Fatal Accident in CO_2 Removal System

Remedial action after unusual incident in hot potassium carbonate service includes change to stainless from carbon steel for large elbow that had ruptured

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Investigation of a major fatal accident due to the rupture of a carbon steel elbow in the carbon dioxide removal system of an ammonia plant showed the probable cause to be erosion by impingement of a high velocity stream of hot liquid from a faulty control valve upstream of the elbow. This article describes the incident and remedial actions.

It took place on June 22, 1974, at Madras Fertilizers Ltd., in Madras, India. When the 16-in. elbow ruptured, hot potassium carbonate solution splashed into the control room, killing nine operators and seriously injuring a tenth.

The 750-metric ton/day ammonia plant, based on naphtha reforming, had gone into commercial operation in November, 1971. Madras Fertilizers' complete complex includes an 885-metric ton/day urea unit and a 1,100-metric ton/day NPK complex unit.

The carbon dioxide removal system is based on a proprietary process which has been used in more than 50 plants around the world since 1964. However, in India this is the first ammonia plant to adopt this process.

Referring to Figure 1, the converted gas from the shift reactors is scrubbed under a pressure of 28 kg./sq. cm. with a 25% potassium carbonate solution containing a corrosion inhibitor and a catalyst to promote carbon dioxide absorption and regeneration. The rich solution from the absorber goes into the regenerator operating at about 2 kg./sq. cm., at a temperature of 108°C through a letdown turbine. From the regenerator a semi-lean solution is pumped to the middle of the absorber at a temperature of 117°C through the control valve FCV-453 located at the ground level with carbon steel elbows on either side. A lean solution taken from the bottom of the regenerator is cooled and pumped to the top of the absorber at 70°C.

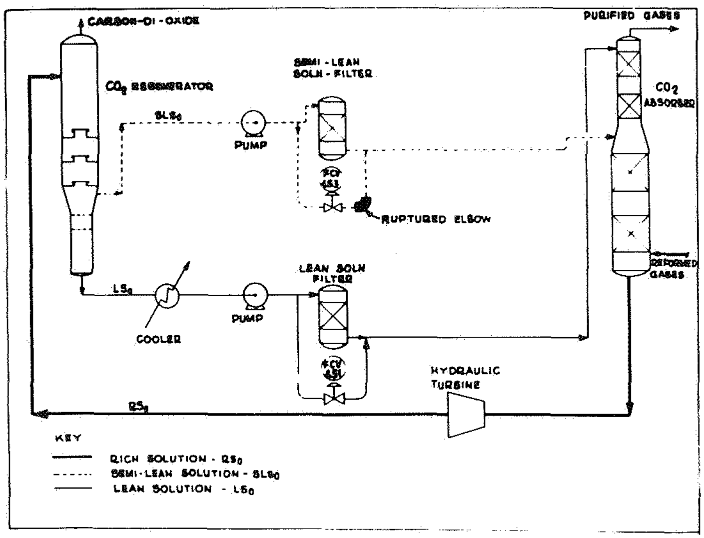

Figure 1. Carbon dioxide removal system, simplified flow diagram.

On the day of the accident, the ammonia plant was running smoothly at about 70% load. Around 7:30 pm, the 16-in. carbon steel pipeline carrying the semi-lean solution from the pump to the absorber ruptured suddenly, splashing the hot solution into the control room located directly opposite, after shattering the toughened glass panels. The nature of opening and the relative position and location of the failed elbow near the control room can be seen in Figures 2 and 3. The photograph taken from inside the damaged elbow on Figure 4 shows clearly the rupture facing the control room windows.

