Catastrophic explosion of a cyclohexane cloud

June 1, 1974

Flixborough

United Kingdom

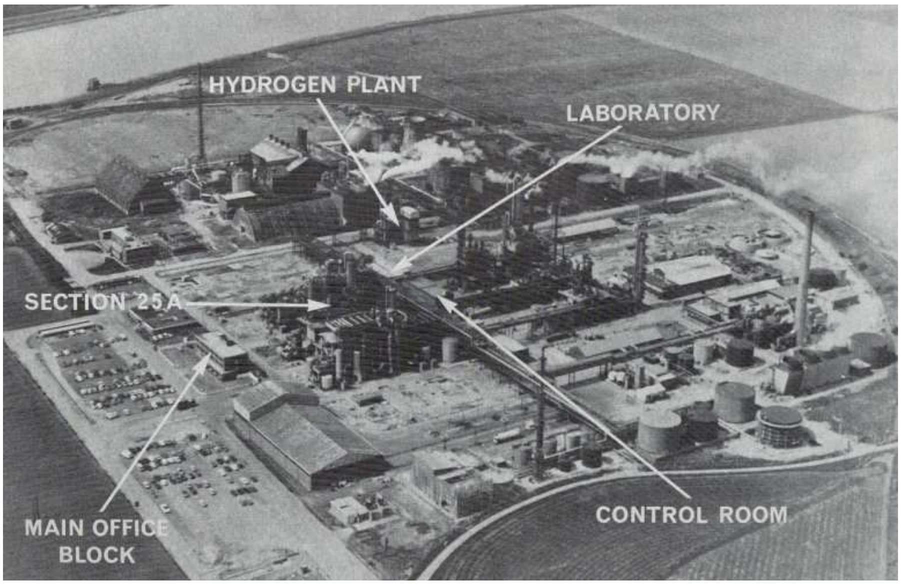
Chemistry
Piping
Expansion bellows
Casualties
Property damage
Modifications / repairs
Human factor
Stress corrosion
***Seveso* Directive**

THE FACILITIES INVOLVED

Accident site

In 1974, the chemical plant employed a workforce of 550 and occupied a 24-ha site set amidst the farmland of Flixborough, 260 km north of London. The two closest villages, Flixborough and Amscott, are at a distance of 800 m from the plant; the larger towns of Burton and Scunthorpe are located 3.5 and 5 km away, respectively.

Built in 1938 to produce fertilizer, the plant changed ownership in 1964 with the aim instead of producing caprolactam, an intermediate compound used in the fabrication of nylon. An initial unit with an output of 20,000 tons of caprolactam per year, by means of phenol hydrogenation, began operations in August 1967. By 1972, caprolactam production capacity had risen to 70,000 tons/year following the construction of a new unit designed to use a cyclohexane oxidation process.



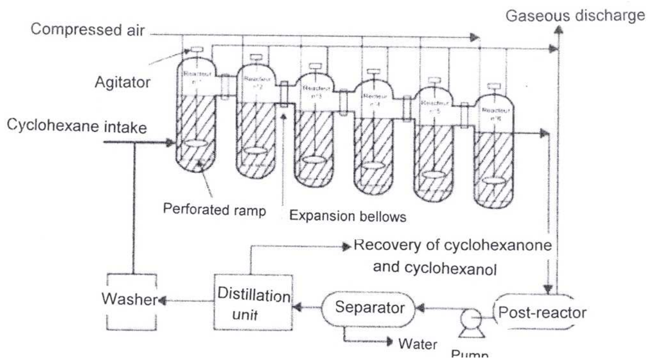
Aerial view of the site before the accident - Source: Secretary Of State For Employment (1975) *The Flixborough Disaster.* London: HSMO

