



Figure 1.
The starlike pits forming on the titanium lining are linked by cracks (mag. 20X).



Figure 2. Enlarged cross section of typical starlike pit showing significant metal contamination (Fe, Si, Al) in the root of the pit (mag. 400X).

Materials and Corrosion Problems in Urea Plants

The most severe corrosion in a urea plant can occur in the reactors, but as shown here, it can be controlled through the careful selection of construction materials and initiation of proper corrosion control procedures.

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OVER THE PAST SEVERAL YEARS ESSO AFFILIATES HAVE experienced materials and corrosion difficulties in urea plant process equipment. In several instances these difficulties have led to premature unexpected shut-downs resulting in loss of product and a safety hazard. The following is a review of the more troublesome problems encountered, together with an explanation of the causes and the proposed methods for overcoming them. In particular, the following difficulties will be discussed.

1. Corrosion and failures of titanium linings in the urea reactor
2. Corrosion of steel multilayers and buckling of titanium lining
3. Cracking of stuffing boxes and working barrels of carbamate charge pumps
4. Failure of tubes in urea ammonia condensers

Titanium linings in urea reactors

Probably the most severe corrosion in an entire urea plant can occur in the reactors. Fortunately, this corrosion can be controlled through careful selection of construction materials and initiation of proper corrosion control procedures. (Table 1 shows the material specifications used in Esso reactors.) The major attack occurs at the bottom 3- to 10 ft. of the reactor directly above where NH_3 , CO_2 , and recycle (ammonia carbamate) are introduced through separate nozzles. Operating temperatures and pressure are 375°F and

3,000- to 3,300 lb./sq. in. gauge.

Esso has used both type 316L stainless steel and high purity titanium to combat this attack. Type 316L (extra low carbon—0.03% max.) stainless steel is preferred over pure titanium (99.0% or greater) from an ease-of-maintenance and cost viewpoint, but either of these materials must be used together with air or oxygen injection to maintain a passive protective film on the metal surface. However, the use of stainless steel such as type 316L with air or oxygen is patented and therefore, can only be used on a licensing basis. Titanium is not covered by the license and air or oxygen injection can be used without licensing. Esso experiences with the use of type 316L with air injection has been trouble free but, unfortunately, difficulties have been experienced with titanium. The three more serious problems encountered are:

1. Corrosion and cracking from surface contamination of the titanium
2. Titanium weld embrittlement and cracking
3. Corrosion of steel multilayers and buckling of titanium lining

Surface contamination of titanium

As previously discussed, the corrosion resistance of titanium is highly dependent on the formation of a continuous protective oxide film which is maintained by air or oxygen injection into the feed stream. However, as reported by Cotton (1), tramp metallic iron

which is embedded into the surface of the titanium during fabrication, or later during either inspection or maintenance, can destroy the protective oxide film and permit the ingress of hydrogen with "the rate of penetration increasing with temperatures between 100°C to 300°C and with pressure between zero psig and 800 psig." (1) Similarly, it is possible to experience hydrogen penetration from iron in the alloy or that entering through the feed streams.

Esso has experienced failures of titanium liners in reactors at two separate plants. The failures were lo-

cated in the base plate at positions removed from welds, and were confined to specific plates near the center of the reactor. Visual examinations of samples removed from the titanium liner revealed that all the cracks observed were associated with small irregular pits. These cracks generally linked several pits, Figures 1 and 2. Leakage occurred only at the larger crack(s) and not at the superficial ones.

Microprobe analysis of the corrosion product found in the pits revealed significant amounts of iron, silicon, and aluminum. Evidence of these contaminants

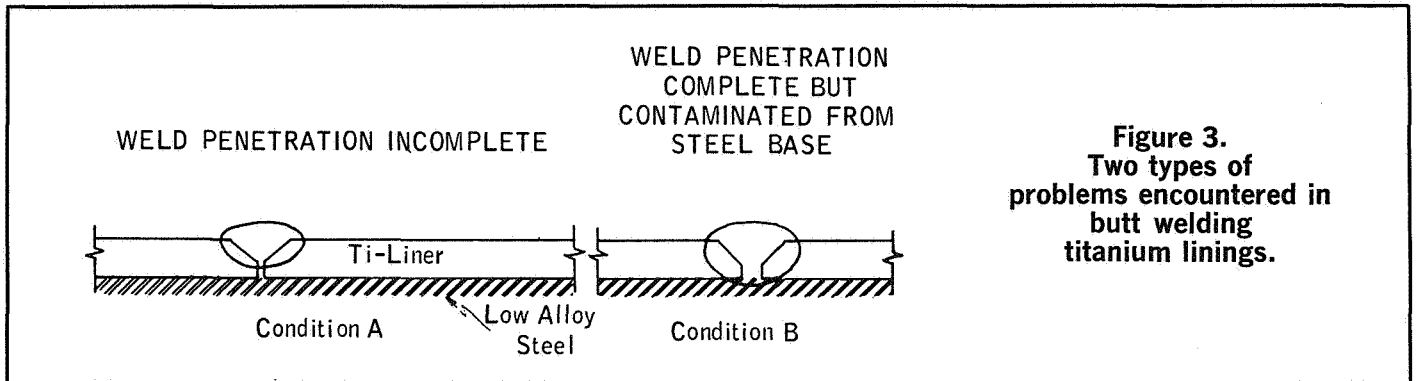


Figure 3.
Two types of problems encountered in butt welding titanium linings.

