

# Rupture in Ammonia Shift Conversion Unit

Investigation of incident showed direct cause was corrosion, itself a result mainly of poor water distribution and a lack of good pH control

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Investigation of a serious rupture in the injection cooler on the shift conversion unit of an ammonia plant has led to an improvement in the pH control arrangements which is the mainstay of a program to prevent any recurrence.

The rupture was followed by an explosion and fire of short duration. No one was injured and the damage was confined mainly to the unit. The incident was at the fertilizer facility of Nitrigin Eireann Teoranta (Irish Nitrogen Ltd.) at Arklow, county Wicklow.

The ammonia plant is based on the Shell partial oxidation gasification process using heavy fuel oil as feedstock. The process stream, after initial gasification, consists of

gas cleaning in the form of carbon removal and hydrogen sulfide removal, followed by a shift conversion unit which is the area in which the explosion occurred.

In the shift plant, diagrammed in Figure 1, gas (containing 1.5% CO<sub>2</sub> at 30 atm., 40°C) is fed to the saturator where it is saturated with water, and raised to a temperature of 200°C.

Steam is added, and the gas passes to the shift converter. The gas (now 30% CO<sub>2</sub>) leaves the reactor at 400°C and is cooled to 200°C before passing to the injection cooler (a column with two beds of Raschig rings), where it is further cooled by a countercurrent stream of water to

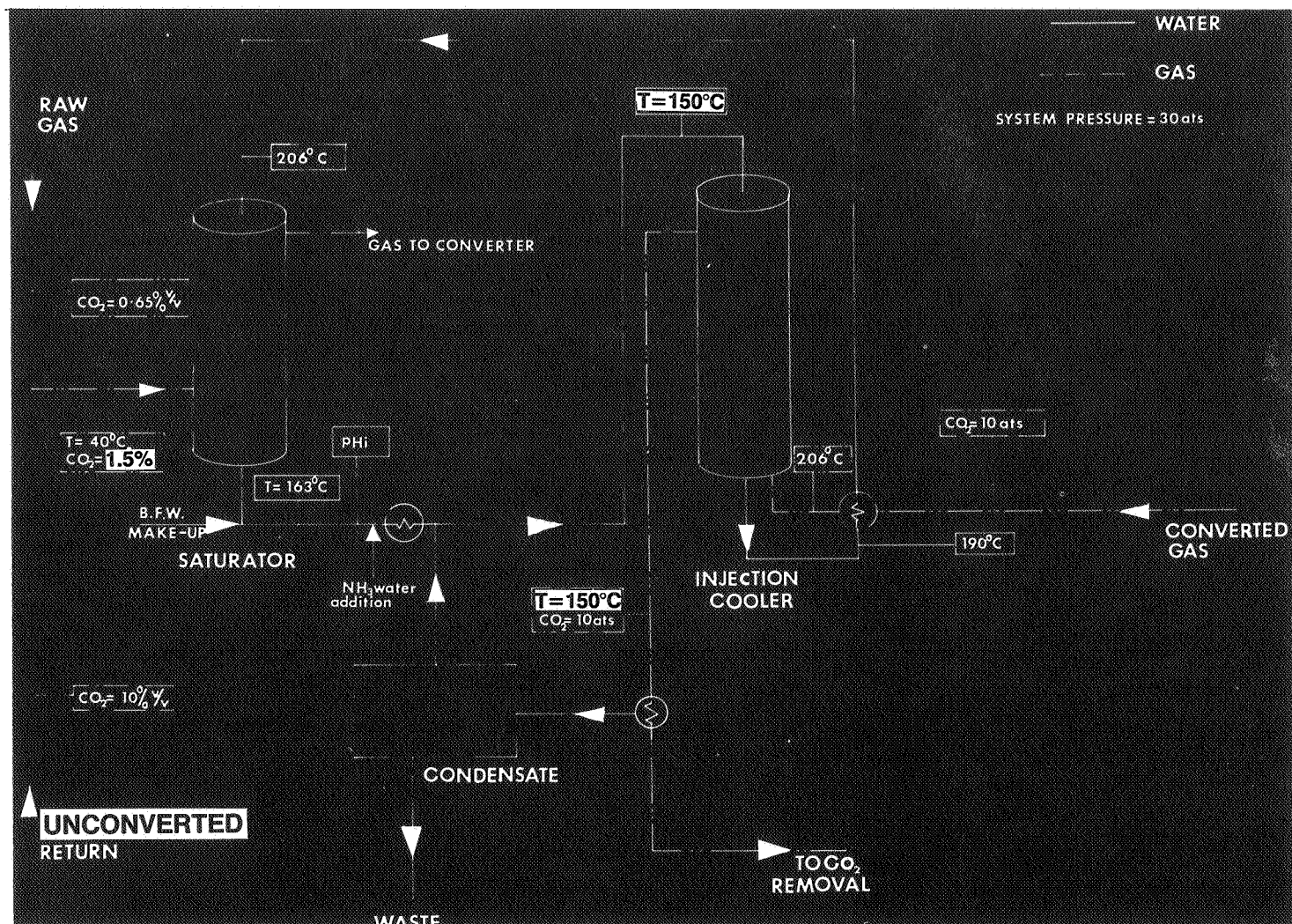
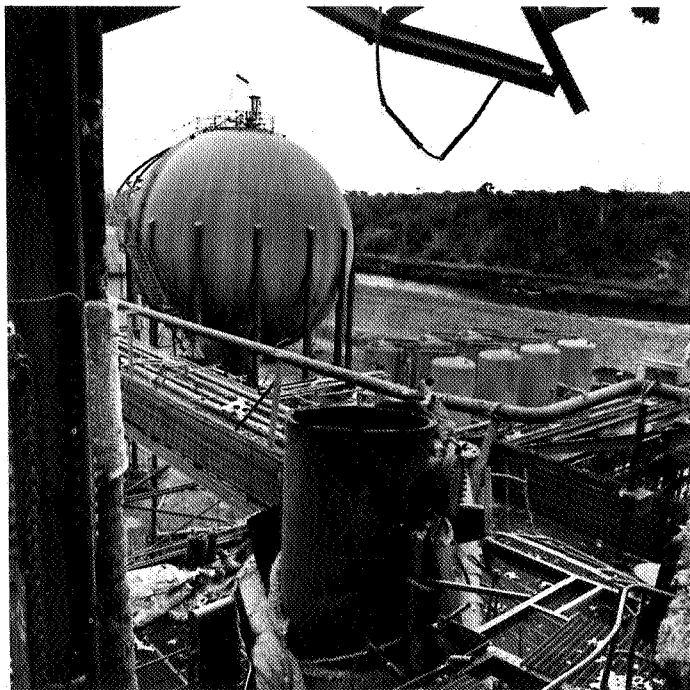