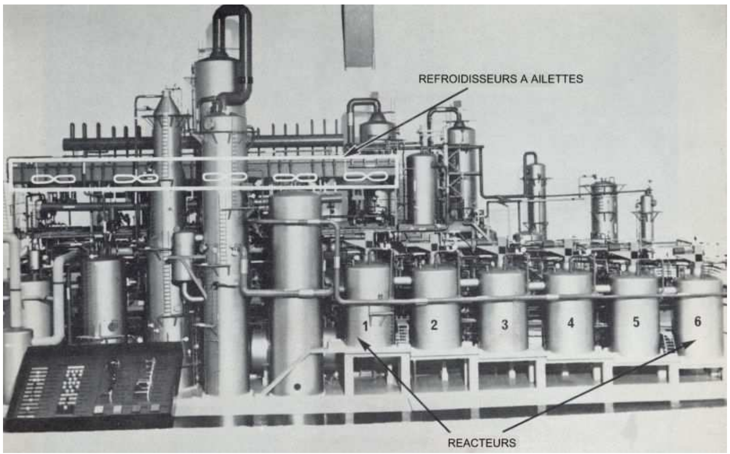
The unit responsible

Built in 1972, the caprolactam unit (Section 25A) performed cyclohexane oxidation in a series of 6 successive reactors. Each reactor, equipped with a unit capacity of 45 m³ (5 m high with a 3.5 m diameter), was made of a 13-mm soft steel plated on the inside by stainless steel (3 mm) and featuring a central agitator.

The oxidation step was carried out in the presence of a catalyst, by means of injecting compressed air using a perforated ramp inside the reactors loaded with 25 m³ of cyclohexane at 155°C under 8.8 bar of pressure; this set-up enabled obtaining both cyclohexanone and cyclohexanol, yet with a relatively low output that necessitated introducing large quantities of cyclohexane as well as a recirculation circuit. A 250 to 300 m³/hr liquid flow was circulating between reactors via 28-inch (711-mm) diameter pipes fitted with stainless steel expansion bellows.

For safety purposes, nitrogen was used to render installations inert; moreover, the valves protecting the unit against pressure surges were set at 11 bar.





THE ACCIDENT, ITS CHRONOLOGY, EFFECTS AND CONSEQUENCES

The accident

With the new caprolactam production unit only operating at full capacity since the beginning of 1974 due to both technical and labour problems (see the section below on Circumstances), additional difficulties arose at the end of March of the same year, once again jeopardizing plant productivity.

On March 27, a cyclohexane leak was observed on Reactor no. 5 at the level of a vertical crack within the sidewall. The facility operator decided to conduct a thorough inspection of the reactor during the unit's next scheduled downtime.

By the next day, this detected crack was already extending a full 2 meters in length; the installation was closed and Reactor no. 5 withdrawn for inspection. In order to resume production as quickly as possible, it was decided to build a bypass between Reactors 4 and 6 and then implement the modified configuration without any specific preliminary study, based on a drawing produced on the shop floor.

On April 1st, following a leak test, the unit resumed operations with a 20-inch (508-mm) diameter elbow pipe connecting the two 28-inch diameter expansion bellows on Reactors 4 and 6 via a plate and flange, with the entire assembly being supported by scaffolding placed so as not to interfere with pipe movement.

Until May 29, this stopgap installation operated normally without any special problem reported.

