogen and having occurred before 1 July 2007<sup>2</sup>, aims at doing so. In light of the available data, the abstract which does not seek to provide statistical information, helps nevertheless drawing lessons on the risks involving hydrogen using specific indicators from the accidentology.



<sup>1</sup> The ARIA numbers included in the text correspond to a non exhaustive selection of accidents illustrating this document. The summaries of the accidents whose number is underlined are listed at the end of the document or in a box. The list of the 215 accidents or incidents, among them 92 abroad, that were used for this abstract is available on the [www.aria.developpement-durable.gouv.fr](http://www.aria.developpement-durable.gouv.fr) website, part « Analysis and feedback ».

<sup>2</sup> Data collection is organised in France since 1st January 1992, when the ARIA database was set up. Nevertheless, accidents that occurred prior to this date might be also recorded, depending on the available data.

### a) Types of accidents and their consequences

One of the specific characteristics of accidents involving hydrogen is the seriousness of their consequences as illustrated by the table below :

Consequences	On a sample comprising 213 cases with known consequences	
	Nb of cases	%
Deaths	25	12
Serious injuries	28	13
Injuries (including serious ones)	70	33
Internal material damage	183	86
External material damage	17	8
Internal operating losses	89	42
Evacuated population	8	3,8

Thus, 25 mortal accidents involving hydrogen including 5 French accidents (ARIA 169, 170, 176, 3512 and 7956) are recorded in the ARIA database and constitute 12 % of the studied sample. These accidents have resulted in 80 deaths including 9 in France.

Accidents with and without serious injury respectively account for 13 and 33 % of the studied sample.

However, it must be noted that the human consequences for hydrogen-related accidents mainly target employees of disaster sites. Rescue workers and the general public are only rarely affected. Thus, all mortal accidents whose deaths are detailed concern employees.

These facts are related to the accident typology involving hydrogen, as well as the rapid kinetics of the underlying phenomena : **84% of the studied events include fires and/or explosions**. The remaining 16% concern non-ignited H<sub>2</sub> leaks, runaway reactions without explosion or corrosion detected prior to accident.

### b) Main activities concerned

The following table lists the main sectors of activity concerned by accidents involving hydrogen.

Activities	On a 215 cases sample	
	Nb of cases	%
Chemical sector*	84	39
Refining / petrochemical industry*	47	22
Transport, packaging and storage	35	16
Metallurgy / metal works	17	7,9
Waste treatment / recycling	8	3,7
Nuclear industry	5	2,3

\* excluding transport, packaging and storage

Two types of activities can be identified :

- activities where hydrogen is either produced or used : chemical, refining, transport, packaging, nuclear industry,
- activities where hydrogen is accidentally produced : metallurgy and metal works, sanitation, waste treatment and recycling.

In Saint-Fons (69), in 1988, grinding operations were scheduled on a tank having stored sulphuric acid. All operation procedures were properly carried out. Nevertheless, a deflagration occurred inside the tank at the start of the operation. Casualties include one death and two cases of serious injury. The tank was partly destroyed. The explosion occurred due to the presence of hydrogen (100 g) in a dead area where no measurements were taken. The hydrogen resulted from the corrosion of the iron tank under the action of sulphuric acid. (ARIA 169)

## II. PROPERTIES OF DIHYDROGEN AND ASSOCIATED RISKS

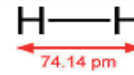
Dihydrogen is gaseous at room temperature and pressure. It cannot be detected by humans as it is colourless, odourless and non-toxic and is found in trace quantities in the atmosphere.

In the XVIIIth century, Lavoisier suggested to re-name the gas previously referred to as "flammable air" by Cavendish referring to its combustive nature as "hydrogen" which literally means "that produces water".

The main physico-chemical properties of hydrogen give rise to specific risks discussed later. These include :

- low molar mass and small size giving it a high tendency to leak,
- extreme flammability and low ignition energy,
- ability to embrittle metals and alloys by altering their mechanical properties,
- violent reactions with certain compounds due to its reducing properties.

### Dihydrogen



Formula	H <sub>2</sub>
Molar mass	2,016 g/mol
Mass per vol. of gaz (20°C/1 atm)	0,08342 kg/Nm <sup>3</sup>
Water solubility (vol/vol at 15,6°C)	0,019
Boiling point (1 atm)	-252,8 °C
Mass per vol. of liquid at boiling point	70,96 kg/m <sup>3</sup>

Source : IRH, University of Quebec

### a) Hydrogen : a light weight compound

Hydrogen is the smallest atom and in its diatomic form is the lightest of all gases. In its liquid or gaseous state, H<sub>2</sub> has an **especially high tendency to leak** due to its low viscosity and molecular weight. Its low viscosity alone makes the escape rate of liquid hydrogen 50 times greater than water and 10 times greater than liquid nitrogen [1].

In its gaseous state, hydrogen also has the lowest viscosity at room temperature among all other gases. Therefore, it easily crosses porous walls and easily escapes through the smallest gaps. It can thus leak from a device or circuit that is tight to air or any other gas (ARIA 7518).

Consequently the weak points of facilities to **monitor** naturally include **insulation valves** (ARIA 170 and 176), **connecting and related joints** (ARIA 7518, 19490, 23140, 26429, 26619, 30720, 31715, and 32147) while ensuring that such **equipment is properly tightened** (ARIA 26616, 26617, 32174, 32147, 32817 and 32796).

### b) Hydrogen : an extremely flammable substance

Hydrogen is classified among the "extremely flammable" substances as shown by its properties compared with methane and petrol in the below table:

Properties		Hydrogen	Methane	Petrol
Ignition limits in air	(vol. %)	4 - 75	5,3 - 15	1,0 - 7,6
Detonation limits in air	(Vol. %)	13 - 65	6,3 - 13,5	1,1 - 3,3
Minimum ignition energy in air (MIE)	(mJ)	0,02	0,29	0,24
Heat of combustion	(kJ/g)	120	50	44,5
Self-ignition temperature	(°C)	585	540	228 - 501
Flamme temperature	(°C)	2 045	1 875	2 200
Theoretical explosion energy	(kg TNT/m <sup>3</sup> <sub>gaz</sub> )	2,02	7,03	44,22
Diffusion coefficient in air	cm <sup>2</sup> /s	0,61	0,16	0,05

Source : Hydrogen, the energy carrier, TÜV Bayern Group

As mentioned before, the main **risk** involved with hydrogen is that of **fire or explosion** (84% of recorded accidents) due to its very **wide flammability range** (from 4 to 75 % in air, even more in atmosphere rich in oxygen or chlorine), as well as its very **low ignition energy**.

Accidentology has recorded several ignition sources of flammable clouds formed by hydrogen : hot spot (ARIA 169, 15339, 27273 and 30365), lightning (ARIA 343), electricity (ARIA 542 and 25112), mechanical sparks (ARIA 10095) and even static electricity (ARIA 6716).