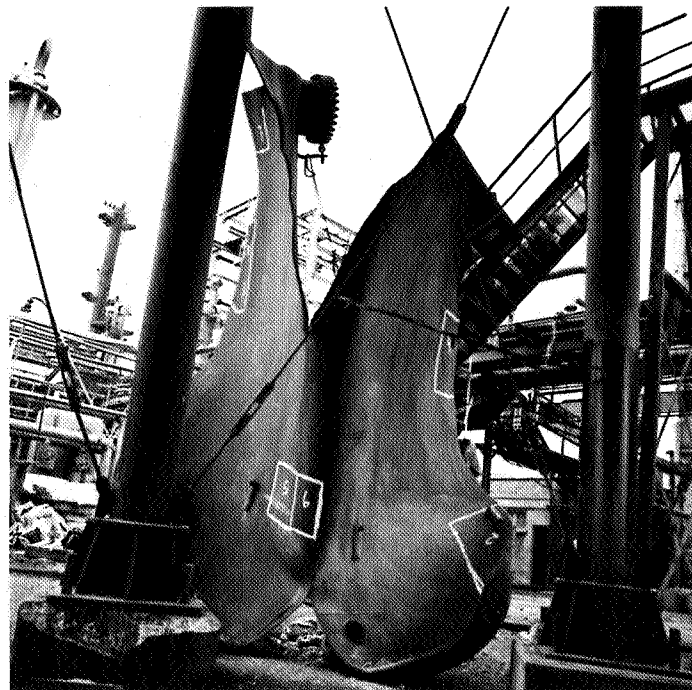
Figure 1. Flow diagram showing water circulation in shift plant.