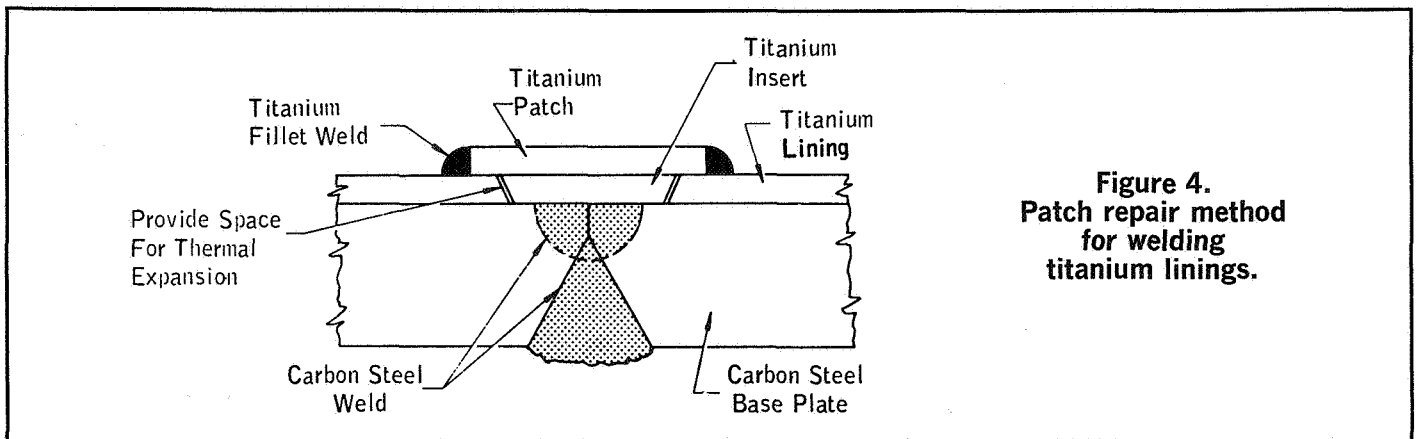


Figure 4.
Patch repair method for welding titanium linings.

Table 1. Material specifications for Esso reactors.

	High Purity Titanium (1)
Shell	Multi-layered (2) (3)
Top and Bottom Head	Forged (4)
Liner, Bottom 1/3	5 mm. thick titanium (5)
Liner, Middle 1/3	4 mm. thick titanium (5)
Liner, Top 1/3	3 mm. thick titanium (5)
Gasket	Titanium (6)

Notes:

- (1) Materials specification shall follow ASTM B-265 Gr. 1.
- (2) Shell shall be multi-layered construction and welded to the top head forging and forged ring circumferentially. Each shell unit shall have two weep holes and two vent holes. High strength steels (Welcon 2HS) must meet the requirements of Esso Basic Practices particularly regarding hot tensile and notched beam ductility tests.

- (3) Innermost liner shall be a specially welded loose strip lining of titanium with a *minimum thickness* as indicated in the above table. All welds made inside of vessel shall be designed to avoid possible iron contamination from base metal.
- (4) Top and bottom head forging shall be of integrally clad construction fitted with a special welded orange peel type strip lining of titanium, 7/32 in. minimum thickness with all but 0.040 in. considered as corrosion allowance.
- (5) Titanium lining is designed for service in excess of 10 years. Bottom third of shell (also top and bottom head) assumes 15 mils./yr. erosion-corrosion rate, middle third assumes 10 mils./yr. and upper third assumes 5 mils./yr. corrosion rate. In all cases, 0.040 in. may be used for mechanical strength and the remainder is corrosion allowance.
- (6) Flat type titanium gasket 1/8 in. (3 mm.) thick per ASTM B-265 Gr. 1.