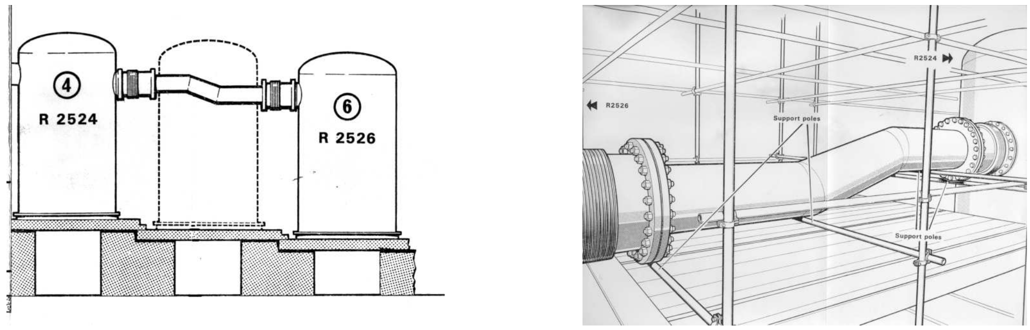


Diagram of the bypass between Reactors 4 and 6

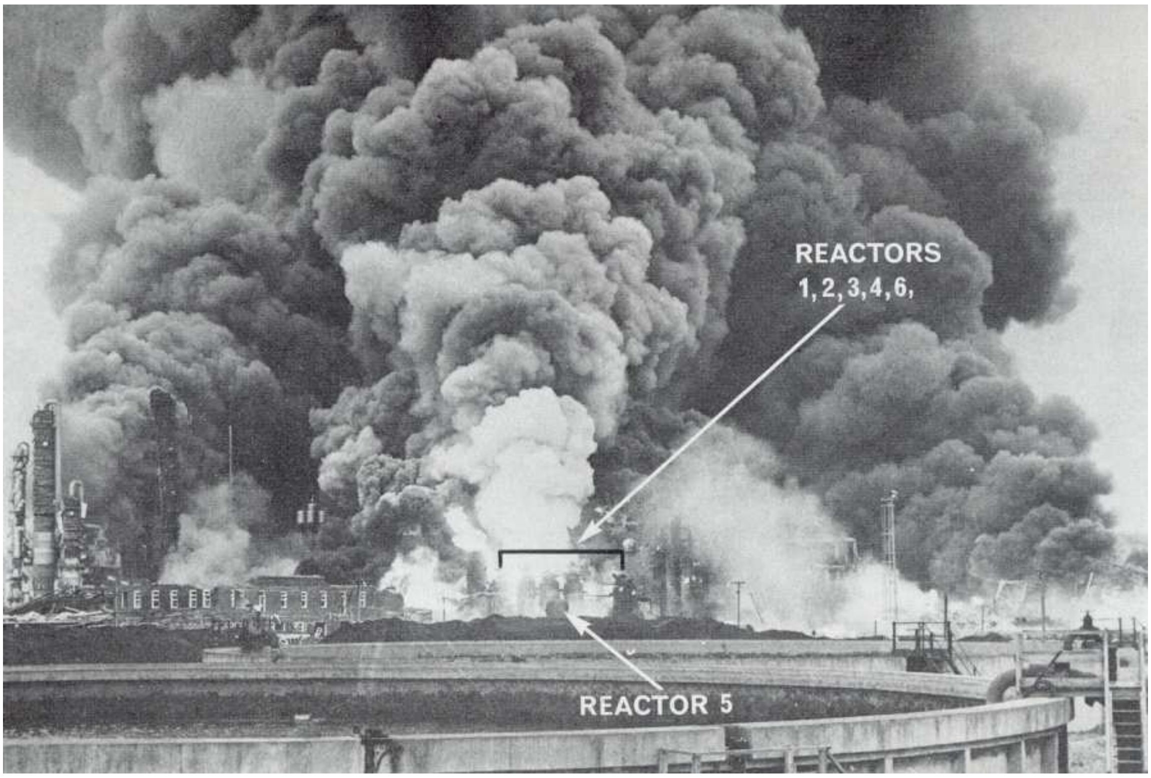
Source: Secretary Of State For Employment (1975). *The Flixborough Disaster.* London: HSMO.

On May 29, the installation was shut down after discovering a cyclohexane leak.

Subsequent to repairs and testing, the unit was started up during the early morning hours on Saturday June 1st. At 4:00 am, a new cyclohexane leak was observed, followed by several others. The installation was once again stopped before reactivation an hour later, with the leaks being "self-contained". Shortly thereafter, another discovered leak forced the operator to cease production, since the specific repair tools required were not available onsite.

At 7:00 am on June 1st, the unit was placed back into service, yet a new round of difficulties were noticed as the equipment was warming up, including a lack of control over temperatures and pressures within the installation (resulting in a power shut-off).

At 4:53 pm, a deflagration noticeable up to 50 km away practically levelled the entire site. In many sectors of the plant, intense fires ensued, with flames flaring 70 to 100 m high. The instantaneous jump in pressure at the epicentre of the explosion, calculated at over 2 bar, destroyed all stationary fire protection equipment, further complicating the work of emergency and rescue services; the main sources of ignition would not be extinguished until two and a half days later.