## II. PROPERTIES OF DIHYDROGEN AND ASSOCIATED RISKS

Even though completely dust-free hydrogen does not catch fire easily upon leaving a pipeline or escaping from a leaking joint, ignition follows quickly when the gas comes in contact with dust particles [2], which is often the case in an industrial environment (ARIA 170, 1089, 4799, 26619 and 30720). The presence of fine water droplets in the gas can also trigger ignition [2].

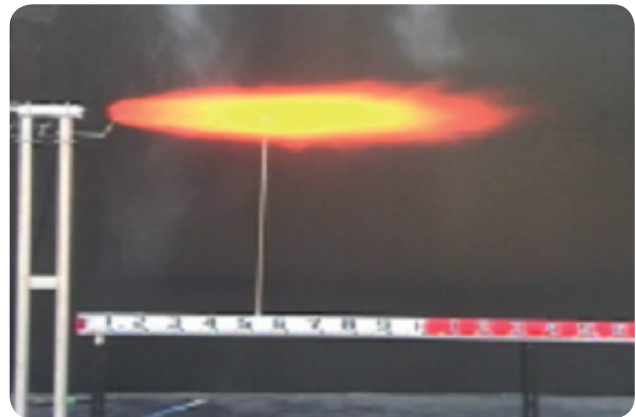
Moreover, hydrogen's combustion flame is extremely dangerous as it is not very visible in general (colourless except when impurities such as carbon particles are present).

In some cases, the ignition of a flammable hydrogen cloud can result in an **explosion in form of a deflagration or detonation** (ARIA 29864). The theoretical detonation limit of hydrogen in air ranges from 13 to 65 % in volume, but several other parameters come into play in the explosion : turbulence on account of obstacles in the environment, etc.

A **high concentration in a specific zone** (above 4% in air), for instance in a dead zone or above a capacity is hazardous as illustrated by the explosion of hydrogen during works on a tank. Explosimetry measurements did not allow the detection of hydrogen accumulated in the tank at height, with difficult access (ARIA 169).

However, the high rate of diffusion of  $H_2$  gas in the air ( $0.61 \text{ cm}^2/\text{s}$ ), 3.8 times higher than air itself can prove to be an advantage in safety matters. In fact, its rapid dilution when released into the atmosphere reduces the risk of an intrinsic explosion. An experiment illustrated that when 500 gallons ( $1.89 \text{ m}^3$ ) of liquid hydrogen was released, its diffusion helped obtain a non-explosive atmosphere after 1 min [1].

**Thus, preference should be given to systems in an unconfined, non-congested and preferably open environment with good ventilation.**



Ignited stream of pressurised hydrogen in the laboratory  
Source : Research Core for Explosion Safety, AIST (D.R.)

### c) Degradation of metals and alloys by hydrogen

The degradation of metals and alloys continuously exposed to hydrogen can cause substances to leak or equipment to break suddenly. Two modes of degradation can be distinguished for steels : hydrogen embrittlement and hydrogen attack.

From a theoretical standpoint, these phenomena have not been fully understood and are rather complex. Basically it involves the diffusion of hydrogen (atomic or not depending on the case) in the materials and especially in the cavities, grain boundaries or interfaces. The recombination of atoms (to form  $H_2$  in the case of embrittlement and to form methane ( $CH_4$ ) at high temperature in the case of hydrogen attack) exerts a pressure on the matrix that irreversibly damages the material. [8] [9]



Hydrogen blistering on the wall of a capacity.  
Source : www.maverickinspection.com (D.R.)

**Hydrogen embrittlement includes several phenomena:**

- hydrogen blistering : absorption of atomic hydrogen on the surface of low resistance materials resulting in blisters (ARIA 324 and 33330).
- hydrogen embrittlement : absorption of atomic hydrogen on the surface of high resistance materials resulting in low ductility and increased internal stress (ARIA 437 and 14666).
- hydrogen induced cracking and hydrogen stress cracking : blister formation that may effect the integrity of materials especially when stressed (ARIA 2903, 7315 and 22229).



## II. PROPERTIES OF DIHYDROGEN AND ASSOCIATED RISKS

**High-temperature hydrogen attack** leads to loss of resistance and ductility resulting in internal cracks and decarburization due to the reaction of the absorbed hydrogen with the carbides of the material (ARIA 26621).

It must be noted that the two above-mentioned modes of degradation depend on a large number of parameters and especially the material (state, composition, microstructure, etc.), the environment (gaseous, watery, temperature, etc.) and the mechanical strain (static, dynamic, cyclic, etc.) [8]

Accidentology shows that the phenomena is frequently observed at elbows of pipes or under specific conditions of stress (ARIA 324, 11282, 13392, 20356, 21196, 22229 and 23175).

Various **preventive measures** may be planned depending on the type of damage : **choice of materials** (low impurities, specific alloys such as aluminium alloys, one of the rare metals less sensitive to hydrogen attack, etc.), **use of coatings, elimination of stress, improved design and fitting, etc.**

### d) Reaction with chlorine

Chlorine reacts spontaneously with hydrogen as shown in the following reaction  $H_2 + Cl_2 \rightarrow 2 HCl$ . The reaction is slow in the absence of light but explosive when light or heat are present (ARIA 17070). It can also be triggered by the energy resulting from the turbulent flow of fluids against the walls of a pipeline (ARIA 26208). In the worst case scenario, the lower explosive limit of hydrogen can drop to 3.1 % in the presence of chlorine (ARIA 10316, 14987, 22101).

The rise in temperature after an explosion can moreover lead to chlorine / metal combustion (ARIA 6511 and 6818), causing the equipment to be consumed (ARIA 26208). In fact the maximum temperature up to which an equipment can resist chlorine is 100°C for lead, 120 °C for soft steel, 150 °C for stainless steel and tantalum, and 200 °C for silver and copper. This is a parameter that must be taken into account in electrolysis facilities that use both chlorine and hydrogen (ARIA 6444 and 30637).



ARIA 26028 - Missing section of a pipeline due to iron/chlorine combustion

### e) Special feature of cryogenic hydrogen

Cryogenic hydrogen is stored in liquid form at -253 °C (ARIA 2915). At this temperature, many materials become brittle or friable. Therefore, the design of facilities must take this phenomenon into account.

Moreover, at this temperature, solidification of nitrogen or air gases may obstruct the pipes and prevent machine parts from working properly. The contamination of liquid hydrogen by oxygen or air can thus lead to explosions (ARIA 26618).

In Belgium, in 1992, process gas (80% hydrogen, 14% methane, 1.8% hydrogen sulphide, C2, C3 and C4 gases at 50 bar and 300°C) leaked from the elbow of a desulphurisation unit pipeline. The inflammable cloud released into the air exploded and triggered a fire. The refinery was shutdown, and a major part of the facilities destroyed. Traffic in the adjoining roads and in the town of ESCAUT was interrupted for 1 hour.

The elbow, already corroded, had been replaced in 1989 and a follow-up was done regularly. The enquiry following the accident revealed the source of the leak to be a spontaneous crack at the 90° elbow on the 8'' pipeline. The facility was rebuilt by reducing the use of the 90°C elbow and the gas transfer speed by increasing the diameter of the pipelines. (ARIA 22229)



### III. ACCIDENTAL GENERATION OF HYDROGEN

In 21% of the 215 accidents of the sample studied, i.e. 46 cases, hydrogen is generated accidentally. Such circumstances are even more hazardous as very often the risk is not taken into account or not properly assessed. Consequently, no measures are implemented to counter the risk.