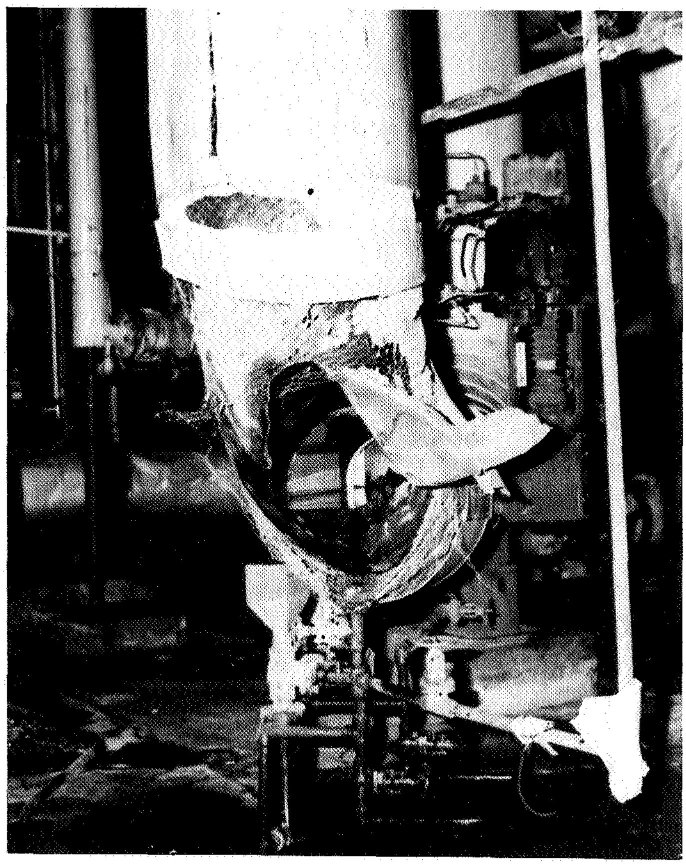

Figure 2. The failed elbow with the rupture.

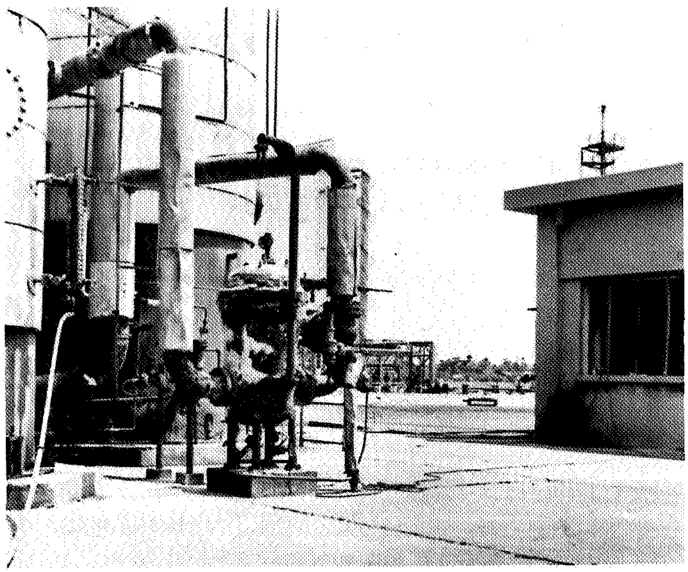

Figure 3. The relative position of the ammonia control room and the failed elbow (see arrow).

Of 10 persons in the control room at the time, 8 died almost instantaneously, one died after 5 hours in the hospital, and one recovered after long hospitalization.

Fast action prevented further injuries

The hydrogen gas from the absorber that escaped through the ruptured elbow caught fire and it took about half an hour to extinguish. Conditions were difficult because the control room as well as the front-end of the ammonia plant was in darkness.

Since the control room staff had died, and no one from outside could enter the room immediately, the ammonia plant was shut down on a crash basis under very exacting circumstances by the night superintendent and the operating staff remaining outside. It was a good job done with great presence of mind with no mishap or incorrect operation.

The synthesis gas compressor and the other compressors were manually tripped, the vent valves opened, and the process naphtha to reformer shut off. Many pumps were also tripped. Though the fire did no damage, the false ceiling and the light fittings and cables in the control room were badly damaged by the impact of the hot solution. Instruments and control circuits and switches in the control room were badly affected by the potassium carbonate and were out of action.