Source: Secretary Of State For Employment (1975). *The Flixborough Disaster.* London: HSMO.

Consequences of the accident

The human toll

Among the 72 individuals present inside the plant at the time of the explosion,

- 28 were killed, including the 19 working in the control room,
- 36 were injured.

Outside the facility, 53 injuries were reported, but hundreds of other people who sustained more mild injuries were not officially counted.

Confronted with the risks caused by combustion fumes from the solvents and chemical substances directly involved, nearly 3,000 residents from neighbouring localities were evacuated and spent the night of Saturday to Sunday in makeshift shelters set up by the British army. They would return to their homes by Sunday afternoon.

This casualty tally, already quite dire as it is, would have been of a completely different order of magnitude had the accident occurred on a weekday, with the onsite presence of all 550 plant employees, given that the site's administrative buildings, technical offices, control room, laboratories and maintenance workshops were totally devastated.

Property damage

The property damage caused by the explosion covered a vast zone:

- all buildings lying within a radius of 600 meters around the explosion epicentre were destroyed;
- a total of 1,820 housing units and 167 retail businesses in the vicinity were damaged to varying degrees, this disastrous consequence concerned 72 of the 79 houses in Flixborough, 73 of the 77 homes in Amscott and 644 of 756 in Burton;
- missile-like debris projection due to the explosion was considerable: a large piece of equipment would be found 6 km from the plant and smaller debris could be found as far as Anlaby, 32 km away.

Estimations of the cost of this disaster varied tremendously from one source to the next; nonetheless, it is quite likely that the cost topped USD 100 million (in 1974 dollars).

Environmental impacts

The River Trent, whose bed flows close to the Flixborough site, was closed to all fishing activity.

On the European scale of industrial accidents

By using rating rules applicable to the 18 parameters of the scale officially adopted in February 1994 by the Member States' Competent Authority Committee for implementation of the '*SEVESO*' directive on handling hazardous substances and in light of the information available, this accident can be characterized by the four following indices:

The parameters composing these indices and their corresponding rating protocol are available from the following Website: http://www.aria.developpement-durable.gouv.fr

The "hazardous materials released" index equalled at least 4, as the sheer power of the explosion was comparable to that of 16 tons of TNT (parameter Q2) [3]. Moreover, given the quantity of cyclohexane present in the unit at the time of the accident, it is likely that at least a hundred tons of cyclohexane contributed to the incident (explosion + fire), which represents 50% of the *Seveso* threshold for the substance (parameter Q1).

Since over 50 bystanders were seriously hurt (i.e. requiring hospitalization of more than 24 hours) due to the accident, the "human and social consequences" index was set equal to 6 (parameter H4).

By virtue of pollution caused to the River Trent (triggering a fishing ban on the river), the "environmental consequences" index registered at least 1 (parameter Env14).

With the cost of property damage alone caused by the accident exceeding USD 100 million in 1974 dollars (i.e. over 300 million in 1993 euros), the "economic consequences" index climbed to at least 6 (parameters €15 and €16).

THE ORIGIN, CAUSES AND CIRCUMSTANCES OF THE ACCIDENT

Circumstances

Economic context

Ever since its construction, the unit had experienced multiple difficulties that would prevent production activities from reaching their objective, set at 70,000 tons of caprolactam / year.

In November 1973, the situation was compounded by a miners' strike that led the British government to declare a state of emergency and restrict industries to just 3 days of electricity use per week. The Flixborough plant, which was unable to adapt to such a mode of operations, turned on its backup electric generating sets so as to keep running equipment essential to the production activity. As a result, reactor agitators in the caprolactam unit were deactivated. In January 1994, the miners' strike was settled and plant production returned to normal, yet the agitator on Reactor no. 4 in the caprolactam unit, which for an unknown reason had become deteriorated, was not placed back into operation [8].

Towards the beginning of 1974, the plant was operating at a production pace of 47,000 tons/year. Faced with the prospect of sizable financial losses, the plant's holding company, Great Britain's sole caprolactam producer, requested the Government's Pricing Commission to authorize a 48% increase in the price of caprolactam, but was refused.

