Repairing Titanium-Lined Urea Reactors

Experience in several British plants of ICI with corrosion in titanium-lined vessels led to the development of a number of useful repair methods.

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Useful repair procedures have been developed in Imperial Chemical Industries' ammonia-urea facilities over recent years on the basis of direct experience with three Mitsui-Koatsu type units, involving five reactors lined with sheet titanium and made in Japan. Discussions with Kobe Steel, the makers, who were very helpful, shows that the ICI experience is typical.

Figure 1 shows the general arrangement of a lined urea reactor. The liner corrodes slowly but uniformly, the rate of loss being about 0.1 to 0.2 mm./yr. at the bottom, and 0.1 mm./yr. at the top. Inasmuch as the thickness is only about 5 mm., this loss rate will ultimately require replacing the entire lining; but that should not be necessary for more than 20 years, based on calculation. The first titanium-lined reactor is still in good condition after 11 years of service, and shows no immediate necessity to replace the liner within the next 10 years.

More severe corrosion, perhaps mainly erosion, is found at the inner end of the CO_2-inlet nozzle (which also carries the injected air) and in the exit nozzle. We have fitted an internal standpipe to the CO_2 inlet and sleeved the exit nozzle so that the erosion affects only an item which can readily be replaced.

Small cracks appear at welds

The major cause of trouble is that small cracks appear after a period in service, almost always at welds, most commonly in the butt-strap welds between barrel and head of the liner, and in the petal plate butt welds. Propagation of these cracks is slow, and if the weld regions are crack tested by the dye penetrant process at each scheduled turnaround (annual or biannual) it is likely that they will be found before a leak occurs. Repair is not difficult if the cracks are found in time.

In one vessel which leaked the cracks had initiated at a local hard spot which could have been caused by hydriding that arose from local corrosion resulting from iron contamination of the surface. This is a well-known cause of corrosion and hydriding;ICI practice is: 1) to use low-iron titanium (0.05% max. instead of 0.2% allowed by, e.g., ASTM B265); 2) to take all possible care during fabrication and during inspection (e.g., special footwear, no steel scaffolds, etc.); and 3) to make doubly sure by anodizing the vessel *in situ* before start-up. None of the ICI reactors which have been anodized has suffered this hydriding and cracking, although this is of dubious significance since there is only one case among the much greater number not anodized.