**Figure 2. View of the units and the sphere.**

150°C. It then passes to a final cooler and water separator.

Water is circulated in the system from the saturator to the injection cooler as shown in Figure 1. Make-up to the system is either condensate from the gas or boiler feed water. Before the explosion, the pH measuring point was after the saturator and pH was controlled by NH<sub>3</sub> water addition through metering pumps.



**Figure 3. View of the top section against the sphere.**

#### **Incident started with rupture in cooler**

At 00:50 hrs. on August 18, 1974, the injection cooler on the shift unit ruptured. The plant had been operating quite normally prior to the explosion. Operators reported seeing a purple-blue flash followed by a bang and a fire of short duration. No personnel were injured.

Debris was scattered over a wide area. The top section of the injection cooler was thrown against one of the ammonia sphere stanchions. Damage was confined to the immediate vicinity of the unit. Figure 2 shows the general area with the damaged unit in the center and the ammonia sphere in the background. Figure 3 shows where the top section of the vessel ended up at the sphere.

Figure 4 gives an idea of the damage done to the unit and what remained of the injection cooler. The saturator, a similar vessel, is the one beside the injection cooler.

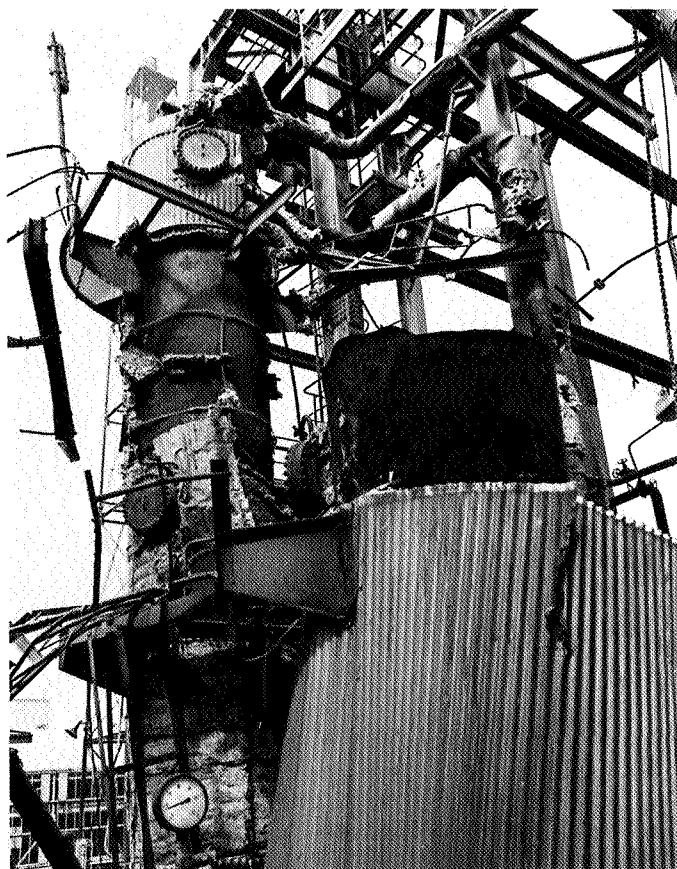
Figure 5 illustrates the distribution of fragments of the vessel after the explosion. XA is the top section of the vessel at the sphere; XB the distribution nozzle at the river bank; XC the gas outlet baffle of the vessel at the No. 2 compressor house; and XD sections of support grids scattered over a wide area of the plant.

Following the explosion, the plant was quickly and efficiently shut down by operating personnel.