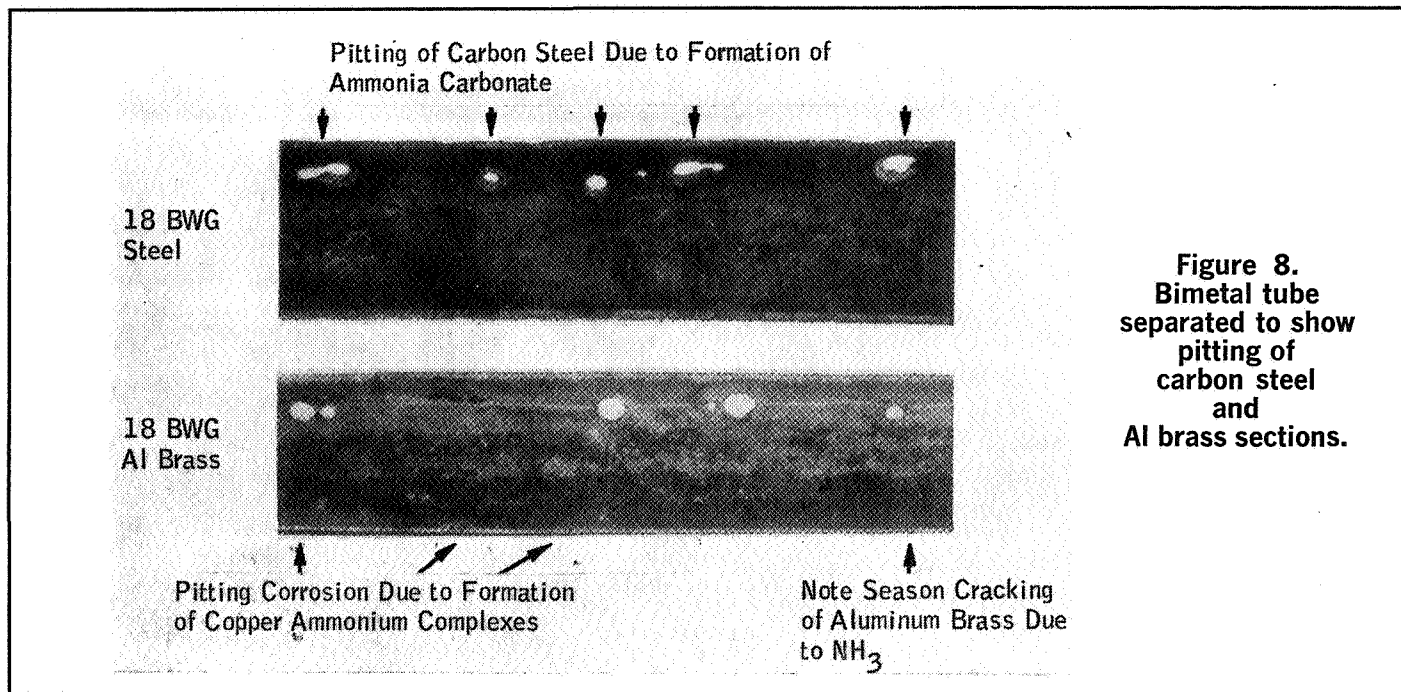


Figure 8.
Bimetal tube
separated to show
pitting of
carbon steel
and
Al brass sections.

ferricyanide test shows to be positive, swabbing this area with 20-30% nitric acid will be necessary until further testing with ferricyanide shows to be negative.

An alternative approach for cleaning titanium surfaces was reported by F. Clarke, ICI, Billingham, England at the 1970 Seminar of the Ammonia and Related Process Safety Symposium. In this method, the titanium surface is anodized by filling the vessel with a dilute solution of ammonium sulfate and impressing a small current through the use of welding generators. Further details of the method are described by Cotton (1).

Titanium weld embrittlement and cracking

Similarly, welds are subject to surface contamination from extraneous sources and failures from this source can be expected particularly if carbon steel brushes are used for surface preparation. However, the welding of titanium, particularly in the field, is extremely difficult and requires utmost precaution. The presence of oxygen, nitrogen, or hydrogen in the atmosphere will seriously embrittle titanium if these gases are allowed to make contact during welding when the titanium is molten or cooling to cherry red. Also, the welding of strip or clad titanium linings is difficult since iron contamination from the steel backing causes similar embrittlement problems. As a result, field welding of titanium should be attempted only by a specially trained welder who is familiar with the important techniques required to obtain sound welds. A discussion of the proper welding specifications, procedures and inspection requirements is beyond the scope of this article particularly since comprehensive information on the subject is available in manufacturers' brochures. Sticha (2) has published some worthwhile information in this regard, and the American Welding Society Handbook (3) also has useful general information on titanium welding.

One vessel fabricator of Esso urea reactors experienced two types of difficulties when butt welding titanium linings as illustrated in Figure 3. When using a small route gap (condition A, Figure 3) pene-

tration was incomplete. When using a wider gap (condition B) penetration was complete, but the weld was contaminated from the steel base. Both types of joints showed evidence of gas contamination and neither stood up in service.

To overcome the excessive iron contamination it was necessary to fillet weld strips of titanium over the contaminated welds. These strips were about 1 in. wide by 0.25 in. thick, and were welded with the TIG process after the area was thoroughly cleaned.

All repair work on existing equipment which is subject to iron contamination is covered with special patches of titanium over the weld. It must be emphasized that the patch technique is used no matter how small the area to be welded, including nicks. Under no circumstance are butt welded or weld overlay repairs made. Detail for patch repair are shown in Figure 4. It should be noted that others (2) sometimes use a silver insert which can be brazed directly to steel and titanium. However, Esso experience has found this to be unnecessary and the use of titanium inserts to be entirely satisfactory.

For new construction, Esso now requires all longitudinal welds of the titanium liner be made outside the vessel where the welding can be shielded with inert gas from both sides of the weld. The welded section is then slid into place within the vessel. All butt titanium welding which is required inside the vessel is subject to iron contamination, and is covered with fillet welded strips of titanium as described previously.

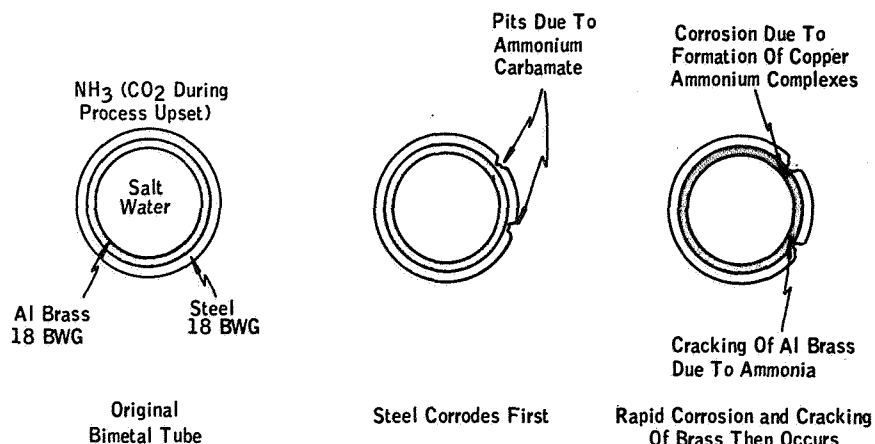
Buckling of titanium lining

A most serious problem resulted due to corrosion of the steel multilayer underneath the titanium which caused it to buckle. Figure 5 shows the mechanism by which the difficulty is believed to occur, and the sequence of events that lead to failure are outlined below:

1. Microcrack through the depth of the lining occurs either at weld or pit. Liquid ammonium carbamate seeps through microcrack.