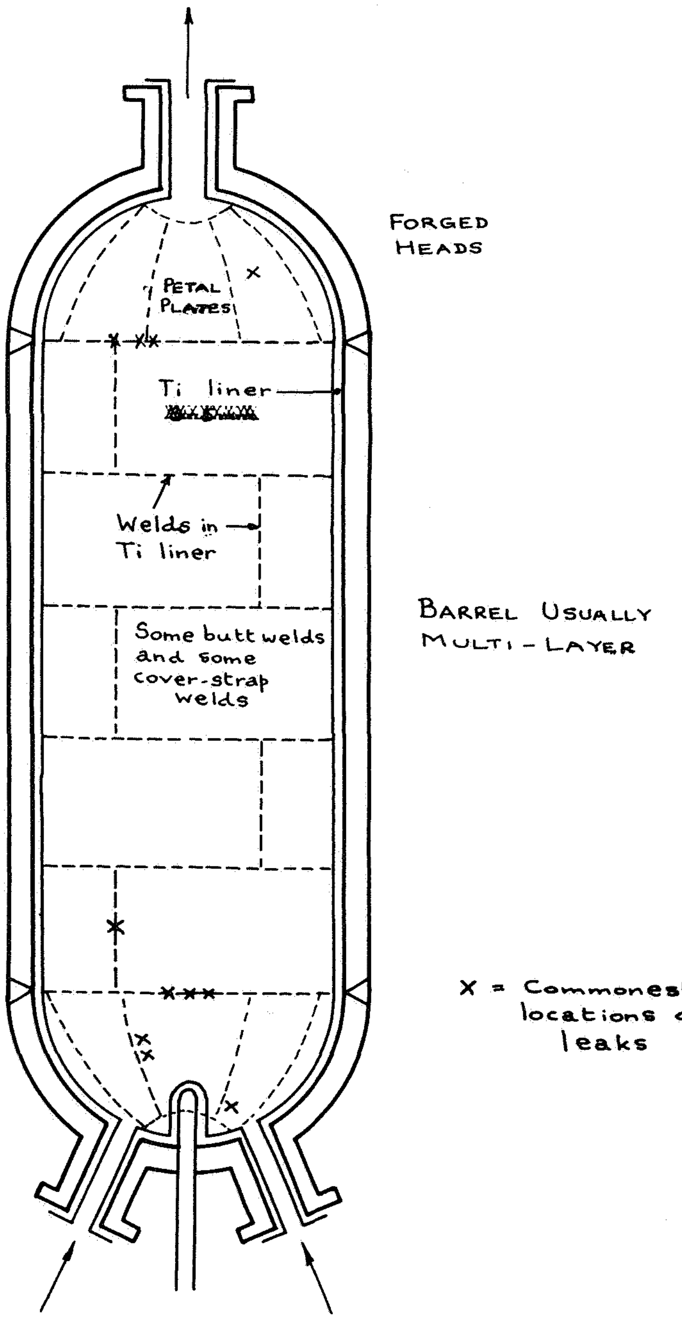


Figure 1. The general arrangement of a lined urea reactor.

It is also usual to find that the welds appear pitted, though close examination suggests strongly that these are spherical gas pores which have been exposed by the general surface corrosion. They cause some worries if they seem deep or a number are closely aligned.

It is well-known that if the liner leaks, whether it is silver, austenitic steel, titanium or any other metal, corrosion of the base steel by the urea melt can be very rapid. Standard practice with vessels having loose liners is to have a number of weep holes through the pressure shell so that liner leaks can be detected. To avoid damage, a reactor should be brought off line within a day after a leak starts. Various arrangements are in use which detect when a weep hole starts to blow, and signal this to the control room. No time should be spent in arguing whether it is a false alarm: the reactor should be brought off line immediately.

When cold, urea melt can solidify, and if a reactor is shut down without consideration, the leakage path may be blocked with solidified melt and be very difficult to find. The reactor should be kept hot and under pressure until the contents have been replaced with water which follows the leakage path and sweeps away the melt. Then, on cooling the leakage path is not likely to be plugged. This practice also sweeps away some of the urea melt usually behind the liner, and makes repair easier.

When the reactor is entered, the leak may be evident. More often it is not, and it may be difficult to find. Attention should first be paid to the area near the weep hole which gave the signal. However, it is not uncommon to find the fault in an area which would be expected to signal through a different weep hole. All internal welds may need to be dye-checked; a few areas may be found suspect and marked for repair.

Another method is to plug all weep holes, apply hydrostatic or gas pressure behind the lining, and look for inward leaks using one of the standard techniques. This is somewhat dangerous because the collapse pressure of the liner is very low and carelessness can destroy it.

Methods using gas with a tracer (organic halide or helium) are also suspect in that the lower part of the liner/shell gap is presumably full of water (or urea melt) and the gas may not reach the leak path.

The only leak we have had at Billingham was found more easily. It was at a fillet weld on a thermosheath in the bottom head; and when the inspector stepped onto the flat bottom water squirted onto his ankle! The original fillet weld had less than full penetration, and there was also a gas pore. Surface corrosion had caused a local leak.

In general, the damage to the liner is small—a crack an inch or two long in a fillet or a butt weld. If the leak has been allowed to persist for many days, there will also be attack on the steel of the shell, usually as a groove or cavity close to the leak, diminishing to negligible attack further away. It is not usual to find trouble near the exit weep hole. The extent of attack on the steel can be assessed by ultrasonic thickness measurements from the outside, except on the barrel of multilayer vessels.

One converter had lost about 2 in. of thickness of steel in the middle of a 20-in. diameter cavity. There is no doubt that a urea converter which is operated while leaking could cause a major accident.