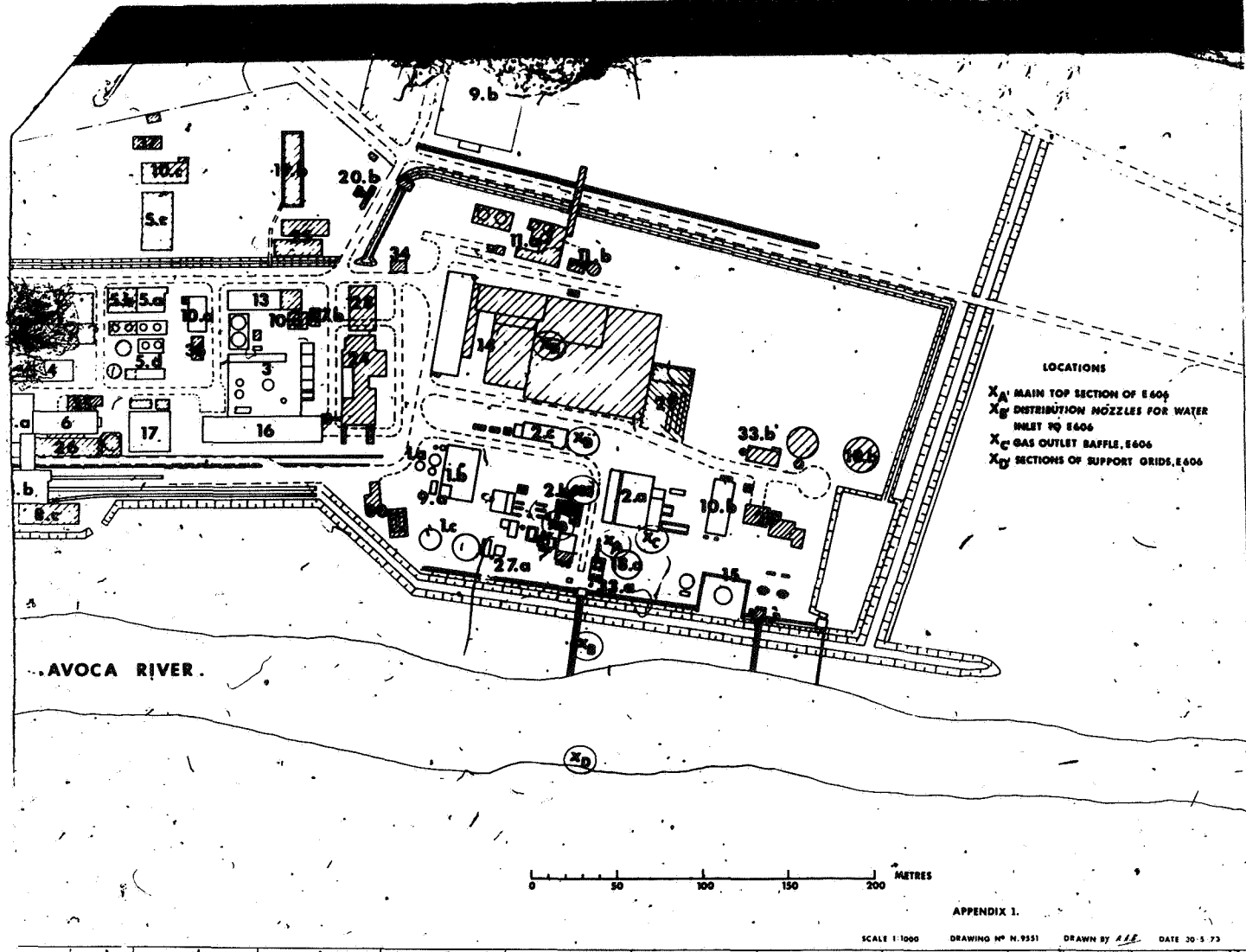
#### **Metallurgical study shows ductile fracture**

An investigation into the cause of the explosion was carried out by N.E.T. technical staff in co-operation with an Imperial Chemical Industries (ICI) investigation team and a metallurgist from the Irish Institute of Industrial Research and Standards.

The metallurgist's examination found no evidence of a brittle fracture, the whole fracture area having a ductile appearance. Sections taken show the fracture passed through a weld which seemed to have preferentially cor-



**Figure 4. View of unit 600 after the explosion.**



**Figure 5. Plot showing distribution of fragments.**

roded. This can be seen in Figure 6, which shows a microsection through part of the fracture area. There was considerable thinning of the vessel wall in a fairly localized area.