Accidentology shows that various phenomena can lead to the generation of hydrogen especially :

- corrosion of steels,
- reactions water / metal,
- formation of water gaz,
- other chemical reactions involving hydrides.

#### a) Corrosion of steels

In the ARIA database, 13 accidents have been identified where hydrogen was formed due to the corrosion of steel. Iron and other usual metals (zinc, aluminium) are attacked by diluted acids and release hydrogen according to the following reaction :



Stainless steel is especially sensitive to pitting corrosion in the presence of aqueous solutions charged with chlorine, bromine or especially hypochlorite ions. In the nucleus, an oxidation-reduction couple is created between the discontinuous zones that constitute small anodes where the metal is dissolved and the rest of the surface where the cathodic reaction takes place generating hydrogen.

All types of facilities are concerned by this phenomenon : firstly, the acid storage tanks (ARIA 169, 22278, 27273 and 31082), but also retention tanks (ARIA 6346 et 24977), reactors (ARIA 22101 and 23017), transport pipelines (ARIA 29864), tanker trucks and rail tankers (ARIA 7192 and 9477) etc.

The risk increases especially when water is added to an equipment containing or having stored concentrated acids (dilution of acid), either accidentally (ARIA 31082), or during cleaning (ARIA 9477).

As mentioned before, the generation of even very small quantities of hydrogen this way is enough to cause an accident as soon as the concentration of  $\text{H}_2$  crosses the flammability limit e.g. in an unused pipeline or in the upper portion of the tank (ARIA 169).

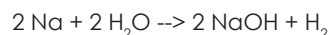


Source : DRIRE Rhône-Alpes  
ARIA 29864 - Hydrogen explosion in a chlorine transport pipe

#### b) Reactions of water / acid with metal

The studied sample includes 20 accidents resulting from contact between water or acid with metal.

Alkaline metals (lithium, sodium, potassium, etc.) and to a lesser extent alkaline earth metals (magnesium, calcium, etc.) react rather violently with water and generate hydrogen that can subsequently ignite or explode depending on the exothermicity of the reaction (ARIA 14162, 15018, 15532, 18298, 28513, 30857 and 31605). The reaction for sodium for instance is as follows :



These reactions are even more violent when the metal is in a divided state like aluminium powder (ARIA 8966, 13017, 22518 and 25689) or at high temperature. Most metals that are not sensitive to the action of water at temperatures below 100°C can decompose even very pure water when the temperature is high enough, leading to the generation of hydrogen.

For example, the layer of hydroxide formed on magnesium on contact with water ( $\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg}(\text{OH})_2 + \text{H}_2$ ) protects it from any further corrosion (passivation). On the contrary, at a temperature above 70°C, magnesium decomposes water producing hydrogen and Magnesia ( $\text{MgO}$ ). The higher the temperature is, the faster the reaction takes place [2] (ARIA 4525).

In Italy, in 1985, a sulphuric acid ( $\text{H}_2\text{SO}_4$ ) container exploded while two technicians were performing oxyacetylene cutting operations in the vicinity to remove plates fixed by nuts. The two technicians died in the explosion. The capacity was projected across the workshop and destroyed two other  $\text{H}_2\text{SO}_4$  containers whose contents spilled onto a retention tank. The explosion resulted from the ignition of the hydrogen accumulated in the tank by the oxyacetylene flame. Hydrogen was formed by the corrosion of the steel tank by the sulphuric acid due to insufficient maintenance of the storage equipment. (ARIA 22278)

### III. ACCIDENTAL GENERATION OF HYDROGEN

These oxidation-reduction phenomena are rather frequent in the metallurgy industry when water comes in contact with molten metal (ARIA 3512, 6390, 13182, 15083, 23317 and 23968) that results in projections. For example :

- liquid  $\text{H}_2\text{O}$   $\rightarrow$  gaseous  $\text{H}_2\text{O}$ : the instant evaporation of water causes projections of liquid metal as well as a pressure wave due to the expansion in volume.
- metallic reducing agent +  $\text{H}_2\text{O}$   $\rightarrow$  oxidised metal +  $\text{H}_2$  (e.g. with aluminium:  $2 \text{Al} + 3 \text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3 \text{H}_2$ ): the oxidation-reduction reaction generates hydrogen that gradually burns as it is produced (ARIA 4525) or leads to a very violent explosion which effects similar to the ones caused by several kilograms of TNT (in the order of one kilogram of TNT for a few hundred millilitres of water reacting with molten aluminium [7]).

These reactions likely to lead to explosions are little-known by some operators. The risks must be thoroughly assessed especially when alkaline, alkaline earth or molten metals or metals in powder form (aluminium, magnesium) are involved. The risk assessment aims at implementing adapted preventive measures and rescue means such as good facility design that helps avoiding the addition of water or oxidising agent as well as the training of technicians.

#### c) Formation of water gas

Water gas, that is a mixture of hydrogen and carbon monoxide (CO), is formed when carbonaceous materials at very high temperatures (1 000°C) come into contact with water as illustrated by the following endothermic reaction :

$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$  The explosion of this mixture results in its combustion with atmospheric oxygen :  $(\text{CO} + \text{H}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O})$ .

Several cases of accidental formation of water gas have been recorded in the ARIA database (ARIA 20066, 27877, 29011...). They all involve fire-fighting operations where carbonaceous materials heated to very high temperatures (coke, coal, wood chips) due to a fire result in an explosive mixture of hydrogen and carbon monoxide when doused with water. This phenomenon is sometimes not taken into account. It can nevertheless also occur when a smouldering in a silo, landfill or storage facility is quenched.

Taking the risk into account helps plan fire-fighting measures adapted to such material by avoiding the use of water (smothering, covering with inert materials, etc.)

#### d) Reactions involving hydrides

Hydrides ( $\text{MxHy}$ ) that are currently used to store hydrogen in some fuel cells are compounds that are a natural « source » of hydrogen with a potential risk of accidental release as shown by the 4 accidents involving sodium borohydride recorded in the ARIA database (ARIA 984, 5136, 24767 and 30679).

These compounds are strong reducing agents used in the pharmaceutical industry and react with oxidising agents (especially air and moisture) to form hydrogen. Generally instable at high temperatures, the breakdown of hydrides generates hydrogen (ARIA 9841 et 30679).

Accidentology shows that the risks involving hydrides must also be taken into account in the management of chemical wastes (procedures, training of staff). In two cases, the accident did not occur during their use but after being released into wastewater or waste (ARIA 24767 and 30679).

In Pessac (33), in 1995, a violent reaction occurred between molten metal and water following accidental contact at an ingot mould coming out of a melting furnace. The metal-vapour mixture was projected. Five technicians in the vicinity sustained burns mainly in the upper limbs and head and were hospitalised. The foundry was shutdown and a legal expertise was ordered. The production of parts was not directly impacted by the accident. The material damage stood at 2 MF. (ARIA 6390)

In Champagnier (38), in 2005, an explosion ripped through a pipeline transporting gaseous chlorine between a chemical platform (producer) and an elastomer manufacturing plant (user). [...]