At the time of the accident, the operator was thus enduring considerable economic and commercial pressure.

Company personnel

By June 1974, the post of plant maintenance engineer, vacant since the beginning of the year, had still not been filled. Since none of the facility's other engineers were specifically trained in mechanical engineering, this post was being occupied by the former maintenance engineer's subordinate, who happened to be a technician with 10 years of experience in the electricity department and just 4 years in maintenance. Despite having taken continuing education courses, this individual's qualification remained insufficient for the responsibilities required of the post.

Moreover, the plant's level of engineering competence was on the low side, as both the Director and Technical Director were chemists by training without any qualification in mechanical engineering.

Regarding this particular point, the accident investigation commission concluded that: "*had a suitably-qualified maintenance engineer been present at the time, with an appropriate status and authority to impose his views, we all feel that he would have insisted that no reactivation be attempted before having fully inspected the other reactors and before determining the cause of cracks in Reactor no. 5 (…)*"

Regulatory ramifications

At the time of the accident, over 400,000 gallons (1.5 million litres) of hazardous products were being stored onsite, even though the operator only held a license for 7,000 gallons. This excessive storage included:

- 330,000 gallons of cyclohexane (unauthorized)
- 66,000 gallons of naphtha (vs. just 7,000 authorized)
- 11,000 gallons of toluene (unauthorized)
- 26,400 gallons of benzene (unauthorized)
- 450 gallons of gasoline (1,500 authorized).

While these stored quantities did not contribute to the accident, they raise questions about authority control over the plant; such questions however were not addressed in the investigation report.

Causes of the accident

A determination of the exact causes and processes leading up to the explosion was seriously complicated by the absence of witnesses (all staff present in the control room died in the accident) and the destruction of all unit instrumentation.

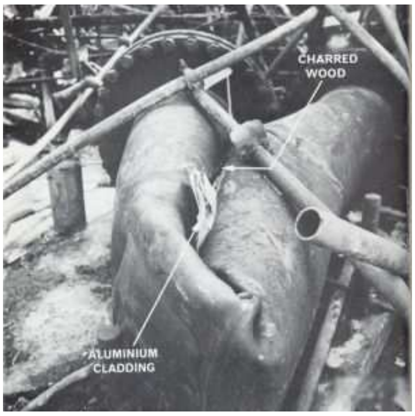
An investigation commission organized by the Secretary of State for Employment was assigned to examine the causes of the accident and assign responsibilities. The commission's conclusions, published in April 1975, were not however unanimously accepted, and a number of theories regarding the accident would provide the topic of scientific publications for decades to come.

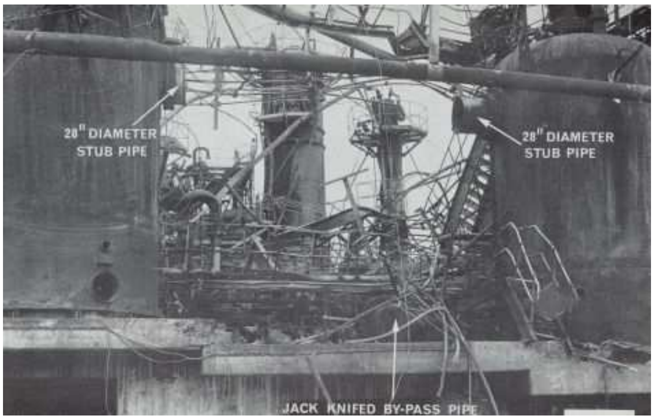
The commission's conclusions along with a summary of three other hypotheses will be presented below.

Conclusions offered by the investigation commission

According to the investigation report, failure at the level of the two connecting bellows on the temporary 20-inch pipe placed between Reactors 4 and 6 caused a massive leak of hot and pressurized cyclohexane. The 40- to 60-ton cloud of cyclohexane created then ignited 25 to 35 seconds later, when making contact with the reforming tower of the hydrogen unit located 100 m from the leak, thereby causing the explosion and ensuing fires.