Figure 7 shows that when the circumferential variation of wall thickness in the top of the vessel was plotted, four areas of severe corrosion were found as can be seen. One of the troughs is predominant and here the fracture occurred.

In Figure 8 the old water distributor is shown as recovered after the explosion. It consisted of four vertical legs, which can still be seen. Attempts to correlate the position of the four thinned areas of the vessel with the distributor legs met with some success.

The main conclusions were that a clear pattern of corrosive attack occurred on the inside surface of the vessel related to the distribution of water through the vessel. This thinned the walls of the vessel, eventually causing a ductile fracture. Although the fracture was through a vertical weld, it was considered that this was coincidental but that the weld corroded preferentially.

The vessel was fabricated in January, 1964. Inspection and hydraulic test (to 46 atm.) were satisfactory. The vessel was fabricated according to German standards and supplied by Lurgi Warmetechnik m.b.h., Frankfurt-on-Main, West Germany.

After the first year of operation, a thorough inspection of the entire plant was carried out, and a plant history record system established. In the second year this was re-

peated and the plant record system established. It was decided at that time that the injection cooler needed only visual internal inspection every two years.

Inspection reports from September, 1966, show that there was corrosion of the support grids and rolled steel joint supports but that the vessel itself seemed to be in good condition. An ultrasonic test in 1969 and again in 1972 on the *bottom* of the column indicated the vessel was satisfactory.

In May, 1973, a visual check on the top and dished ends of the vessel showed it to be satisfactory. In May, 1974, ultrasonics on pipework around the vessel showed no marked deterioration. The vessel itself was not opened at that time.

### Curve of corrosion rates was plotted

Since the vessel appeared satisfactory in May, 1973, changes in process conditions from then to August, 1974, were investigated to see if any conditions were changed which could have accelerated the corrosion rate in the vessel.

All process conditions of interest were plotted from March, 1973, to August, 1974. Among areas investigated were corrosion in heat exchangers in the water circulation system, the fact that the make-up water to the system had been changed from condensate from the gas to boiler feed water, and any change in operating conditions which could have contributed to accelerated corrosion. It was



**Figure 6. Microsection through part of the fracture area.**

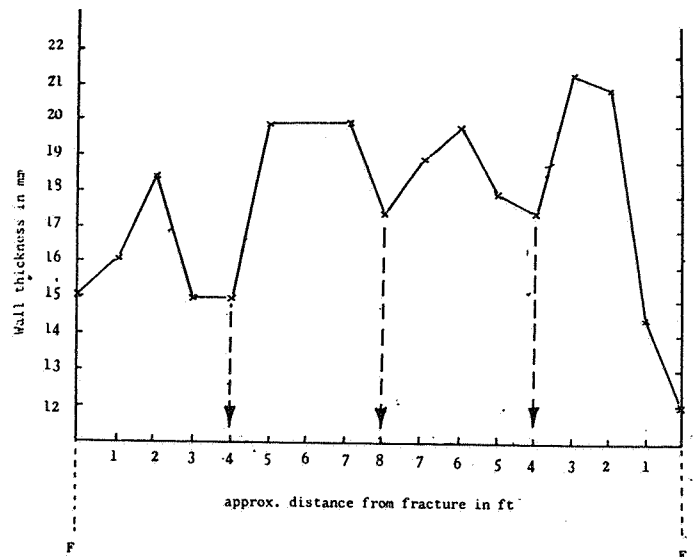
concluded that none of these factors had a marked effect on the system.

Also plotted from 1971 to August, 1974, was the pH of the circulating water taken after the saturator. The main body of readings fell between pH 7 and 8. An analysis of the readings over the period showed a number of trends, as seen in Figure 9. For example: the percentage of readings in the pH range 7-8 decreased sharply, and the percentage of readings of pH < 6.0 and pH < 6.5 increased by a significant amount. Because of these findings, the method of pH measurement and control was looked at in some detail.

### Lack of precise data on pH values

The circulating water system on the unit, shown in Figure 1, is particularly prone to corrosion because of the presence of CO<sub>2</sub> in the water which comes from the shift gas. The pH was controlled in the system by the addition of a 10% ammonia water solution to the system after the pH-sample point at the saturator outlet.