Analysis of the accident showed that an  $\text{H}_2/\text{Cl}_2$  explosion caused the damage. The formation of  $\text{H}_2$  (20%) can be explained by the combination of several elements: The accidental introduction of humidity into the piping during a previous maintenance operation may have led to hydration of the ferric chloride present in the pipe's environment. According to the operator, the change in the deposit's crystalline phase due to excessive heating of the pipe (80 to 90 °C) promoted corrosion in the steel pipe (by the hypochlorous acid) and the formation of  $\text{H}_2$ . This heating is due to a temperature sensor that lost its electrical power supply 3 days earlier after a cable on the user's site was broken when a slab protecting the structure was poorly handled.

In fact, the proportion of hydrogen (20%) released in the gaseous chloride contained in the pipe, which was capped at each end and kept at low pressure (0.25 bar), formed an explosive mixture requiring very little initiation energy to ignite (in the order of a dozen micro joules).

The operator cleaned the inside of the structure (2.5 to 3 t of mineral and organic residues were extracted), and planned to install temperature sensors every 500 m with upper and low safety devices, refurbish and secure the electric (heating) tracing, and perform regular endoscopic inspections. (ARIA 29864)

## IV. CAUSES OF ACCIDENTS AND ORGANISATIONAL FACTORS



ARIA 161 - Explosion in a chemical plant in Auzouer-en-Touraine

External causes are totally or partly responsible for 7 accidents of the studied sample. The causes include :

- weather conditions : lightning causing a cloud to ignite or facilities to trip (ARIA 343 and 11562) or rains leading to accidental contact between water and metal (ARIA 14162 and 25689),
- power supply failure of units leading to the switching over of the facilities to safety mode (ARIA 15757),
- external domino effects such as forest fires (ARIA 27877).

As mentioned before, equipment failure recorded in hydrogen accidentology mainly results from :

- failure of joints, valves, etc. leading to leaks (see II a "hydrogen : a light weight compound"),
- corrosion problems (see II c "degradation of metals and alloys by hydrogen"),
- automatisms and instrumentation failures (ARIA 5136
- failure of an agitator led to a thermal runaway, ARIA 10316

- carbon deposits on a liquid seal led to the accumulation of hydrogen that exploded, ARIA 17070 - pH regulation failure in an electrolysis unit resulted in an explosion, ARIA 22211 - opening of a valve followed by ignition due to error in pressure measurement, ARIA 33838 - ignition of hydrogen leak in a hydrogenation workshop due to error in level measurement, etc.)

**Over 70% of accidents involving hydrogen and whose causes are known are due to organisational and human failure alone or coupled with an equipment failure.**

All stages in the service life of a facility are concerned : design (ARIA 6189, 21196 and 22249), safety report (ARIA 26983), operation (ARIA 15018, 25494, et 32796), maintenance (ARIA 891, 8966, 20274 and 27273), modifications (ARIA 2903, 6189, 7315, 9841 and 22319), intervention (ARIA 3512, 14987, 20066, and 29011).

Hydrogen accidentology highlights two main causes of accidents involving organisational and human factors : **maintenance or upkeep operations and process management errors.**

Out of the 25 mortal accidents recorded in the ARIA database, 48% occurred during maintenance operations. The figure is 100% if only the five French accidents are taken into consideration.

Among the accidents involving **maintenance** as the main cause include :

- maintenance operations at hot spots without ensuring the absence of an explosive atmosphere beforehand (ARIA 4501, 22278 and 27273);
- errors or wrong commissioning of facilities during maintenance operations (ARIA 891, 22319 and 29864);
- rinsing of equipment without a detailed risk analysis (ARIA 7956 and 19461);
- poorly conducted operations (errors in joint assembly or bolt tightening, etc.) resulting in hydrogen leaks (ARIA 14779, 19490 and 32817),
- electrical or automatism failures following maintenance (ARIA 9541 and 19325).

Errors in **process management** mainly include :

- electrolysis facilities (ARIA 6444, 10316, 17070, 20351, 25777 and 30637)
- runaway reactions (ARIA 161, 5136, 7956, 9841 and 15140)
- poor waste management resulting in reactions generating hydrogen likely to explode (ARIA 6759, 13017, 15532, 24767, 30679 and 32897).

The implementation of a **high-performance safety management** tool should allow hydrogen risks to be curtailed especially due to :

- adapted operating, maintenance and emergency procedures (ARIA 14987 and 22319), understood and applied by the technicians (ARIA 14700 and 32796),
- preventive maintenance of equipment (ARIA 22249 and 22251),
- rapid detection of malfunctions (ARIA 9541, 20274 and 22211),
- optimal training of technicians (ARIA 161),
- increased risk awareness in the facility given the permanent risk of ignition due to hydrogen (ARIA 30679).

**R**isks involving hydrogen concern a large number of activities that use or produce the gas: chemical, pharmaceutical, oil refining, nuclear or transport industries, as well as metallurgy, metal processing and recovery or sanitation for which the risks are even more pernicious as hydrogen is often generated accidentally.

Nearly 20% of the studied accidents result from the accidental production of  $H_2$  by contact between water and molten metal, formation of water gas, reactions involving hydrides or by corrosion of steels. The last case may concern several facilities especially the ones using concentrated acids. Accidental dilutions (e.g. addition of water, rinsing, gradual reduction of titer, etc.) are likely to generate hydrogen. The corresponding risks can be curtailed by a better understanding of such dangerous reactions by operators and rescue staff.

The properties of hydrogen such as its tendency to escape due to its small size, wide flammability range, low ignition energy and faculty to detonate make it especially dangerous in confined or semi-confined spaces (high points, recesses of tanks, roofs, etc.) Thus accidents involving hydrogen are 84% fires and/or explosions with serious human consequences. The best strategy adopted in battery charging or electrolysis workshops include opting for unconfined, non-congested open environments or workshops with good ventilation.

With regard to the origin of accidents involving hydrogen, the analysis shows that in over 70 % of the cases “organisational and human foactors” contribute to the deep-rooted causes of the accidents. Constant vigilance must be called for at all hierarchical levels in the facility - management, supervisory staff, technicians, subcontractors – while bearing in mind that there is a permanent risk of ignition in the presence of hydrogen.

**1 NASA GLENN RESEARCH CENTER**

Glenn Safety Manuel, Chapter 6 – hydrogen, mars 2006.

**2 INERIS – R. LODEL**

Incendies et explosions de métaux en poudre, Rapport scientifique et technique, octobre 1992.

**3 INRS – P. GROS**

Projections explosives de métal liquide dans les fonderies d'aluminium – Causes et prévention, in « Cahiers de notes documentaires n°122 », 1<sup>er</sup> trimestre 1986.

Incendies et explosions lors du travail des alliages d'aluminium et de métaux facilement oxydables, Mesures préventives, in « Cahiers de notes documentaires n°140 », 3<sup>ème</sup> trimestre 1990.