For the commission, the 20-inch pipe would have burst during just a single phase, as a result of internal temperature and pressure conditions that, while remaining within the unit's operating range, would have been more severe than is customary. These conditions would have induced the torsion of both connecting bellows followed by the violent sandwiching of the pipe, thus causing the pipe to break. The experiments conducted on full-scale assembly reproductions have moreover shown that the torsion of bellows depends on their axial stiffness as well as on the number and position of supporting struts and the distance between them.





However, the real cause of this accident was indeed the "amateurism" shown by removing Reactor no. 5 and by constructing the bypass in the first place; this risky sequence was not specifically examined in any of the studies or tests undertaken. After the commission's findings, no verification of actual operations was conducted; only a nitrogen test at 9 bar, but this test was designed to assess the leak and not safety (the valve adjustment pressure was set at 11 bar).

The investigation report made special mention of the fact that:

- no calculation was carried out and no one voiced concern over the structural strength of these bellows and the bypass, despite the forces being exerted due to the hydraulic thrust of cyclohexane, assembly torsion movements, etc.;
- no reference was made to standards or guidelines in effect at the time, or to the bellows manufacturer's published user's guide;
- no column or other means were employed to prevent bypass movement.

At the origin of the accidental sequence, the deficiency of Reactor no. 5 stemmed from cracking corrosion caused by nitrates contained in the water used in the past to spray the small cyclohexane leaks, in an effort to limit the risk of ignition. This water had penetrated into the insulation and, during evaporation, deposited nitrates onto the equipment steel.

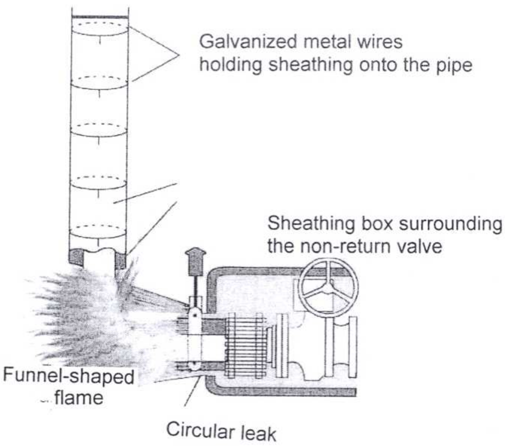
The cause of the leak on Reactor no. 5 should have been analyzed prior to any unit reactivation and the other reactors should have been verified with respect to the degradations sustained by Reactor no. 5. Such an approach however would have required shutting down the plant for a few days; the concern over minimizing plant downtime and production losses actually motivated the stopgap configuration that eventually gave rise to the accident.

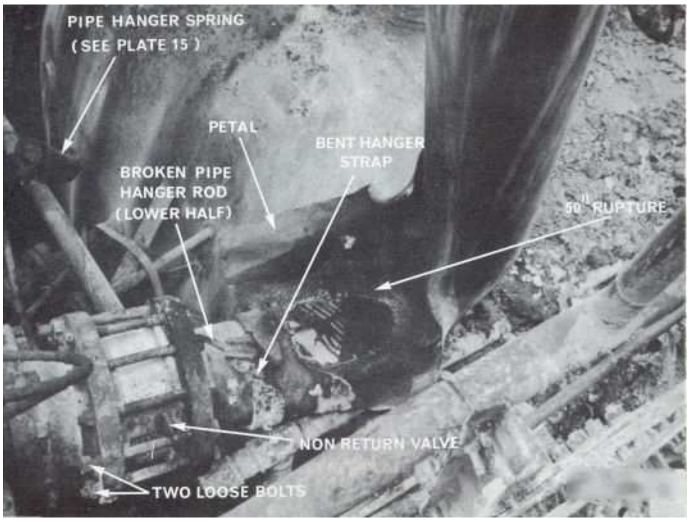
The "8-inch pipe" hypothesis

The investigation commission also examined a second accident scenario called "the 8-inch pipe hypothesis", which it ultimately rejected in pointing out that according to this hypothesis, the accident would have resulted from a succession of events that for the most part remained improbable.