2. With minute crack the amount of liquid oozing through is small. Once the liquid reaches the gap be-

Figure 9.
Cross sectional view
of bimetal tube
ammonia condenser.



tween the liner and the multilayer construction, the liquid flashes since the pressure is essentially atmospheric, releasing NH_3 , CO_2 , and depositing solid carbamate. The gap as illustrated, Figure 2, is highly exaggerated and is actually only a crevice where the titanium lining is resting directly on the multilayer shell because of the high operating pressures (3,300 lb./sq. in. gauge).

3. When the crack is small and the amount of liquid oozing is minimal, continual flashing of the off-gases occur and solids build up behind the liner. The off-gases escape through the vent holes and little, if any, liquid is formed at this stage to escape through the weep holes. Such a condition can exist for weeks, even months without being detected.

4. Corrosion of the inner multilayer high strength steel occurs very rapidly since this type of steel is not corrosion resistant. Figures 6 and 7 show the progressive nature of corrosion which occurred at two separate reactors. Figure 5 illustrates the attack which occurred underneath a small pinhole, and Figure 6 shows the attack caused by leakage at a weld. The formation of solid urea and corrosion projects tend to plug the weep holes and permit a pressure build up behind the titanium liner.

5. Eventually the crack opens wider and larger amounts of liquid flow through until finally all the liquid cannot flash away and it finds a way through one of the weep holes. However, in a multicrack situation some of the other weep holes may remain plugged.

6. The leak is now discovered and shutdown of the reactor proceeds. If the reactor is drained too rapidly, a vacuum can be created which can cause collapse of the thin titanium liner (3- to 5 mm. thick). Also, the back pressure caused by plugged weep holes can exert sufficient pressure to buckle the liner if the back pressure equilibrates slower than the depressuring rate of the reactor during the draining period.

To overcome the buckling problem, an early warning device has been developed which will alert operators immediately in the event of a leak. This early warning device is described in detail in a subsequent paragraph. In addition, the following special operating practices are used:

1. Immediately, upon detection of a leak from the detecting device, the unit is shut down to avoid excessive build up of deposits behind the titanium liner.

2. Drainage of the reactor is carefully controlled to avoid any sudden pressure changes or creation of a vacuum. Each shutdown operation involving the CO_2

compressor, NH_3 charge pump, and carbamate recycle pump is carefully controlled from this aspect.

3. It is most important to clean out deposits between the lining and the multilayer steel sections when a leak occurs. Under these circumstances it is important to hold reactor pressure and to replace the contents with hot boiler feed water or steam condensate using the carbamate pumps until all weep holes are unplugged and free of deposits. If extensive leakage of carbamate has entered underneath the liner, the injection of water may be required for 10 or more hours.

4. The reactor is then carefully depressured, drained and opened for necessary repairs.

5. Similarly, emergency shutdowns caused by power failures are carefully executed to avoid generation of a vacuum within the reactor.

Detecting leaks in multilayer vessels

If excessive carbamate melt should leak out of the wrapped vessel reactor due to failure of the inner titanium liner, serious corrosion and possible rupture of the vessel can occur. Therefore, it is necessary to detect leaks rapidly in order to minimize the corrosion effects and prevent widespread infiltration of carbamate deposits within the steel multilayers of the vessel. The deposits within the layers of the vessel tend to partly solidify so that small leaks may go unnoticed causing serious buildup of deposits which are difficult to remove later.

Therefore, it is important to develop an early warning system which will indicate a leak as soon as it occurs. This can be accomplished by the installation of manometers to the vent holes. This method is particularly effective since the off-gases tend to leak before the carbamate solids do. Alternatively, Esso Research and Engineering has developed an electrical device which is available on a licensing basis which greatly simplifies the manometer system.

It must be emphasized that, once a leak is detected, it is necessary to shut down the reactor immediately to make repairs before extensive damage of the multilayer construction occurs. Also, it is necessary to flush out all urea deposits between layers before the repair and startup using steam condensate or evaporated water.

Cracking of stuffing boxes and working barrels

Esso affiliates have had continual cracking of type 329 stainless stuffing boxes and working barrels in

their triplex positive displacement plunger-type pumps used for carbamate service. Inspection of the stuffing box section revealed a crack running along the oil inlet assembly starting on the inside of the case and continuing outward. A microscopic examination revealed that the cracks were transgranular with branching ends. The appearance of the cracks, and the fact that the stuffing box is exposed to cyclic stress indicated the mode of failure to be corrosion fatigue. Similarly, the failures in the working barrels appear as a crack, starting at the intersection of the plunger port and cross port on either the suction or discharge side and, in some cases, on both sides. Again there was exposure to cyclic stress and the failure was due to corrosion fatigue.