**4 INRS**

Fonderies d'aluminium – Risques et prévention, juillet 1999.

**5 L. MEDARD**

Les explosifs occasionnels, Lavoisier TEC&DOC, 1987, Vol 2, Ch 31, p 809-821

**6 INRS - J. LELEU**

Réactions chimiques dangereuses, INRS ED697 – 1987

**7 INERIS – S. EVANNO**

Référentiels, guides de bonnes pratiques et modes de gestion du REX dans la prévention des projections explosives de métal en fusion. DRA-07-85166-17188A – version B, décembre 2007.

**8 Code de construction des appareils à pression** (CODAP – 2005 – SNCT publications) Annexe MA3 « comportement des aciers en présence d'hydrogène sous pression »

**9 INERIS** « résumé de connaissances sur l'hydrogène pour l'utilisation en tant que vecteur d'énergie alternatif » rapport DCE 07/85165- 15399A - dec 2007.

**10 BARPI**

- [www.aria.developpement-durable.gouv.fr](http://www.aria.developpement-durable.gouv.fr)
- Water pollution after an explosion in a chemical plant in Auzouer-en-Touraine (37), 8 June 1988 – ARIA 161
- Fire Incident in a Multi-Purpose Plant North Rhine-Westphalia State (Germany), in 1997 – ARIA 14700
- Blast in a reactor on a fine chemicals site in Marans (17), 3 September 2002 – ARIA 23017
- Chlorine leak in a liquefaction workshop of a chemical plant in Vieux-Thann (68), 13 January 2004 – ARIA 26208
- Explosion of a wood chip refiner and fire in Corbenay (70), 20 and 25 January 2005 - ARIA 28990 and 29011
- Chlorine pipeline explosion in Champagnier (38), 21 May 2005 – ARIA 29864
- Explosion in a sulphuric acid tank in Pierre-Bénite (69), 26 novembre 2005 – ARIA 31082



## A SELECTION OF FRENCH ACCIDENTS QUOTED IN THE TEXT



Source : SDIS

### European scale of industrial accidents :

The quotation of the four criteria of the European scale is shown for each accident. It provides an indication of the seriousness of the accidents, following their detailed analysis. The scale is based on 18 parameters that are grouped into four indices, namely :

Dangerous material released	 <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	(2 parameters)
Human and social consequences	 <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	(7 parameters)
Environmental consequences	 <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input type="checkbox"/> <input type="checkbox"/>	(5 parameters)
Economic consequences	 <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/> <input checked="" type="checkbox"/>	(4 parameters)

The information used to determine the elementary level of each parameter is available on the site :

[www.aria.developpement-durable.gouv.fr](http://www.aria.developpement-durable.gouv.fr)

on the « Information Tools / European scale of industrial accidents » page. For a given accident, the value of each index corresponds to the highest level of the parameters that it contains. Only some of these 18 parameters, which are designed to cover a broad variety of the possible consequences of diverse incidents, are usually of relevance when characterising an accident..

# ACCIDENTS



ARIA 161 - 08/06/1988 - 37 - AUZOUER-EN-TOURAIN

20.14 - Manufacture of other basic organic chemicals

An explosion and a fire occurred during the night in a chemical plant during the manufacture of a silicon oil- and additive-based waterproofing agent. A junior technician (hired 6 months back), recently assigned to this post, was left without supervision around 1.00 am to manage a process modified in June and implemented for the second time. Since the order of addition of reactants was not specified in the operating procedure, he loaded 800 kg of oil into the tank 1702 on level 1, started heating the reactor, went back to level 0 to pump the reagent. While going up to level 2 to fill a tank with water, he observed a kind of fog escaping from the tank 1702. The explosion that occurred around 3.00 am resulted in the formation of hydrogen generated by the decomposition of the silicon oil after the abrupt and uncontrolled addition of an extremely basic alcoholate. The fire that ensued consumed 500 tonnes of chemicals (mainly alcohols), spread to significant part of the site (7,000 m<sup>2</sup>) and resulted in a huge cloud of smoke.

The technician was thrown 10m away, suffered a concussion and sustained serious burns and injuries. During the rescue operations, 2 fire-fighters were injured and 15 other poisoned. Despite the difficulties encountered, the rescue workers brought the situation under control in 4 hours. Analysis of the air revealed low levels of CO and NOx. The absence of retention devices, unused pipes and malfunctioning of the internal waste water treatment plant led to the disposal of the fire water (cyanide compounds, pentachlorophenols, etc.) in the Brenne river, a tributary of the Cisse river. Both the Cisse and Brenne rivers were polluted over 23 and 5 km respectively wiping out all traces of plant and animal life: 20 tonnes of fishes, aquatic and terrestrial mammals were destroyed. A high phenol index was measured in the Loire river: catchments were shutdown on 9/06 depriving 200,000 inhabitants of Tours and the adjoining area of drinking water. The water supply was restored in 3 days with a ban however on human consumption for 8 days. Drinking water supply was arranged for 10 days. Material damage and operating losses of the company stood at 45 MF and 8 MF respectively.

The chairman of the company was given a 1-year suspended sentence and fined 120,000 F while the plant manager received a 6-month suspended sentence and was fined 60,000 F. The damages to be paid to the civil party stood at 800,000 F.

The accident resulted from a major organisational failure (absence of safety policy, incomplete procedures, etc.).



ARIA 169 - 09/08/1989 - 69 - SAINT-FONS

20.59 - Manufacture of chemicals n.c.a.

Grinding operations were scheduled on a tank having stored sulphuric acid. All operation procedures (neutralisation of residual sludge with carbonate, measurement of oxygen and inflammable gases at various points) were properly carried out. At the start of the operation, a deflagration occurred inside the tank. Casualties include one death and two cases of serious injury. The tank was partly destroyed. The explosion occurred due to the presence of hydrogen (100 g) in a dead area where no measurements were taken. The hydrogen resulted from the corrosion of the iron tank under the action of sulphuric acid.



ARIA 176 - 23/02/1989 - 76 - LE GRAND-QUEVILLY

20.15 - Manufacture of nitrogenous products and fertilizers

In an ammonia synthesis loop, the synthesis gas (75% H<sub>2</sub> and 25% N<sub>2</sub> at 30°C) leaked from a sectional valve of level control device of a capacity at 250 bar. An explosion occurred killing the two workers from an outside company who intervened and triggering a fire in the facility. No consequence outside the site has been reported. Four other operations were carried out on this valve in less than a year without stopping the leak. A follow-up (mountings, bolts) with record of all operations has been implemented for all critical equipment from a safety standpoint. An overall inspection of the sub-contracting process was organised.