This theory, defended in particular by Dr. John Cox, confirmed that the major explosion was due to the "sandwiching" break of the 20-inch bypass, but still contends that this break was due to an external primary explosion caused by the cyclohexane leak on an 8-inch pipe and not under the temperature and pressure conditions internal to the unit.

According to Cox, a break in the seal on the backflow prevention valve, due to poor clamping of both bolts on the valve flange, would have been the source of a small ignited cyclohexane leak heading towards an elbow in the 8-inch pipe section, thereby destroying its sheathing. The contact with zinc contained in the metal wires holding the sheathing with the steel of the 8-inch pipe would have immediately generated a 3-inch crack; the ignited double leak would then have heated the pipe elbow to a temperature of 950°C for at least 4 min, causing a creep-induced break over more than a meter (50"), in the shape of flower petals, as could be found in the rubble. The cyclohexane discharged in this manner would then have produced an explosion at the level of a winged cooler of the unit, which would have engendered a downward force acting upon the 20-inch bypass, which lies at the origin of its failure.





View of the 50-inch break on the 8-inch pipe

Source: Secretary Of State For Employment (1975). *The Flixborough Disaster.* London: HSMO.

The "water" theory

According to the hypothesis defended by Ralph King, the break in the 20-inch bypass resulted from a sudden pressure rise due to the presence of water inside Reactor no. 4, thus forming an azeotrope with the cyclohexane.

Since water and cyclohexane are not miscible, they form at their interface a liquid layer, called an azeotrope, whose boiling point lies below that of either water or cyclohexane.

Under normal operating conditions, this azeotrope cannot be derived because of agitator action. On the day of the accident, the agitator of Reactor no. 4 was not operable due to a mechanical malfunction (see Section on Circumstances). Two phases, one aqueous the other cyclohexane, could thus form in Reactor no. 4, with an unstable azeotrope at the interface. Upon start up with installation temperature on the rise, the boiling point of the reactor was reached, hence triggering a sudden pressure increase and projection of a cyclohexane and overheated water mix, leading to failure of the temporary pipe (which was only supported by thin struts).

More than 25 years after the accident, the Health and Safety Executive (HSE) undertook a series of experiments in order to study this "water theory" more closely. Initial results indicated that the amount of water in Reactor no. 4 was probably significant. Larger-scale testing has revealed an increase in static pressure due to the interaction between water and cyclohexane, yet at levels insufficient to confirm Ralph King's hypothesis.

Venart's theory

Lastly, Jim Venart forwarded the hypothesis whereby the temporary 20-inch pipe would not have broken during a single phase, but instead required 2 stages.

The bellows connected with Reactor no. 4 was likely to have yielded first by fatigue due to the vibrations generated from liquid flow in the installation, thereby freeing a quantity of cyclohexane estimated at 10 to 15 tons (whereas the investigation report noted a quantity of 40 to 60 tons of cyclohexane contributing to the explosion). The resultant explosive cloud formed would have detonated 20 to 40 seconds later. Failure of the bellows connected to Reactor no. 6 and the "sandwiching" of the bypass therefore would have merely been consequence of the explosion.

ACTION TAKEN

On June 17, 1974, the Secretary of State for Employment ordered two investigations. The first, conducted by an Investigation Commission, was to examine accident causes and assign responsibilities, while the other, performed by a committee of experts, was to advise the government on measures to adopt in order to control the operations of chemical plants at risk of creating other major accidents.

At the time of these events, the draft law entitled "Health and Safety at Work" was being discussed in the House of Commons; enacted at the end of 1974, this law stipulated that the operator must adopt all reasonable measures (in conjunction with the level of risk) to ensure human health and safety.

The Flixborough accident like that of Seveso (ARIA 5620), which happened in Italy in 1976, served to build awareness among European Member States of the need to strengthen public authority control over industrial activities presenting major technological risks, in an effort to better manage industrial risks. As a direct result, on June 24, 1982, the European Council adopted the now well-renowned "*Seveso* directive".

Despite local protests, the Flixborough plant was rebuilt in paying strict attention to lessons learned from the accident. In particular, the process involving cyclohexane oxidation was replaced by one making use of phenol hydrogenation, considered to be safer.