Various repair methods used

Repair of the titanium, perhaps involving inserting a patch, is not very difficult. Repair of the steel is almost impossible unless a large area of the lining is taken out, because the steel is normally high-strength and needs heat treatment after welding. If, however, the amount of steel lost is such that the pressure strength of the vessel is not affected, it is reasonable to argue that all that need be done is to fill the cavity with something with sufficient hydrostatic compression strength to support the lining so that it does not deform into the cavity and tear at the edges.

In one case, we considered using a heavily filled epoxy mortar on the basis that it would not matter if it did denature. However, inasmuch as there was only a very shallow groove in the steel it was not considered necessary to do any filling. Other possibilities include a loose block of metal, tailored to fit the cavity. Lead could be used, but a lead tin solder would be dangerous. In one case, steel wires were fed in to fill up a groove under the titanium; this seems to have worked satisfactorily.

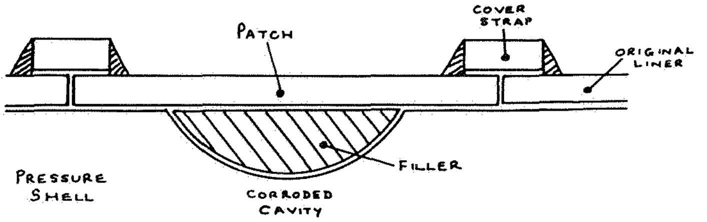
One uncertainty is that the leaking melt has probably spread far and wide behind the liner, even if it has not corroded much steel. It cannot be removed with certainty unless the liner is cut away. Will it have any ill effect (stress corrosion) on the vessel? The practical answer is that this problem has existed with very many converters and associated piping, lined with silver, austenitic steel and more recently titanium, and may have been put back in service with some contamination behind the liner. No ill results have been reported; and when converters have ultimately been stripped, nothing special has been found.

The technique used, therefore, is to cut a window in the liner to expose the cavity, clean and wash out, and fill it up level with the steel. A titanium plate is then tailored to fit the window and lie flush with the adjacent liner. Cover straps of about the same thickness are then pressed down over the joints by suitable struts across the converter, and fillet-welded into position. The heat of the welding is not sufficient to affect the underlying steel. At the corners of the "window frame" a groove-weld is made between the straps. These corners are additionally reinforced by a separate capping piece, accurately shaped to fit closely over the straps and bed down on the liner, and this is fillet-welded to straps and liner.

Figure 2 indicates the technique. Because there is little air behind the various items it is found unnecessary to go to the considerable complication of argon purging behind the straps, long as the fillet welds are at least two runs thick.

For small cavities in the steel it may be simpler to use a single cover patch of titanium rather than a window frame of strip. If there is no cavity, it may be sufficient to do no more than fillet-weld a patch over the leak area. One point is essential: the fit of inserted patches, cover straps, etc., must be very good, otherwise the repair will not last.

The discovery that the cracking in one vessel was associated with hydriding of the titanium added a new dimension to the picture, because welding on hydrided titanium is very likely to cause cracking. Etching



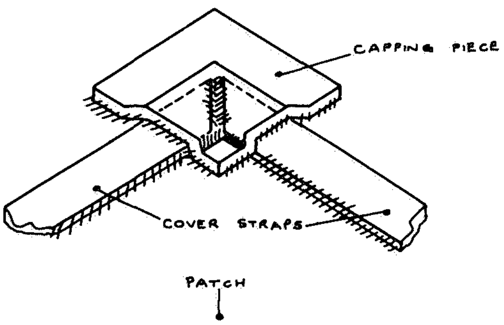


Figure 2. Two views of repair techniques.

techniques exist which can show, *in situ,* whether there is hydriding. If it is found, the repair should involve removal or covering of the hydrided area. ICI will follow this practice in the future.

Plan is to watch the pore problems

As noted above, it is usual to find many pores in the welds, and opinions differ as to their significance. We have taken no action about those problems in our vessels except to record them so that we can tell at the next examination whether they are getting worse. Japanese practice, we believe, is to weld over them, especially if there is a notable aligned group. Much depends on whether any cracks are found that necessitate welding, and on the skill of the available welders.