ARIA 437 - 01/10/1988 - 69 - SAINT-FONS

20.14 - Manufacture of other basic organic chemicals

At 6.10 am, a 3000 litre hydrogen gas tank dating back to 1939 (L=14 m, diam.=570 mm) exploded at 135 bar during hydrogenation in a chemical site. The technicians who witnessed the violent explosion followed by a red-orangey fire ball sounded the alert. The hydrogenation workshop was urgently shut down. The start of fire was quickly brought under control. The H<sub>2</sub> station commissioned in 1986, located in an open underground pit with an asbestos cement roof assembly (L=16 m, B=5 m, depth= 4 m) and 20 m at the boundary of the site housed eight 1,000 to 3,300 litre forged cylinders in horizontal position mounted on metallic supports and connected by pipes with manual control valves. All cylinders were emptied. The single supply pipe was fitted with a pneumatic valve that closed upon lack of air and was controlled by a palm button. Its air supply, cut off by a projected horizontal hydrogen gas tank fragment (a 183 kg fragment was projected at 22 m, a 33 kg fragment was projected at 145 m) isolated the plant from the pressurised units.

No casualties were reported. Internal and external material damage were observed as far as 500 m in the storage axis, most of it being confined within a 350 m radius: rupture of claddings and asbestos cement roof assembly of exposed workshops, window panes, showcases of shops, displaced tiles. The explosion could have resulted in physical injury outside the site at a less favourable moment.

The expert report concluded the differed rupture (static fatigue) of the tank by the embrittlement of steel under the effect of hydrogen. The recycled cylinder was used on other sites mainly to store nitrogen. The site had two H<sub>2</sub> plants to make up for the low flow rate during the various hydrogenation cycles as the compression station did not have a sufficiently high flow.

The use of the network and all pressurised hydrogen capacities (150 bar) of the plant was stopped and replaced with a direct supply under 35 bar.



ARIA 7518 - 31/10/1995 - 76 - BOLBEC

21.10 - Manufacture of basic pharmaceutical products

In a pharmaceutical product manufacturing plant, an explosion occurred when a hydrogenation reactor was commissioned for the first time during joint tightness tests conducted in an atmosphere of hydrogen at very high pressure. The accident resulted due to the rupture of one of the joints tested followed by the auto ignition of a 30 litre air/H<sub>2</sub> mixture. Five employees near the reactor who sustained burns and suffered from ear pain due to the overpressure were hospitalised. Among them, 2 employees were hospitalised for over 48 hours (humming sound in the ears). Material damage was confined to the immediate perimeter of the reactor. The H<sub>2</sub> detectors controlling the closing of the H<sub>2</sub> supply valve were not yet installed but this was not critical (prompt reaction taken by employees). The preliminary tests carried out under nitrogen were insufficient.



ARIA 8966 - 02/02/1980 - 73 - HERMILLON

24.42 - Aluminium metallurgy

In a plant transforming aluminium, an Al powder fire broke out at 8.15 am on a worm supplying a conveyor. The flame cutting operation on the worm shell generated scales that ignited the dust on the ground. The incandescent Al dust swept by the wind spread to the atomisation tunnels, sewers and a lost well. The dust and hydrogen formed upon contact with water caused 4 violent explosions. The fire spread to a stock of Al powder stored in bags and drums. The fire that was violent till 12.00 was brought under control at 3.00 pm and resulted in significant internal damage (roofs ripped out, craters formed, etc.). Projections were found within a radius of 50 m. No victims or environmental damage was reported.



ARIA 9477 - 10/08/1977 - 69 - SAINT-FONS

20.12 - Manufacture of colouring agents and pigments

In a chemical plant during seasonal shut down, a container used to transport fuming sulphuric acid had to be rinsed before reinforcement. During the addition of water, the container was projected against a wall situated 30 m away and a cloud of sulphuric acid was formed. Three employees sustained injuries.



# ACCIDENTS



ARIA 9841 - 02/09/1996 - 63 - VERTOLAYE

21.10 - Manufacture of basic pharmaceutical products

In a chemical plant, a violent explosion took place during the batch production of chlorobenzorex from an aqueous solution of sodium borohydride contained in a feed tank on a movable truck. The workshop was devastated: roof ripped out, light walls displaced, solvent pipes ruptured by the projections. The feed tank was destroyed but the remaining process equipment was not damaged. Outside the workshop but near a door, a technician was projected against the containers by the shock wave. He sustained injuries on the ribs and was hospitalised for a month.

The sodium borohydride solution (44 kg of powder for 130 kg of solution) was prepared 2 hours before production in a closed 630 litre agitated feed tank. Since dissolving was problematic, the operating mode was recently modified to include prior heating of the solution by hot water surface runoff (45-55°C). The reactor was placed under nitrogen circulation ( $N_2$ ) at 2h00 and then connected to the feed tank whose heating was stopped. At 2.15 pm, the feed tank's  $N_2$  inlet was connected to the supply hose. At 2.20 pm,  $N_2$  supply to the feed tank started with the partial opening of the supply valves of the reactor and the valves at the bottom of the feed tank (at a flow rate of 100 l/h -  $P(N_2) = 2.8$  bar). At 2.40 pm, the  $N_2$  hose supplying the feed tank was abruptly torn out letting the gas escape through the opening created. The superfluous staff was evacuated from the workshop and an emergency team installed a valve on the  $N_2$  inlet to stop the leak. The team tried to decompress the feed tank in the reactor by opening the reactor valve to the maximum and then opening the feed tank valve that was difficult to access. At this moment, the feed tank's manhole gave in a few seconds before it exploded.

Post-accident investigations revealed thermal decomposition of sodium borohydride triggered by an excessively high storage temperature (50 °C due to hot water surface runoff). Maintaining the temperature at 50 °C stabilised the decomposition rate in such a way that the small quantities of hydrogen ( $H_2$ ) formed could escape via the leaking feed tank. When the heating was stopped, the system evolved in an independent way: the temperature and pressure increased under the effect of heat resulting from the decomposition causing a thermal explosion. The inspection hole opened under a pressure of 15 to 20 bar followed by the rupture of the feed tank. The depressurisation of  $H_2$  in the form of a shock wave was responsible for the damage caused in the workshop.

Lastly, poor knowledge of the properties of hydride and absence of a critical analysis of the process were also responsible for the accident. Modification procedures and taking into account the various productions incidents would have certainly led to the missing critical analysis.



ARIA 14987 - 11/09/1991 - 13 - MARTIGUES

20.14 Manufacture of other basic organic chemicals

An explosion ripped through a chlorine production site during the restart of an installation. The hydraulic seal had apparently become blocked by fire extinguishing products following a fire on the hydrogen exhaust system. The blockage caused the pressure to increase in the hydrogen manifold and the passage of flammable gas into the chlorine through the diaphragms. The  $Cl_2 / H_2$  mixture then entered the  $Cl_2$  desiccation unit before exploding. The explosion was probably initiated by a discharge of static electricity or UV radiation. The internal contingency plan was put into action. The accident did not claim any victims although the desiccation towers were destroyed and the chlorine manifold was damaged. The increase in the chlorine's hydrogen content had been detected by an on-line analyser 15 minutes prior to the explosion. The accident demonstrated the inappropriate hydrogen fire fighting means or insufficient with regard to the detection of overpressure in the hydrogen manifold and the analysis of this gas in chlorine, as well as inappropriate operating procedures with regard to the intervention procedures in the event of excessive  $H_2$  pressure or chlorine gas polluted by flammable gas. Corrective measures were implemented: Elimination of the causes of pressure build-up in the  $H_2$  manifold, reinforcement of hydrogen overpressure detection systems and the presence of hydrogen in the chlorine, adaptation of the initiator operating procedures ( $H_2$  overpressure and chlorine polluted by hydrogen).