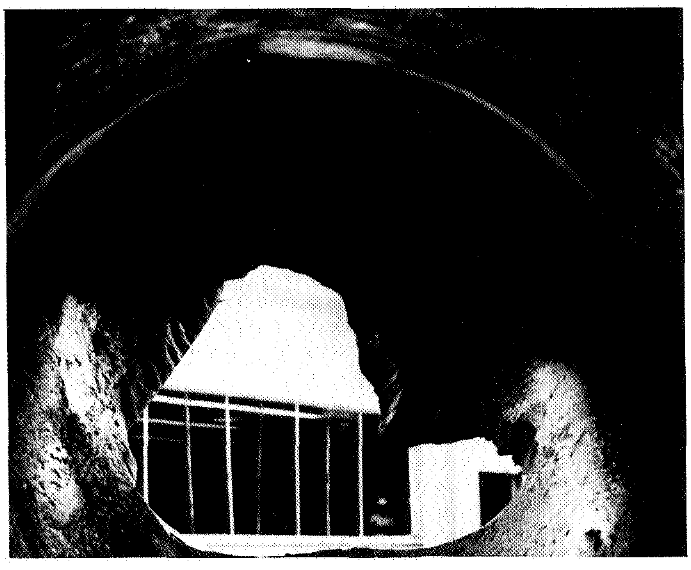

Figure 4. View of the control room windows from the inside of the ruptured elbow.

A departmental inquiry committee, appointed by the management to go into the causes of the accident and suggest improvements in the piping system and control room, submitted its report on July 11, 1974. The accident was considered most unusual because the elbow had eroded over a large area, rather uniformly to about 2-3 mm. thickness, from the original 10 mm., during a period of about three years of operation, and it failed suddenly with a rupture of about 15 × 13 in. opening. Since the rupture faced the control room direction, the consequences were tragic.

Various aspects including specification and quality of material of the elbow, the design of piping, the operating conditions, inspection schedules, and experience in other plants were examined.

Quality of materials used. It is believed from the nature of pattern of wear on the elbow material that erosion by the high velocity solution from the control valve orifice impinging on the elbow, with some possible cavitation by bubble collapse, is the major factor for the failure. The upstream carbon steel elbow and the main carbon steel pipeline have shown no corrosion/erosion during the same service period.

No defective materials were used

Metallurgical examination as well as the physical and chemical analysis of the failed and unaffected portion of the elbow have confirmed that the material used has not been defective and is within specification. Though it was known that high turbulence, and velocities considerably greater than 10 ft./sec., could result in erosive failure of carbon steel piping material, nobody foresaw that the control valve and its location near the carbon steel elbow would pose such a hazard to the safe operation of the plant.

Piping design. The material selection of the piping and fittings was based on previous operating experience and knowledge available from similar plants using the carbon dioxide removal system. In many critical places stainless steel piping and fittings were used. Details of the elbow, control valve, and reducers in the affected semi-lean line are shown in Figure 5. The 16-in. pipeline is carbon steel seamless A 53 Gr. B. The elbows are ASTM A 234 Grade WPB, while the control valve with 10-in. opening and two 16 × 10-in. reducers are S. S. 304L.

While the upstream elbow was supported from the ground, the downstream elbow was not. It is difficult to say whether this arrangement contributed in any way to the erosion.

Average velocity of solution in the different lines in the carbon dioxide removal system is in the range of 5.3 to 8.4 ft./sec., which is well within the 10 ft./sec. considered safe by the designer for carbon steel lines as it ensures satisfactory protective film. For the higher velocities occurring in control valves, orifices and reducers, stain-

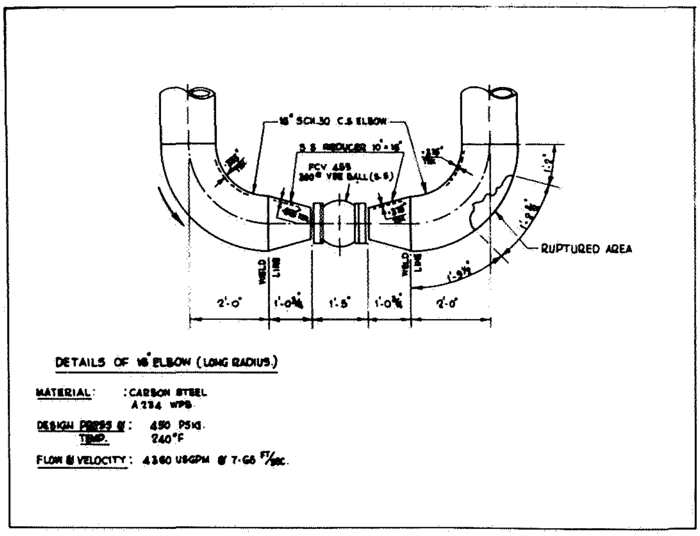

Figure 5. Details of the carbon steel elbow in the 16-in. semi-lean solution pipeline.

less steel is the recommended material.