The failures have been linked in the case of the stuffing boxes, to stress concentrations associated with the flushing port and, in the case of the working barrels, to stress concentrations at the intersection of the cross bore. Frequency of failure of the stuffing boxes and barrels has been roughly 6 to 18 months necessitating a high inventory of spares for replacement and shutdown for maintenance.

The problem can be overcome through redesign of the stuffing box and working barrels to modify the flushing port and the cross bore and thus overcome the excessive stress concentration. The principal drawback is that few parts are interchangeable with the present pumps and a complete pump changeover at considerable cost is required.

Other approaches for reducing the failures which can be employed with the existing pump design are:

1. Coating the internal stuffing box surface with either a 50% Pb, 50% Sn solder or a Penton, or Viton coating. The use of these coatings has not eliminated cracked stuffing boxes but has extended their life to more reasonable levels.

2. Substitute vacuum remelted type 316L stainless in place of type 329 stainless for the working barrels. Again this material substitute is not expected to eliminate the problem, but to extend the life to perhaps 24 months.

3. Shot peen cross bore intersection area to apply compressive stresses which should provide greater resistance to metal fatigue. As with the other methods, shot peening will only extend life and not eliminate the problem. A test is planned by Esso in the future.

4. Substitute other more resistant construction materials such as Ti-6Al-4V (90Ti,6Al,4V) Carpenter 20 Cb-3, (20 Cr, 33Ni, 3Cu, 2.5 Mo) Armco 22-13-5 (22Cr, 13Ni, 5Mn). Another highly promising material reported at the recent AIChE conference in February 1970 as having outstanding chemical resistance in urea synthesis operations which merits consideration is Tenelon (4). Esso has not as yet tested these materials, but hopes in the future to arrange for supply of test forgings by the pump manufacturer.

Tube failure in urea ammonia condensers

Esso affiliates have experienced corrosion and failure of tubes in the urea ammonia condensers. The failures occurred after roughly one or two years service during which corrosion was initiated due to the following situations:

1. During abnormal operation from carryover of CO₂ from the washing tower due to occasional process upsets. This action resulted in the formation of ammonia carbamate which is highly corrosive to carbon steel tubes in the ammonia condenser.

2. During upsets, such as power failures when large

quantities of CO₂ pass through the system because of the discontinuance of the washing system. As a result carbamate forms and the corrosion, as described previously, occurs.

3. Also, during power failures, on occasions when the cooling water level in the condenser drops since the condenser is located above grade, failure of the tubes at the tube sheet occurs. This failure is caused by thermal expansion differences between tubes which were flooded and tubes which were not. As a result, the tubes loosen at the tube sheet and leakage results.

The problem can be controlled for fresh water condensers since solid heavy wall carbon steel tubes are used. These tubes are strength welded to the tube sheet and some corrosion of the tubes can be accepted. However, it still is necessary to carefully control operation to minimize the corrosion during upsets so that excessive CO₂ does not pass into the ammonia condensers. However, for salt water condensers it is necessary to use a tube material which is resistant to both salt water and ammonia. As a result, bimetal tubes are often used, 18 Bwg (0.049 in.) carbon steel on the process side and 18 Bwg aluminum brass on the water side. If active corrosion is experienced due to CO₂ carryover or if power failures cause loosening at the tube sheet joints, ammonia will leak onto the water side and rapid failure of the brass will occur due to formation of copper ammonium complexes and "season cracking" (a form of stress corrosion which occurs to copper base alloys exposed to ammonia). Figures 8 and 9 show a bimetal tube exposed to this type of attack and illustrates the severe pitting and cracking that can result.

The problem is associated mostly with overseas locations where as many as 20 power failures have been experienced per year. The specific action taken to overcome the problem is as follows:

1. Carefully monitor process upsets and operating conditions to detect excessive CO₂ entering the ammonia condensers. The use of corrosion test probes has proven useful for this purpose.

2. Modify cooling water piping so that water cannot drain during a power failure thus eliminating the thermal differences, which can cause tube loosening. In addition, it is recommended that an antisiphoning device be installed in the system to prevent the threat of water drainage due to siphoning action.

3. At sea water locations where numerous power failures are experienced change bimetallic tubes to solid titanium, 18 Bwg. Titanium has superior corrosion resistance to sea water, ammonia and ammonium carbamate. #

Literature cited

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Discussion

Q. When you make the patch where you use a strip, after you've cleaned the carbamate from behind the liner, do you just make that patch over the weld or did you always examine the steel behind the liner?

KRYSTOW: Well in some instances - if we had severe damage behind the liner - we actually cut it out, and in some cases we even had to ship the vessel back to the manufacturer to have the vessel relined in the shop. Small patch repair work was not necessarily checked underneath the patch but this is a matter of judgment.

Q. What thoughts do you have on galvanic corrosion where the tubes go through the tube sheath?

KRYSTOW: Well the use of stainless steel would be one of our first choice materials selections. Unfortunately, this is at a fertilizer plant that utilized salt water cooling and we just could not use stainless steel. We would accept stainless steel, but only at high velocity, with cooling water having less than 500 parts per million chlorides. We'd like to have the water on the tube side, of course, and velocities in the order of 8 to 10 feet per second. However, if the chloride content is substantially lower, in the order of 25ppm, it is possible to drop the velocity requirement to 3 fps. Putting cooling water on the shell side has been disastrous and frequently leads to stress corrosion cracking.