It was found that where the pH should be measured and what the values should be was not really known. The Lurgi operating manual for the plant did not specify where the pH was to be taken from. Also it was vague about the



**Figure 7. Variation of wall thickness in E-606.**

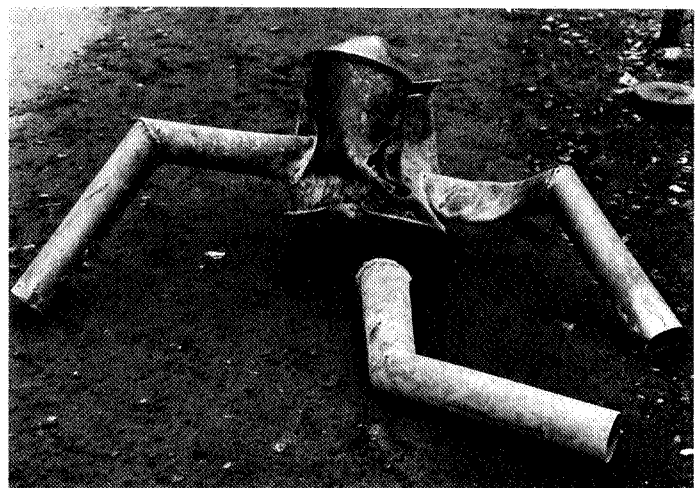
minimum acceptable value, stating at one place 6.5 and a few pages later 6.5-7.0. Lurgi responded to correspondence after the explosion that the pH should be 7-7.5 after the saturator and after NH<sub>3</sub> addition. The practice of taking samples after the saturator was established by following the example of Lurgi commissioning personnel.

The control system was that if a pH reading (taken every 8 hr.) was less than 7.0, then NH<sub>3</sub> liquor was added to the system until the next reading was above 7.0. Due to the time lag between readings and the fact that pH was sometimes difficult to raise, the pH might remain below 7.0 for periods of 24 hours and more at times.

Calculations by N.E.T. research and development personnel suggested that the pH in the injection cooler would be lower than at the measuring point at the saturator. These findings were confirmed by experimental work in the laboratory.

The reason for the difference is the much higher CO<sub>2</sub> partial pressure in the gas in the injection cooler. It was found that pH in the injection cooler would be 1 to 1.5 units lower than at the saturator after NH<sub>3</sub> addition.

Thus, a pH of 6.5 at the saturator could mean one of about 5.28 at the injection cooler, assuming 10% loss of circulating water (blowdown etc.) and 0.75% CO<sub>2</sub> in the feed gas.



**Figure 8. The old distributor (after the explosion).**

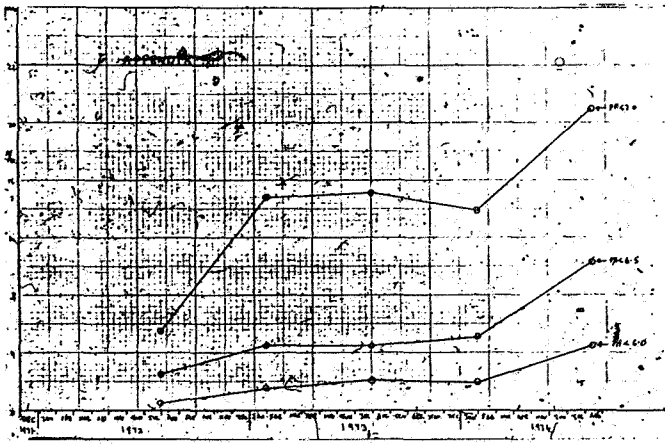


Figure 9. Variation of pH.

Precise information on corrosion rates for the condition in the injection cooler was difficult to find. There is general agreement in the literature that carbonic acid, like any other acid, has a corrosive action on iron and steel. Direct dissolution with attendant hydrogen evolution occurs at pH 5.0-5.5 at ambient temperature and increases progressively with further lowering of pH. The presence of  $O_2$  accelerates this reaction. It was considered unlikely that much  $O_2$  was in the water system. This was confirmed later.