Inspection and operating conditions. The extent of inspection of the pipelines and vessels in the ammonia plant was decided before the plant start-up by the foreign and Indian experts, based on their earlier experience. The failed elbow was not in the inspection schedule because the semi-lean service was not considered corrosive.

Ultrasonic thickness measurements carried out exhaustively subsequent to the accident in 170 critical locations in the entire carbon dioxide removal system showed that only in three places (two condensate lines and the reboiler nozzle) was the thickness reduction substantial but still above discard thickness. This confirms the uncommon and unexpected nature of the failure of the concerned elbow.

The condition of potassium carbonate solution in regard to concentration, catalyst and inhibitor content, extent of impurities like iron, chloride, silica, and suspended matter was checked and found normal and within the limits prescribed.

Comments of others found helpful

Experience in other plants. After the accident, we tried to get some information on the problems we faced, from similar plants in Europe and the U.S.A. and from the control valve manufacturers.

The replies show that many plants have changed carbon steel pipe and fittings in carbon dioxide removal systems to stainless steel after experiencing corrosion and erosion due to high velocities.

One plant in Europe with an MEA-TEA system has written about their experience in March, 1970:

"Due to such a construction elbow-valve-elbow and high velocity of fluid, the erosion took place on the outer radius of elbow and a strong explosion occurred."

A more-or-less similar rupture in a carbon steel reducer elbow of an 18-in. line in their system downstream of control valve has been reported by this plant. A 6 × 12-in. hole developed due to erosion caused by high velocity solution. The rupture was just below the elbow on the eccentric reducer.

We were also informed that outlet velocity of vee-ball control valve is greater than that of other types of valves like single or double plug, butterfly, etc. The valve's vee-ball characteristic may have been a factor in the elbow failure in our plant. Modifications adopted and recommended by these firms are: use of some straight length pipe after control valve; stainless steel elbow in place of carbon steel; and fixing the control valve in the vertical line after the elbow.

Remedies taken

To commission the ammonia plant after the accident, the following short-term remedial measures were taken.

The carbon steel elbow was substituted temporarily by a new one, lined with stainless steel weld overlay, and provided with some sentry holes to monitor possible erosion (so that the plant could be restarted early). This is to be replaced by a stainless steel elbow later after receipt of the imported piece.

The glass panels in the control room were reduced considerably in size without sacrificing visibility and operating convenience.

For psychological reasons, strong steel shields were installed protecting the bends in the lean and semi-lean lines from the control room direction.

With these modifications, and after cleaning the many instruments in the control room and carrying out inspection of other critical areas, particularly in the piping system, the plant was restarted July 8, and ammonia production was resumed from July 14.

As a long-term measure, stainless steel elbows have been ordered to replace all carbon steel elbows downstream of the control valves in the semi-lean, lean, and reflux lines.

There is a proposal to modify the semi-lean pipeline to the absorber in such a way that the control valve can be fixed after the elbow in the vertical section of the pipeline.

The schedule of periodic ultrasonic inspection in this section will include additional points considered vulnerable. It is expected that there will be smooth and safe operation of the carbon dioxide removal section with completion of these measures. #

T.R. Visvanathan

DISCUSSION

R.M. OSMAN, Exxon Chemical: Exxon operates four Catacarb units, and our general practice is to not use carbon steel where the velocity exceeds 6 ft/sec, not 10 ft/sec as you mentioned earlier. Also we find that even with velocities below 6 ft/sec, we need a very thorough wall thickness monitoring program in the Catacarb area, and have often found it necessary to go to stainless steel in elbows even when the line velocity itself is below 6 ft/sec.

VISVANATHAN: Thank you for the information. The 10 ft. per sec. was recommended by the designer himself. I was not aware that below 6 ft. is the current practice in your plants.