Q. What do you have to say regarding fatigue cracking in high pressure ammonia pumps?

KRYSTOW: Well, of course, we did cover these points in the paper. The most important point I can make at this time regarding the pump failure is that it appears to be associated with the particular pump design and manufacturer, and I'd prefer not to mention the pump manufacturer. However, our investigation did reveal that there are other pump designs and suppliers that have also experienced these difficulties. But it is a significant fact that most Urea manufacturers do not have the problem. We are still continuing our investigation for the best approach. I personally believe that getting a more corrosion-resistant material, that is, one that completely resists corrosion, and has higher fatigue strength, such as the ones that I mentioned in the paper will probably yield the eventual solution.

Q. I understand you are using a stainless steel liner in a plant in Holland. Have you had any chance to examine the corrosion rate on it?

KRYSTOW: I have not heard anything yet. We also have a stainless reactor in the Philippines, and to my knowledge, this reactor has been inspected and there has been no observable corrosion after more than a year of service.

W.D. CLARK, ICI, Billingham: We've been making urea for 20 years I suppose - originally in silver plant - lately we've had a Tojo Koatsu unit. And one or two points which may be of interest come up from this. Our reactors - titanium lined, have given no trouble except in one small point. That is at the bottom branches, where the CO₂, carbamates and ammonia come in, they were originally fitted with thermal shields.

These were titanium sheath pieces separated from the wall of the vessel by about an eighth of an inch, and going round the corner. There was probably about 6 inch total

length. We did, in fact, have some corrosion behind those shields, and we have since then removed them. We thought this was possibly oxygen starvation behind the shields.

The other point, which is general to all titanium equipment we touch. We are dead clean on getting rid of iron. We insist on clean shops and so forth. In fact, Mr. Cotton, whose remarks you referred to - he supplies us with the titanium - very low iron content and so forth - but even so, we make sure and doubly sure by anodizing every bit of titanium plant we put in.

We fill it up with a cheap electrolyte and connect up a couple of welding generators and make it fizz for a few hours, and then we know there is no iron left on the surface. This is fine as regards iron contamination from hob-nailed boots and things of that sort. It is no protection if you've had iron on your welding surfaces, and you've diffused the iron in by the welding process. But it has done quite a lot of good. We've actually had corrosion coupons in, some of which were anodized, and some of which had not been anodized, and were pleased to find that the ones that hadn't been anodized were not corroding, so we think the money we're spending there, which is not an awful lot, is well worthwhile.

As regards weepholes, on our urea plants and on some other plants where we are working with rather nasty process fluids, we have connected all the weepholes together to a manifold - your sort of system. I think that we don't work on pressure. We work on passing a flow of a carrier gas around the system, and having some sort of analytical check on this. We're also considering putting in some sort of electrochemical probe in the weepholes, or immediately adjacent. There are several ways in which if you want to detect whether a weephole is showing anything, you can bring it down to a central point, whereas if a weephole is 50 feet up in the air, a lot can be coming out that you'd never know.

As regards injector blocks, I was rather interested by what you say, because we started off with 316L injector blocks, and every one we've got cracked. The cracking starts at the junction between the crossbores, and it works out, and we're now reasonably confident that all that happens is that you get a slight weep. It is not a catastrophic failure, and so we have been able to carry on. And one of the improvements we are trying is something which sounds rather like 329. Perhaps we are going to be disappointed. Perhaps you are going to be disappointed, trying 316L.

Another of the things we are trying is 316L strengthened by the addition of nitrogen, which puts its tensile and fatigue strength up quite a lot, and does not greatly affect its corrosion resistance. We think this might be the answer. On the other hand, we have now got a centrifugal pump installed, and it looks as though this might be another answer.

KRYSTOW: Well, I'd like to make some comments, - not in rebuttal, because I think they're excellent comments - but as additional support. I think this procedure of strengthening type 316L with nitrogen is very attractive because the most corrosion resistant grade of type 316L is one that has a completely austenitic structure. We know that small amounts of ferrite in the austenitic stainless will tend to decrease its corrosion resistance. And nitrogen's a very

strong austenite former, so that you can probably obtain by this addition, a grade of type 316L which is completely austenitic. I was going to make another comment on your second point, but I forgot what it was now. Did you recall the second point that you made?

CLARK: Anodizing.

KRYSTOW: I think we heard about this technique through you people and we agree that this is an excellent approach. However, my main discussion here is what do you do in existing equipment if you have to go in and repair and you find you have some iron embedded in the titanium. This anodizing technique gets to be very difficult, since it requires an awful lot of acid. Do you actually do this in existing equipment after repairs?

CLARK: Yes, we do it in existing equipment. We don't use acid. We use ammonium sulfate; I think 1%.

KRYSTOW: I see.

CLARK: And its throwing power is very high; it will go down a 6 inch pipe for a half a mile or something, and so there is no great difficulty there. If I could return to one point you made about the 329 and ferrite. We heard about ferrite, and we have been restrictive on this, but we have made one discovery which surprised us: That is you use 316L with 4% of ferrite - OH, it starts to corrode. But the material which we are using, which I think is similar to 329, is an alloy sold in England under the name of Ferralium, which is misleading because it contains no aluminium - it is in fact, I think, 25 chrome, 6 nickel, 2 or 3 copper, 2 or 3 molybdenum, and it is 50% ferrite, 50% martensite and it has much better corrosion resistance than 316L, and you can weld it and do what you please with it.