What happens when  $H_2$  evolution occurs can be seen in Figure 10, which shows corrosion rate vs. pH for the HCl system (the carbonic acid system is similar.) The corrosion rate increases very rapidly after hydrogen evolution starts. At increased temperature, the pH for hydrogen evolution also increases. Thus, for conditions in the injection cooler it could be as high as 6.0.

Therefore, it can be seen that the increase in the percentage of low pH's over the period 1972-1974 is significant because: (a) the pH in the injection cooler is lower than that at the saturator; and (b) a pH of 5.0 to 6.0 is critical for carbonic acid.

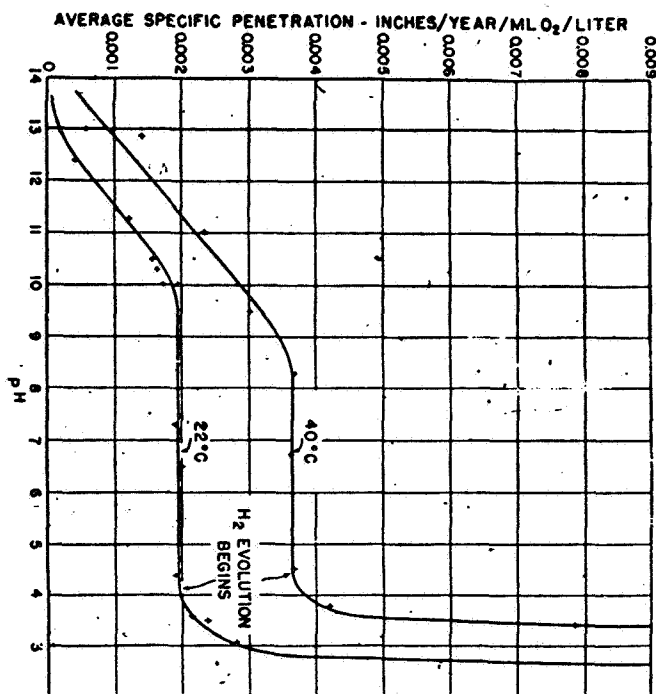


Figure 10. Critical nature of pH on mild steel corrosion.

Why there should have been this increase in low pH was never precisely determined, but there was a general lack of emphasis on pH control which started with Lurgi's initial attitude toward the problem and continued under N.E.T.

Calculations on the loading of the column indicated the top section was operating under the lower loading limit curve. The implications of this are that probably some channelling and possibly film washing of the vessel walls would occur. According to the I.C.I. team, film washing is the most severe flow regime where  $CO_2$  corrosion is involved. This sort of regime would not occur in the bottom of the column.

## Conclusions

Rupture of the injection cooler was caused by loss of metal in the area of fracture in the upper part of the vessel, a vertical weld being particularly badly corroded.

No abnormal corrosion was reported in May, 1973, so an increase in corrosion rate sufficient to reduce the wall thickness below the minimum took place in the period May, 1973-August, 1974. It was considered that the increase in corrosion rate was due to at least two mechanisms: 1) an increase in the number of low pH excursions below the recommended figure of approx. 6.5; and 2) maldistribution and possibly film washing on the upper walls of the vessel. The primary cause was felt to be the increase in low pH.

The pH measuring point did not record the lowest pH in the system; and this was not appreciated by Lurgi when they commissioned the plant nor afterwards by N.E.T., nor was the actual importance of pH itself in  $CO_2$  corrosion.

The main measures taken to avoid a recurrence of the corrosion problem were as follows:

1. pH was now to be measured at three additional points on the water system: a) after  $NH_3$  addition and before the injection cooler; b) half-way down the injection cooler; and c) after the injection cooler.

It was hoped to keep the pH in the cooler as high as possible (7.0 if possible), but it was felt that with such a pH in the cooler, the pH into the cooler would be so high that Raschig ring softening would occur.

2. The pH readings were to be taken more frequently (initially hourly).

3. A distributor tray (weir trough type) was provided for the new injection cooler to improve the water distribution.

4. The injection cooler was coated with an aluminum spray paint.

5. Corrosion probes were placed around the water circuit.

6. Spot checks were made on oxygen levels in the system.

7. Laboratory experiments were to be done to provide accurate corrosion rates vs. pH from the system under simulated plant conditions.