There has been a fundamental change over the years. Originally, it was thought essential that any joints in a liner should be butt-welded, and radiographed. More recently, this has been the aim but fillet-welded straps have been accepted where it was not practicable to use butt welds. Service experience with these, and with repairs made by fillet-welded straps, has been such that they are acceptable. When our titanium liners get dangerously thin, there is little doubt we shall consider relining the reactors *in situ* by this technique, using specially formed petal plates in the ends, etc. #

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DISCUSSION

Q. After how many years did you notice the corrosion?
CLARK: It's been on line something like seven years. We think it has been corroding uniformly from the word go. It appears to be a steady rate of corrosion.
Q. Well I ask that question because last month we just had a turnaround, after operation for one year and we did not notice any corrosion at all, of the liner.
CLARK: Well what I'm saying here is that the rate of corrosion is between 1/10th and 2/10ths of a millimeter a year, generally uniform, so you've got to be pretty clever in thickness measurement to find it after only one year.
Q. Second, do you set a limit, to the H_2S content or sulfur content in the CO_2 which is going to the reactor?
CLARK: We probably do but I don't know what it is. That's not been a concern of mine. John Livingston, do you know? 112S content CO2?
LIVINGSTON: The answer as far as we are concerned Willy, is that we operate the Vetrocoke CO_2 removal process. All our attempts to find sulfur in the CO_2 have proved negative, not detected. That's the situation.
CLARK: All right, thank you.
Q. The third question is what is your operating temperature because the temperature affects the rate of corrosion.
CLARK: About 190° centrigrade
MAX APPL, BASF, Germany: I have to add a little of our experience which is perfectly fitting to that what Mr. Clark said. We operate at Ludwigshafen a similar urea converter, also titanium lined. The lining is made in a little different way because we have fixed different cylindrical pieces of lining by making the circumferential welds on stripes of titanium which are inserted in the pressure shell. After about 6 years of trouble-free operation, we detected a leaking weeping hole. The reason was a small crack between welding seam in the upper spherical part. We repaired it by covering it with a small piece of titanium. Two months later we observed a large leakage at the inlet nozzles caused by circumferential crack about 7 mm long. Another defect was detected between the cylindrical part and the upper spherical part. Apart from that, we observed four big bulges in our lining, about in

the midst of cylindrical part, approximately 4 feet long and one feet broad, which probably were caused by some differential pressure between reactor and the space behind the liner. It could well have been the case when we had depressurized the reactor, some ammonia being behind the liner had expanded and caused that trouble. Because in the case of an untightness of the liner, urea and carbamate melt, together with ammonia, can come into the inner space between the liner and the reactor wall, and by solidifying the melt it's well possible that a given volume of ammonia gas is enclosed.

We succeeded in repairing those bulges. First we cut some holes in it and rinsed with water and in one bulge, we cut a window to look behind. We could see no severe damage of the pressure shell because we acted rather quickly in that case, and started repair activities immediately after leaking. It was relatively easy to bring the bulges back. We simply pressed them mechanically and they sprung back like bulges in a car door for example. Afterwards we only had to hammer a little to get final fitting.

All other things you mentioned, are perfectly in accordance with our observations.

Q. How carefully do we have to control oxygen for titanium-lined converters?

CLARK: Oxygen I think is less necessary for titanium than it is for austenitic steel, but it is beneficial. We ourselves, I haven't mentioned this previously, anodise our converters before we put them in operation. We anodise them after any repairs. There's a little bit of argument as to whether this is very important. But it does provide a good strong oxide film to start with.

Q. What is your opinion about the reason for the growing tiredness of the reactors? One are pinholes, the other cracks. We suspect pinholes.

CLARK: I would accept low-cycle fatigue as the cause of the cracks but as I don't know what stresses are acting I don't think it is a helpful explanation.

As regards porosity, it puzzles me a little because by and large if you make titanium welds with decent control, they are not porous. Pores of the size that you find after service would easily be detected radiographically. So I feel it a little unsatisfactory that the amount of porosity shown up by corrosion is far more than ought to be there anyhow. I don't know.