So ferrite in 316L is a very bad thing, but there are other kinds of steel alloys in which ferrite is no problem.

KRYSTOW: This recalls, of course, the papers presented at the February AIChE meeting where it was cited that substitution of manganese for nickel in type 316 stainless confers surprising corrosion resistance and that this may become a new material for urea plant service. It certainly is worth checking further.

A.J.P. TUCKER, African Explosives & Chemical Industries, Ltd.: In our Urea Plant we use Uracha pumps which are apparently not quite so sensitive to cracking as some of the other pumps but we do have cracking of the valve blocks. The cracking goes around the valve ports and then spreads generally around and down into the whole valve block.

From the comments made by other people, our experience might be of interest to you. We started off with columbium stabilized 317 blocks. We were then forced to change, because we cracked nearly all of them, to straight 316. We then got some made of HVD1, which I think is like your 329. It's about a 28 per cent chrome, four per cent nickel molybdenum steel with other additions. We ended up with nitrogen strengthened 316L. All of these have cracked in time, but roughly in order of preference, the HVD1 was the worst of the lot, cracking in under 100 hours, followed by 316 and columbium stabilized 316. The 316 LN has given us the best life of the lot by a factor of about three. This I think might help Mr. Clark and yourself in your thoughts about 329. The 329 (or equivalent) was definitely the worst from the cracking point of view.

As far as our reactors are concerned, we have a secondary reactor which is lined with 5mm thick stainless steel, 316L. This has shown no sign of corrosion whatsoever during two and a half years operation. We have, however, had a little cracking in the top liner butt weld which we managed to repair satisfactorily.

The lead through the crack was detected very rapidly. In our case we have a carrier gas of steam bought from each tell-tale down to a central point - a row of tundishes - which operators can smell from time to time, and the leak was picked up quickly enough so that there was absolutely no corrosion of the low alloy steel behind. We had a good look and it was absolutely clean.

In our first reactor, we do have a serious cracking problem on our inlet carbamate recycle branch. This is a lined vessel and we have done two repairs on this branch which is cracking on the inside where the branch joins the lining. We have now designed and sent out enquiries for a solid stainless steel vessel with proper welded on branches with full penetration welds, which we think will give us a better time.

KRYSTOW: It's interesting to hear that there are other people with similar problems to those experienced in Esso plants. This indicates that more engineering research is needed since the problems are widespread. Hopefully, we'll have some worthwhile results with some of these special alloys that are planned for test in the future and I'm interested in following up on some of the leads that you have cited.

IAN McFARLAND, ICI-America: I was very interested in your remarks on multilayer construction. I have two points which I would like to make on this. The first one is that I will name no names, but I think three people have now found evidence of cracking on the outside of the multilayer vessel.

The three people concerned I think also make ammonium nitrate. Now whereas there doesn't seem to be any specific evidence of ammonium nitrate causing the stress corrosion cracking, this is just purely statistical: three people have suffered this; one in a very severe manner. These cracks have been showing up, particularly around the welds in the outer layer of the vessel. They've been showing up around fillet welds where such things as insulation support rings have been put on.

This is to be expected to a certain extent in that we have a fairly high strength low alloy steel which has not been stress relieved after welding, in fact, cannot be. So one might have fairly high Brinell figures around these welds. Secondly, you showed in your sketch this morning the vent holes which go right through the core tube. Now if you get a lead in the titanium liner you get a corrosion product formed which may in fact block off for some time the route to these vents.

Now whereas you may, if you have detection apparatus available, have detected this before this situation arises, if you do get to this state, there is a possibility that you may break through the core tube itself. Once you get outside the core tube, you find there are other vent holes through the outer layers and these are not connected by means of a tube or a weld through.

So once your corrosion product gets out into this region it can disperse itself within the layers of the multilayer vessel. I mention this because we have seen evidence that this

has happened on a converter and, in fact, there was corrosion product lying about eight layers out. Now how one can get this out I just do not know. But it seems to be something that really needs to be taken care of in that this can get out to a position where you cannot clean it.

KRYSTOW: That's a very worthwhile comment. I might mention when we first heard of the trouble with external cracking on high strength steels from nitrate containing fertilizer dusts, we were also quite concerned. As a result, a full scale inspection was made of our multilayer vessels, particularly that portion of the shell at the support structure. This inspection did not reveal any cracking even though high strength steels were used for the multilayer shell. Later, we discussed the problem with the licensor of our plants, and they now recommend substituting carbon steel for the outermost layer in place of high strength steel to avoid direct exposure to fertilizer dust.

McFARLAND: There seems to be a certain amount of evidence which has shown that after the vessel has been fabricated and checked for lack of cracks on the outside, after it has undergone hydrostatic test cracks have shown up. Now, true, if one puts a nice layer of mild steel on the outside, this will protect you from environmental stress corrosion cracking. But if cracking occurs during stressing of a vessel on the outside layer, what happens on the ones inside?

Q. Would you run the hydro before the carbon steel, as a layer was installed or after?

KRYSTOW: Well, that's an interesting question. We're not faced with it, and it's something that I can't decide right now. We would have to review the problem with the various engineering specialists on our staff and a decision would have to be made. I myself would favor perhaps some kind of a nondestructing test or better yet, to limit the yield stresses to 90,000 pounds or even less.