However, this second plant was closed just a few years later for economic reasons, and its industrial installations were definitively destroyed in 1981.

THE LESSONS LEARNT

A considerable number of technical and organizational lessons could be drawn from the Flixborough disaster in terms of installation design, facility modification management, maintenance, supervision, etc.

Installation design

The death of 19 people present in the unit's control room demonstrates the necessity to carefully design the **layout and location of control rooms** so as to mitigate the risks borne by personnel inside the facility. Furthermore, the placement of onsite occupied premises (administrative buildings, laboratories, etc.) must be studied in depth to isolate the most hazardous units and limit their access to just authorized staff.

One of the means available for reducing the risk of major accidents is to **limit the hazard potential present onsite**, specifically through lowering the quantities of hazardous materials being stored or handled.

Management of facility modifications, maintenance and personnel interventions

The design, construction and control of modifications for hazardous installations must be undertaken according to the same standards as the original facility since **any modification, no matter how small, can engender risk**. Even if completeness cannot be guaranteed, the risk analysis conducted prior to any modification must focus not only on the target unit, but also on all connected units, whether by their proximity, a shared utility, measurement chains or common safety features, etc. Any modification must then undergo construction inspection, which was sorely lacking in the Flixborough situation.

Moreover, temporary repair work is never justified, and this requires even more emphasis when the repair tends to become definitive.

Beyond reducing risks strictly related to physical deficiencies, an organized and planned preventive maintenance program is always preferable to any kind of emergency intervention. In addition, resuming installation operations after an incident requires a preliminary analysis of the causes leading to the shutdown. This accident clearly highlights **a flaw in managing feedback**, given that the other reactors escaped investigation even though cracks had already appeared.

The "theory of the 8-inch pipe" is based on the fact that two flange bolts of a cyclohexane pipe were found loosened. The number of clamping points along with the equipment clamping torque constitute critical safety specifications that must not be overlooked, especially in the presence of a high hazard potential as in the Flixborough case.

The crack in Reactor no. 5, which served as the source of the accidental sequence, stemmed from corrosion caused by spraying the reactor with drinking water (hence high in nitrates) in order to dilute cyclohexane discharge and limit the risk of ignition. Any intervention procedure needs first to be examined and its consequences assessed prior to adoption, since an ill-suited intervention could give rise to risk.

Other technical lessons

The majority of pipes involved in the accident had undergone cracking due to weakening as a result of liquid zinc (see Appendix 2 of the investigation commission report). According to Cox, this phenomenon lies at the very origin of the accident, i.e. breaking of the 8-inch pipe. Studies have shown that the steel pipe failure phenomenon due to zinc may arise below a temperature of 800° to 900℃ and at a tension of 5.8 kg/mm² within just a few seconds. The potential sources of zinc identified include galvanized railings and staircases, galvanized sheathing support wires and the primer paint coat.

When zinc is in contact with steel equipment under pressure, the slightest small fire that sends temperatures near 800℃ could weaken equipment to the point of failure.

The crack in Reactor no. 5 indicates that drinking water contains nitrates capable of causing steel corrosion when under tension. In the case of fire that incites use of nitrate-loaded water for example, it would be necessary to verify the structural integrity of pressurized steel equipment, given the potential for nitrate-induced corrosion to occur.

Management, the human factor

A shortage of the right senior personnel inside the plant constituted one of the causes of the Flixborough accident.

A well-trained staff, aware of the hazards inherent in operating their facility, with access to necessary information sources (such as design standards or technical guidelines for the equipment in use) and possessing multidisciplinary knowledge or knowing how to recognize their expertise limitations by requesting advice from more specialized third parties when appropriate, proves essential to introducing a safety program for a hazardous installation.

Only a well-skilled and experienced workforce will thus be able to recognize precursor signals of an accident (such as cyclohexane leaks that "seal up on their own") and to adopt necessary measures to halt the accidental sequence.

In closing, installations must be designed and operated so that the personnel is not faced with having to chose between safety and productivity since a company's key goal is not only to produce, but to produce under the safest conditions. In this instance, hurrying to restart operations under economic pressure no doubt proved to be a determinant factor in this accident.

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