ARIA 23317 - 15/10/2002 - 52 - BROUSSEVAL

24.51 - Iron foundry

In a foundry, while transferring a ladle of molten iron from one production building to the other, the handling equipment fell into the MOULINS canal. An explosion was heard under the nearby bridge. The neighbouring buildings were damaged (windows smashed, siding and roof partially ripped out) and the bridge destroyed due to the projections and blast effect. Fourteen people sustained injuries including two people who were hospitalised. The explosion occurred due to the contact of molten metal with water.



ARIA 25112 - 26/06/2003 - 38 - LE PONT-DE-CLAIX

20.13 - Manufacture of other basic inorganic chemicals

Two successive fires broke out in an interval of few minutes in 4 cells (1 isolated + 3 successive) in the electrolysis room of a chlorine production plant. The technicians brought the fire under control using the fire-fighting equipment located nearby. The presence of hydrogen ( $H_2$ ) and a spark resulting from a short circuit was responsible for the two accidents. In the first case, the  $H_2$  leaked when a rubber-plastic pipe was manually disconnected from a  $H_2$  trap. The preceding operation that is subject to a procedure was performed when  $H_2$  quality was not good enough to be collected. During the 2nd fire, a sleeve pierced by corrosion was responsible for the  $H_2$  leak. Several causes were identified to explain the short circuit: defective or inappropriate insulators (their properties were not studied), absence of anode / cathode tightness, closeness of anode and the  $H_2$  flange following a modification of the  $H_2$  outlet and deviation in the alignment of cells. The analysis of the accident and the corrective actions retained were presented in the company CHSCT (committee on hygiene, safety and working conditions) before operations could resume. These included deciding on a better suited insulating material, improving process orifice to reduce the presence of chlorine in the hydrogen and avoid disconnection of the pipe from the trap, improving quality control and supervision by team leader, planing  $H_2$  flanges to space them out from the anode, communicating the lessons learnt from the accident to the staff, improving procedures and guidelines, taking stock of all insulation malfunctions of all cells, etc.



ARIA 26208 - 13/01/2004 - 68 - VIEUX-THANN

20.13 - Manufacture of other basic inorganic chemicals

During the re-start phase of an electrolysis workshop in a chemical plant, chlorine ( $Cl_2$ ) gas leaked from a pipeline in a confined chlorine liquefaction unit. The operators shutdown the facilities and evacuated the premises. The internal emergency plan of the site was triggered and lifted after 1 hour and 30 minutes. According to the operator, out of the hundreds of kg of  $Cl_2$  emitted in the building, only 3 kg were released into the atmosphere thanks to the dynamic confinement system that opened into a neutralisation tower. The  $Cl_2$  detectors indicated the 5 ppm threshold was crossed for 20 seconds at the boundaries of the site and for 20 min near the workshop. No environmental or human (including both staff and civil population) consequences were reported. The leak linked to the missing of a few dozen meters of pipeline (pipeline carrying "residual" chlorine from a gas/liquid separator to a liquid bleach manufacturing plant) is responsible for the accident. This absence was due to the combustion of the pipeline steel by chlorine, which in turn according to the operator was caused by the presence of hydrogen ( $H_2$ ) in the pipeline due to lack of monitoring. The  $H_2$  concentration in residual chlorine that must be below the LEL (4.6 %) was manually controlled by the rate of evaporation of chlorine in the gas/liquid separator and monitored through analysis. During the accident, the technician failed to take any action to reduce the increasing  $H_2$  concentration in the pipeline that reached 6.7%, crossing the LEL. To bring down the concentration, the evaporation rate of chlorine was increased causing thus a rise in the residual chlorine flow rate that probably provided the low energy needed to start combustion. The flame stabilised near a valve and a flow meter caused the combustion of iron / chlorine when the temperature reached 130 °C. To reduce the chances of reoccurrence of such an accident, the operator decided to increase monitoring of the  $H_2$  concentration and shutdown the electrolysis workshop when the  $H_2$  concentration crosses 3.5 % in residual chlorine. Furthermore this concentration was guaranteed by continuously performing the material balance of pure chlorine.

# ACCIDENTS



ARIA 26618 - 04/12/1991 - 27 - VERNON

30.30 - Aviation and space construction

On 4 December 1991, in a space equipment testing site, internal combustion occurred in a liquid hydrogen tank ( $H_2$ ) under a high pressure of 12 m<sup>3</sup> (700 kg of liquid  $H_2$ ). The test was stopped as the malfunction was detected by the indicators. No consequences were reported. The tank commissioned in 1988 was connected to  $H_2$  gas and liquid oxygen ( $O_2$ ) storage tanks. The tank structure included a double casing separated by vacuum. The multilayer inner wall was made of austenitic stainless steel and 157 mm thick. Its maximum operating pressure was 400 bar, with a service pressure of 250 bar.

In July 1991, the test tank was emptied and purified (by injecting helium) as the  $H_2$  gas network was suspected of being polluted in October 1990 following an intake of air from a compressor.

On 4 December 1991, a test was performed: the liquid  $H_2$  tank was pressurised by a control device (+ 250 bar in 30 sec). While the pressure in the tank reached 160 bar, a noise indicating a pressure drop was observed and the detectors recorded a pressure fluctuation of 10 bar. The sudden and significant fluctuations in the measured parameters (temperature of wall, pressure, flow) led the test to be stopped. The combustion of an  $O_2$  pellet in an abandoned pipe of the tank's drain pipe was responsible for the accident. The  $O_2$  pellet was formed by the regular addition of air due to the impurities present in the  $H_2$  and the accidental pollution of the network in October 90, the presence of air in the abandoned pipeline during purification in July 91 (helium is lighter than air), re-solidification of the air while refilling the tank with liquid  $H_2$ . The abandoned pipe was thus obstructed by the air pellet causing a mixture of air and  $H_2$  to be trapped in its lower portion.

Several combustion spots were detected: in condensed phase between solid  $O_2$  and  $H_2$  gas, in less dense phase between  $H_2$  and  $O_2$  gas. The combustion was undoubtedly triggered by the friction of the pellets against the walls and the adiabatic compression of the  $H_2/O_2$  gas mixture. The tank was re-commissioned 4 months later after investigation and implementation of a bleed valve to regularly drain the abandoned pipe and avoid the accumulation of  $O_2$  particles.



ARIA 29864 - 21/05/2005 - 38 - CHAMPAGNIER

20.13 - Manufacture of other basic inorganic chemicals

An explosion ripped through a pipeline transporting gaseous chlorine between a chemical platform (producer) and an elastomer manufacturing plant (user).