KEES VAN GRIEKEN UKF: I would strongly suggest you to be sure that welds in erosive MEA conditions are flush on the inside irrespective of whether it is carbon steel or stainless. Especially behind the welds you get increased material wastage due to local turbulence.

JERRY SCHILLER, Amoco Oil: We've experienced quite a bit of erosion downstream of the control valve also. We went to a stainless steel elbow and reducer. We have often noted quite a bit of erosion upstream of the control valve in the reducer, and last shutdown, we stainless overlaid that reducer section.

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VISVANATHAN: Thank you for the information. We didn't observe any erosion on the control valves, and the reducers on either side.

Q. We have also a similar system of Catacarb for carbon dioxide removal, and although the piping is stainless steel we have the problem with control valve, which is also stainless steel. The spindle of the valve got damaged, and there is so much noise and vibration in that valve, due to the high velocity, we are having all of this trouble.

I. WARDIJASA, Indonesia: We have a Kellogg plant with Catacarb for CO_2 removal, and we have very, very bad corrosion in the absorption tower near the distributor. Do you have similar experience like we do have?

VISVANATHAN: Anywhere else in the system we didn't have any corrosion. The inhibitor and solution concentration is kept all right and so far we have not observed any corrosion in the entire system, except this particular elbow which failed.

I. WARDIJASA, Indonesia: Well I would like to elaborate the problem. The problem is—this vessel is fabricated in Japan, and Kellogg specification calls for carbon steel. And apparently, they fabricated the distributor also in just plain carbon steel and now the distributor is finished—I mean, you know, corroded, and well that's I guess what started the corrosion in the absorber wall. Now, we put stainless steel in that part of the vessel.

VISVANATHAN: We didn't have any such experience. There was no corrosion at all in the entire system so far. May be the type of design for the inlet gas distributor makes a difference.

SHAUKAT MIRZA, Esso Fertilizer, Pakistan: We have also experienced a number of failures on our catacarb piping, but most of these have been confined in the vicinity of the rich solution letdown valve both in the main line as well as bypass line of the valve. The failures in the bypass line have probably been due to dead end corrosion resulting from concentration gradients. We also experienced erosion of the weld joint of an elbow, downstream of the catacarb regenerator lean section level controller. At every opportunity during a planned or emergency shutdown we dismantle the critical control valves and inspect them from inside. This is how we found heavy erosion in the weld joint of this elbow which then was repaired in good time before it could cause another shutdown or an accident.

We have now instituted a very elaborate program of monitoring which includes radiographic survey of critical bends, certain straight portions of the pipeline and certain reducers, ultrasonic thickness measurements, and of course actual inspection whenever a suitable opportunity arises.

I wonder if you have experienced any corrosion problems on the rich solution line, upstream of the Control Valve?

VISVANATHAN: The rich solution line is all stainless steel, right from the beginning. With this material we didn't have any problem of corrosion in this line. All the available previous knowledge was utilised in the design of the plant and very well we knew there wouldn't be corrosion in these critical areas which are of stainless steel. But about this particular elbow, I don't know why this was not considered critical from previous experience. It seems the type, size and location of the control valve or the material of elbow or this combination perhaps used for the first time seems to have done this damage.

JOHN LIVINGSTON, ICI, Billingham: We do not in fact operate the Catacarb process, we operate the Vetrocoke process. But we do in fact approach these sort of solution velocities and we have in fact evidenced erosion on bends in similar positions. Evidences that this is being a slower process over quite a long time—we are talking now of pipe work in a plant with the age of 10 years. I just wonder though if some of the people who have already spoken in the room have any indication of what sort of corrosion rates they are in fact measuring when they are doing the ultrasonic thickness tests, because we are coming around at Billingham to considering a policy of ten years change out of pipe work. Because it does seem, and I don't know whether there is any corrosion potential measurements done at all in the Catacarb plants, but we in fact continuously monitor corrosion potential, or solution potential, and we have evidence of start of conditions where corrosion begins to operate at rather a faster rate than normal and here you must then obviously have a very very careful monitoring situation to see just how fast the piping is going.