G.F. POLLOCK, Atlas Chemical Industries: There are some question in regard to the use of oxygen for anticorrosion in the reactor. We don't use oxygen at that point, but we do use it at another place. In the first year of our operation we lost the gas line going from the separator to the primary rectifying column, a six inch line. It was schedule 40 line initially. We replaced that line with schedule 80. And at the same time theorized that the oxygen was not getting past the heater and protecting that area of the plant.

We did put oxygen in at the separator, and that line now has lasted for seven years with no evidence of corrosion.

KRYSTOW: As an important point, with air or oxygen injection, you have to monitor the injection at initial startup to determine if the injection is doing the job that it is supposed to do, not only in the reactors but downstream of the reactors. If after initial startup, you should determine that the portions of your downstream piping and separators are not being adequately passivated by the air injection, it will be necessary to provide additional air injection, particularly in the vicinity where inadequate passivation is experienced.

Q. You mentioned contamination with iron on the surfaces. Did you do anything particular about the titanium metal itself in controlling iron chemistry?

KRYSTOW: As I mentioned in the paper, the iron content was examined to see exactly how much iron was in the base titanium alloy itself, and we found it to be all within

the normal specifications for high purity titanium. However, despite the fact that the iron was within specifications, it is possible that there was sufficient iron to cause the attack. However, I do not personally believe the iron within the titanium was the cause since if it were, there would have to be other similar cases of the attack reported in the literature. On the other hand, it is possible that the iron deposited from dissolved iron in the feedstream. However, in my opinion, the most likely source of iron contamination was through some kind of contact with steel during inspection or maintenance since the defects were located in one specific area over only a few of the vessel plates and far removed from the feed inlet nozzles.

CLARK: Two points, sir. First going back a little bit to the high strength steels and the deterioration in plant atmospheres. We've been very interested in this, and we have been over our urea converters, which are multilayer, Japanese, with a fine toothcomb, and we found rather a lot of small cracks. I think we found 20 or 30 cracks, half inch long across the weld beads in the external layer. All except one were the sort of crack which you could very easily get in original fabrication, and so we have marked them all up and we are taking the lagging off in certain areas every six or twelve months and having a look to see whether they are growing.

But this is only one aspect of a fairly general subject; that is to say, how far up in strength of steel can you safely go for equipment which is going to be exposed in the somewhat murky atmosphere of a large chemical plant? We are doing our best to clean it up, but I think it will take us a few years yet. Rather to our surprise while they do drop in ductility and a little in the energy absorbed in breaking them, they don't seem to do terribly badly...

So this is a slight consolation. Then a question I'd like to put to you, sir, if I may: how much oxygen or air do you add to your urea streams? Our tendency is to add I think four times as much as we think would dissolve.

KRYSTOW: The normal rate of air injection is controlled to deliver 500 ppm oxygen content to the feedstream.

QQ. Do you know if these corrosion problems occur in the liquid phase or the gas phase?

KRYSTOW: Well, that's an interesting question. It's my personal opinion that the attack occurs in the liquid phase. You need an electrolyte for electrolytic attack, and I don't believe that the temperatures in the reactor were high enough to get direct vapor attack of the metal.

Getting back to Mr. Clarke's point, I think that we need to explore the levels of nitrates in fertilizer dust, which will promote cracking of high strength steels. Also, there is a need to ascertain whether there is a threshold value of nitrates below which attack will not occur.

I'd like to make an important point. The reactors which experienced the difficulty described in the paper were fabricated five years ago. If we were to build the reactor today, we'd follow a lining thickness much closer to what you just described; we do not feel now that the three millimeter - that roughly an eighth of an inch thick - is adequate at all. We believe that at least a quarter of an inch thickness is required.

An eighth inch thick loose liner is so thin that it is subject to failure even during mild upset operation. For example,

if you suddenly have to rapidly drain the reactor or if you happen to condense steam in the reactor, it is possible to create a slight vacuum, and with thin loose liners you could get buckling and collapse of the liner. Therefore, from the operational stability standpoint, I think a thicker titanium liner is in order, something like a quarter of an inch.

As far as iron oxide versus metallic iron promoting the attack, I believe it's quite possible that iron oxide could promote the attack, and if it does, this would mean that we would have to have to maintain a pretty clean system after each shutdown, and moreover, make sure that we don't entrain rust through the ammonia feed lines.

And, it's probably a good idea to keep your system sealed off from weather and atmospheric moisture and thus avoid conditions where you can form rust in the carbon steel parts of your process which can be carried into the reactor.

L.W. ZINN, Gulf Oil Chemicals Co.: Subject to memory, in 1950 or 1951, Dr. Norman Hackermann of the University of Texas performed tests relative to the corrosion of carbon steels in ammonium nitrate solutions. I believe the results indicated an improvement in both corrosion and stress corrosion cracking characteristics in carbon steel that was in the fully stress relieved condition.

In commenting on the procedure for determining I.D. protective liner pinhole penetration in urea reactor service, our experience has been to introduce a condensate wash following product removal. This is done while the unit is still in service. Salting out of the product is thus prevented, from I.D. failure to O.D. weep hole. Introducing nitrogen gas from the O.D. weep hole makes detection of the liner failure a simple matter of observation.