## Performance of plant since start-up

Since plant start-up in November, 1974; average pH into the injection cooler are 9.0 and in the vessel itself

about 6.5. The old pH point now registers 7.5-8.0.

pH control is now achieved by a 20 to 30% NH<sub>3</sub> water solution and a large slug dose of NH<sub>3</sub> water can be added to the system to raise the pH quickly if necessary. pH is now monitored every two hours into and out of the injection cooler.

When the plant was shut down in May, 1975, no serious corrosion was found in the vessel. #



G.B. Casey

## DISCUSSION

**GENE COMEAU**, Farmland Industries: Could you tell me the reforming pressure of your plant.

**CASEY:** The operating pressure is 30 atmospheres.

**COMEAU:** I'm familiar with a similar situation at the saturator and cooler but the pH always ran very high, without any ammonia injection. It seemed that there was enough ammonia made in the shift converter that ammonia injection was not needed. I thought maybe you had a low pressure reformer but that's not the case. Do you have any idea why, without knowing the detail of my plant, we had a high pH and you have a low?

**CASEY:** Well first, in part of the Paper I said that 18 months ago we stopped returning condensates from the gas. These condensates contained some ammonia. The reason we stopped it was the injection pumps which were positive displacement pumps were giving an awful lot of trouble and it was easier to supply makeup for the system from the boiler feedwater system. There is a school of thought which says that ammonia in the returned condensates maintains the system in balance, but we cannot prove that beyond the shadow of a doubt. So that's one thing that was changed and may have caused the pH to come down, partly. Also, we have our return gas from a copper liquor system in the synthesis end of the plant, and when that gas compressor is out of operation you don't get the return gas into the shift conversion unit, so that the ammonia in this gas is not available for pH control. This return gas system was out of operation for a significant length of time in the period of this review.

**COMEAU:** Just where is the cooler located in the process?

**CASEY:** The cooler—the injection cooler?

**COMEAU:** Yes

**CASEY:** First of all it's a Shell gasification plant. You gasify heavy fuel oil, you remove carbon, and then you remove hydrogen sulfide, and the gas comes then. The first vessel in the conversion plant which this gas meets is the saturator, by which it is saturated. Then the saturated gas goes to the converter, and then the gas coming from the converter goes into this injection cooler.

**COMEAU:** I see. Well the one I was familiar with was in a different place, so it actually had a water make, so you didn't inject water.

**CASEY:** Normally you should not have injected water in

this one either. There was a water makeup because condensates were allowed to drain continuously.

**ANON:** We also are operating a high temperature shift conversion at a temperature of 50 atmospheres. The gas is also coming from a partial oxidation so it's quite similar to your unit. In the first three months after start-up, the first start-up, we were not aware that this pH must be controlled in a really narrow range. After three months operation we inspected several parts of the CO shift conversion and realised that very heavy corrosion had taken place, together with erosion coming from cavitation by releasing the carbon dioxide when the fluid passes a control valve.

After this we first lined up all elbows and all piping downstream of control valves in the water system with stainless steel lining, and second, we installed an automatic on-line analyser, which gives us the pH value upstream of the injection cooler, but downstream the saturator all the time. The question which I would like to ask you—how do you measure the pH value. If you take only the fluid and you allow the carbon dioxide to release you never would get a correct pH value, so that's my question.

**CASEY:** The method of measuring pH is done by laboratory personnel who cool it down to a set temperature so that there is a minimum amount of flashing off, and then the pH is measured. The pH they report is derived from this measurement and is based on a formula worked out by the laboratory personnel. In other words, you are quite right—you can't get a proper true value of pH because you do release the CO<sub>2</sub> from the water when you take the sample, but our laboratory personnel have derived a system but I am not familiar with it quite frankly.

**CHUCK McCOY**, Chevron Research Co.: I'd like to go back to the comments made by the gentleman from Farmland. It's my impression that most of the ammonia is made in the secondary reformer, and not in the shift converter. This becomes pretty important to the man who is running his first steam methane hydrogen plant after ammonia experience—if he relies on that few hundred parts per million ammonia to prevent condensate corrosion, it isn't there. Corrosion can be aggressive.