VISVANATHAN: In our monitoring, we try to determine if we could come up with some sort of relationship between corrosion and reduced wall thickness, but what we have experienced is that in many places there is hardly any corrosion. Whereas it is possible that some corrosion may be localized in certain areas and in a very intensive way. And you could do a very thorough ultrasonic monitoring and yet discover afterwards that you have missed this particular single area, where the corrosion had concentrated, and that might leak through, leading to a plant shutdown.

So we haven't as yet really found any way of being able to prescribe a certain life for replacement of reducers or bends on the basis of corrosion measurements. We just want to replace with stainless steel those areas which appear critical from thickness measurements.

Q. Why do you need these windows? I can't understand it.

VISVANATHAN: Some of the operators are used to seeing the plant from there and watch for any happenings.

Q. That's not the same thing.

VISVANATHAN: If something happens they can get out and see.

Q. No, there's nobody passing outside, except the operators. What he has to see he can see on the panel.

VISVANATHAN: Everything is on the panel of course. But it is a sort of habit and it appears convenient to see the happenings outside.

Q. I still can't understand it.

VISVANATHAN: In the control room perhaps we don't need the windows, and one can manage without them. But more important I think is such hazards as pressure pipe lines and equipment being so near. That's also equally important I think, because even without the windows an accident like this can still damage the control room if it is so near, about 30 feet.

DON LUTZ, Consumers Power Co.: We operate two Benfield systems and have had similar problems. On this subject of erosion rates, we've seen erosion rates of as much as 500 thousandths or half an inch in 25 days. This was on regenerator reboilers right through the shell or nozzle areas.

JAN BLANKEN, UKF-Holland: A question was raised with regard to the plug coming off the stem of a catacarb solution let down valve. We had quite a number of failures of let down valves in our CO_2 removal systems and as far as I know we brought up the diameter of the stem to its maximum and we made sure that there was no thread of the stem-plug connection outside the plug which could act as a stress raiser.

As regard to corrosion in general in the Pernis plant, where we operate a MEA wash without inhibitor, after seven years of operation, we found corrosion in the discharge line of the pump, which is not abnormal. But as I understand the corrosion was limited to a piece of piping which nobody expected to corrode more than the piece of piping next to it.

You have to be very careful when inspecting piping you could have some piping for unknown reason corroding more than the other.

Because of this should it not be considered, with due respect for the sophisticated non destructive testing techniques, to use the old fashioned method of hydrostatic testing lines in CO_2 removal systems say every planned shutdown.

This applies especially to the older plants.

J.A. LAWRENCE, CF Industries: I'd like to give my opinion about control room windows. Actually I spent many years working in control rooms and I personally feel if you have shatterproof windows, that a window is a big safety aid in a plant—to be able to look out and see little flange leaks, or just for sheer pleasure of working there, to be able to see what the heck is out there. And I don't agree with my friend here who raised all the hell about windows.

I do think the control room should be located where you are not too close to hazards, but to be able to look out across that plant and see it, to me seems to be a safety feature of a plant.

I do think the control room should be located where you are not too close to hazards, but to be able to look out across that plant and see it, to me seems to be a safety feature of a plant. And in our plants, I still think we want to have control room windows.

JIM BORSO, DuPont: It seems to me that the piping system ought to be upgraded at least to stainless steel in these locations, and I wondered if the equipment manufacturers and suppliers are doing this in the Catacarb system. Have you got any input from Eickmeyer or whoever built the plant?

VISVANATHAN: Yes, we wrote to him and we got the information that this should be changed to stainless, and so we shall do it.

JIM BORSO: The entire system or just the elbow?

VISVANATHAN: Only the elbow.

PAT LOMBARDI, Esso Chemie, Netherlands: There's a lot to say for having no windows in control rooms, but I'm going to admit that there is a case for having something the operator can look out of. I don't know whether Guy Legendre remembers, but when Monsanto at Luling was starting up I happened to look out a window just as an insulator tripped the CO2 system let down valve.

It was fortuitous that the window was there and I was looking out and was able to get out in a hurry to reset the trip. That could have led to a disaster too, so we must maintain our perspective in deciding we want to eliminate all control room windows.