Now as regards hydriding, there is one case known where the cracking took place in a part of the titanium which was hydrided. A piece of the lining had been cut out, and analysis showed that it contained far more hydrogen than should have been there, and it's well known that this makes it brittle, more liable to crack, and so forth. We believe that hydriding wholly resulted from a significant iron inclusion in the surface of the titanium; under such conditions the corrosion of the iron releases hydrogen on the surface of the titanium and that hydrogen then can dissolve into the titanium and embrittle it.

There are etching techniques which can prove whether the titanium is hydrided. They do it very well in the laboratory. We've tried it in vessels without much success. Perhaps we haven't any hydriding. If we found any hydrided area on the titanium liner, we would cover up the area by putting a patch on top of it, even if it wasn't cracked already.

JOHN LANCASTER, Kellogg International, Ondon: Without knowing anything about urea, may I comment on this question of fatigue? Experience with aluminium loose liners in times past did show this type of cracking in welds. And we were able to convince ourselves in those days that this was, in fact, due to flexure of the lining causing fatigue, which was concentrated in the region of the weld. I think it's useful to think about this question because if, in fact, it is a fatigue problem, then the solution might be to fix the liner by explosion bonding or other means.

CLARK: True, it is relevant as I said in the beginning. Most of these cracks appear in the welds of the petal plates for the top and bottom heads, and those are the places where probably the fit is least good, and you get the most straining as the pressure goes up and down.

As regard integral clad vessels, I'm just a fraction nervous about this in that you cannot have weep holes if you've got a clad vessel. And if for some unfortunate reason, such as getting some iron on the surface of the titanium, cracking or corrosion of the cladding lets the urea melt get at the base steel, you may not know anything about it until the vessel goes pop unless you are keeping a close watch on the iron content of the urea and see this rise, indicating a failure of the cladding.

BERNARD BRODWIN, M.W. Kellogg Co.: I'd like to comment about your field welding. Many people are not aware of it but poorly welded or unblanketed titanium welds look horrendous. They are purple, green and all sorts of shades, and as you purify it you get a much less color. I think your associates at IMI·have run some experiments and shown that you can go to something like a pale straw color and not lose any corrosion resistance.

If it's done perfectly of course it will be bright, shiny, but apparently there is no change in chemical resistance even if you get this pale straw color.

CLARK: Correct. You can tolerate some coloration of titanium by welding. I think the damage caused by oxidation is more to the ductility than to the corrosion resistance. But okay, we take great care to screen well, very carefully, on the working side of titanium. If you do these cover strap fillet welds with no argon at the interface between the titanium strap and the liner, you probably have got colors in that zone at the back, but it doesn't matter there.

BRODWIN: Just one additional point. You touched, kind of briefly, I assume from what you said that you don't anodize the patches that are put in. Do you see any difference in the corrosion resistance of these areas?

CLARK: Up to the moment we have re-anodized every repair that we've done. You can do this quite simple with a sort of cotton wool pad and a battery and so on. It's quite simple to do really, if you know how. We'll tell you how.

Q. I have three questions. One is the titanium gasket? Can it be used agains—that's the first question. Second, what is the material of the outlet of the reactor, I mean the spool piece outlet of the reactor upstream of the letdown valve. Is it titanium lined? and the third is, at what level do you maintain the oxygen content in order to reduce the corrosion.

CLARK: The titanium gasket is always renewed. The let-down valve is attached directly to the reactor and is titanium with zirconium trim. We have used Ferralium (Langley Alloy Co) rather like AISI 329 plus copper—25 Cr, 5 Ni, 2 Mo, 3 Cu—which is remarkably good in many urea environments. I do not know the oxygen content.

Q. Have you had any experience with stainless steel linings?

CLARK: We ran some stainless steel lined vessels for a small number of years. These were vessels from an old ammonia plant and we put a lining inside ourselves, and they gave pretty good service, even though at least one of them—what we called the bottle vessel, it looked very much like a wine bottle with a type of bottom end which was very difficult to line. We had leaks on those and there was one very unhappy occasion when one of the weep holes was observed to leak; they went inside the vessel and couldn't find anything wrong with it, and they took out the lining piece by piece, and they never found where the leak had been. And finally the plant manager who had seen the leak himself and shut the plant down began to wonder if he'd been dreaming.