The piping, built in 1961 to transport hydrochloric acid (HCl), was being used to convey deoxygenated and dried  $Cl_2$ . Measuring 200 mm in diameter and 3,600 m in length, the painted, lagged steel pipe was equipped with an external skin effect heating system and operated at 4 bar (relative) and 30 °C. Production operations had been stopped the day earlier for a 10-day maintenance shutdown period, and the pressure in the chlorine pipeline had been lowered to 0.25 bar.

The explosion occurred 150 m from the delivery point, in an area outside the user's site. The pipe ruptured in 4 locations along a 70 m section and showed traces of internal shock waves. The accident did not claim any victims despite a large amount of pipe debris projected in a 150 m radius. An estimated 475 kg of  $Cl_2$  was released following the explosion. The damage observed (helical rupture, pressure wave...) indicates the explosive character of the accident. The 4 other pipes on the aboveground rack (dia. 100 mm) suffered extensive damage: the 2 nitrogen lines (13 bar, 2 to 3,000 m<sup>3</sup>/h) were deformed although were not leaking, and their pressure as reduced to 10 bar; the oxygen line (10 bar), was also damaged and was drained. The last line was no longer in use and was kept under  $N_2$  at atmospheric pressure.

Analysis of the accident showed that an  $H_2/Cl_2$  explosion caused the damage. The formation of  $H_2$  (20%) can be explained by the combination of several elements: The accidental introduction of humidity into the piping during a previous maintenance operation may have led to hydration of the ferric chloride present in the pipe's environment. According to the operator, the change in the deposit's crystalline phase due to excessive heating of the pipe (80 to 90 °C) promoted corrosion in the steel pipe (by the hypochlorous acid) and the formation of  $H_2$ . This heating is due to a temperature sensor that lost its electrical power supply 3 days earlier after a cable on the user's site was broken when a slab protecting the structure was poorly handled.

In fact, the proportion of hydrogen (20%) released in the gaseous chloride contained in the pipe, which was capped at each end and kept at low pressure (0.25 bar), formed an explosive mixture requiring very little initiation energy to ignite (in the order of a dozen micro joules).

The operator cleaned the inside of the structure (2.5 to 3 t of mineral and organic residues were extracted), and planned to install temperature sensors every 500 m with upper and low safety devices, refurbish and secure the electric (heating) tracing, and perform regular endoscopic inspections.



ARIA 31082 - 26/11/2005 - 69 - PIERRE-BENITE

20.13 - Manufacture of other basic inorganic chemicals

An explosion occurred in a chemical site causing the cover of a 99.2% sulphuric acid tank (filled to 300 t of its total 1500 tonne capacity) to open partially. The cover opened along the circumference of the tank at the dome / shell fitting. The POI (internal emergency plan) was triggered. No emission or leak was reported except for the emission of fumarole at the opening. No environmental or human consequences were reported. Material damage was limited to the equipment located above the tank (acid supply pipes, air pipe going to the dryer, walkway, steam pipe, etc.). The presence of hydrogen (a few dozen grams), generated by the corrosion of steel by the weak acid was responsible for the explosion. The accident was further to a series of incidents in the unit manufacturing  $H_2SO_4$  through the absorption of  $SO_3$  in packed columns: two successive piercing incidents of the water/acid heat exchangers of the transfer columns on the day before the accident caused an around 85% titer to flow into the acid storage tank (1st incident), followed by acid with a practically zero titer (2nd incident). Before the explosion the tank contained a heterogeneous mixture with a weaker surface titer. The explosion occurred 1 hour and 15 minutes after the tank had been agitated. The ignition of  $H_2$  (requires very low energy) was probably electrostatic. The two piercing incidents of the heat exchanger were due to a phenomenon of corrosion by pitting near the seam welds on the side of the cooling water. Modification of the anti-legionella biocide treatment since the previous year may have favoured the phenomena of corrosion by pitting. The use of liquid bleach instead of bromine greatly increased the oxidising power of water and thus lowered the starting temperature of corrosion pitting. Decreasing the speed of passage of water (on account of the drop in the workshop activity for a long period) contributed to increasing the temperature of the medium, is another aggravating factor for the accident. The measures taken include water treatment (temporary use of a non-oxidising biocide and study of a continuous chlorine-bromine treatment), detection of any abnormal arrival of water in the process (temperature detector with alarm, titrators), operating procedures (prohibition on adding weak acids to storage tanks).



ARIA 33330 - 01/06/2005 - 76 - GONFREVILLE-L'ORCHER

19.20 - Oil refining

The inspection carried out during a major shutdown of a reformer in a refinery using techniques such as AUBT (Advance Ultrasonic Backscattering Technique) of metal sheets, welding checks by TOFD (Time of Flight Diffraction) and magnetoscopy on steel shells weakly alloyed with 0.5 % Mo aimed at identifying thermal etching by hydrogen on the feed/effluent exchange column.

The initial AUBT checks carried out from the outside revealed degradations. These observations were confirmed by the appearance of blisters on metal sheets and cracks at the longitudinal welds when the equipment was opened. The operator had planned to urgently build and replace the corroded equipment with 1.25 Cr 4 steel shells.

The resistance of 0.5% Mo steel to thermal etching by hydrogen was gradually questioned since the 1970s. It is currently considered to be similar to non alloyed carbon steel. In the old units, the materials were selected in accordance with the Nelson curves used at the time of their construction but were potentially sensitive to thermal etching by hydrogen. Equipment in 0.5 % Mo steel operating under hydrogen must be identified and classified according to their criticality, inspected using AUBT and welding checks (TOFD, Magnetoscopy) to identify damage on account of hydrogen and be replaced systematically in the event of appearance of degradations in especially highly-sensitive equipment.

## TECHNOLOGICAL ACCIDENTS ONLINE

Safety and transparency are two legitimate requirements of our society. Therefore, since June 2001 the website [www.aria.developpementdurable.gouv.fr](http://www.aria.developpementdurable.gouv.fr) of the Ministry of ecology, energy, sustainable development and town and country planning has been putting lessons learnt from the analysis of technological accidents at the disposal of professionals as well as the general public. The main sections of the website are presented both in French and English.

Under the general sections, the Internet user can, for example : inquire for the state's action, access to wide extracts of the ARIA database, discover the presentation of the European scale of industrial accidents, inquire for the "dangerous substances parameter" used to complete the "communication on the spot" in case of accident or incident.

Accidents description, which is the raw material of any method of feedback, constitutes an important part of the website : when known, events, consequences, origins, circumstances, established or presumed causes, actions taken and lessons learnt are compiled.

Over a hundred detailed and illustrated technical reports present accidents selected for their particular interest. Numerous analyses sorted by technical subjects or activities are also available. The section dedicated to technical recommendations develops various topics : chemistry, explosives, surface treatment, silos, tyre storage, hot work permit, waste treatment, handling ... A multicriteria research engine enables getting information about accidents arisen in France or abroad.

The website [www.aria.developpement-durable.gouv.fr](http://www.aria.developpement-durable.gouv.fr) develops constantly. Currently, more than 32 000 accidents are online and new topics will be regularly added.

The summaries of the accidents presented in this document are available at :

**[www.aria.developpement-durable.gouv.fr](http://www.aria.developpement-durable.gouv.fr)**

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