Corrosion in CO2 Removal Plant Towers

Stress corrosion cracking only took place when the electrochemical potential of the steel in contact with the solution lay within a well-defined range of values.

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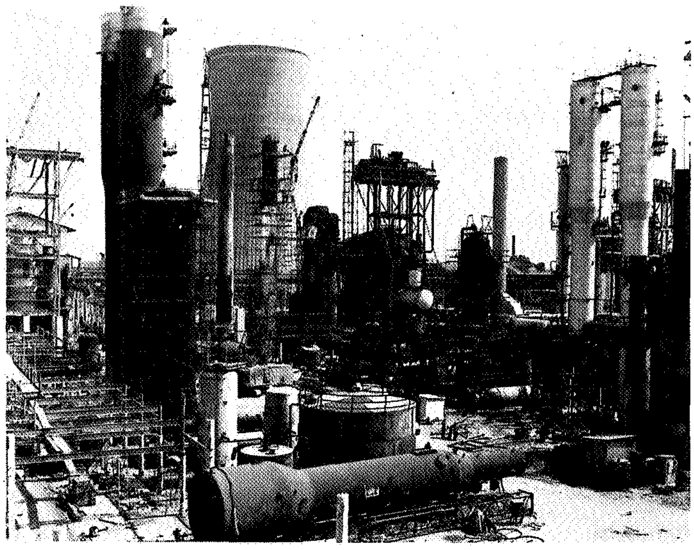

Billingham LP Ammonia unit in construction, ca 1966 *showing top half of absorber lying in foreground.* Weld to bottom half stress relieved on site. Stress corrosion cracking found in this weld, 1972.

Several types of corrosion can occur in CO_2 Removal plants. General corrosion of carbon steel by acid gas condensate occurs in the upper levels of strippers although at a sufficiently low rate to enable planned replacement of items such as packing support grids.

Erosion/corrosion causes damage much more rapidly but this problem tends to be confined to plants using inhibitors in low concentration. Vetrocoke units, using high concentrations of arsenite in solution, rarely suffer erosion/corrosion. Erosion/corrosion can be designed out of any system by avoiding excessively turbulent/high velocity liquor flow conditions, coupled with a suitable choice of materials and a close control of inhibitor level.

Recent experience with Vetrocoke plants has confirmed another corrosion hazard—that of stress corrosion cracking (SCC) of carbon steel. This is of considerable concern because of the possibility that a stress corrosion crack, growing to critical dimensions in the wall of pressurized equipment, could propagate in a fast ductile mode with catastrophic consequences.

Cracking of Vetrocoke units outside ICI

To our knowledge at least 15 Vetrocoke units throughout the world have experienced SCC of carbon steel equipment. There may be unreported cases or plants yet to reveal cracking since the period between commissioning and the first evidence of cracking varies from 6 months to nearly 6 years. Cracking has been almost invariably associated with welds but has varied in severity. In some cases complete towers have had to be replaced. In others only isolated welds have cracked.

Of great concern is that nominally stress relieved welds have cracked, although, in retrospect, there was often a doubt about the efficiency of the original stress relief heat treatment. Conversely, there are instances of non-stress relieved towers not suffering SCC suggesting that a factor or factors in addition to stress must be satisfied for SCC to take place.

Cracking of many types of carbon and low alloy steel used in Vetrocoke plant construction has taken place, e.g. A212 Gd B, 19 Mn 5, HSB 50. Neither is cracking specific to equipment normally in contact with liquor of any particular range of carbonation index. No cases are reported where the liquor in contact with the cracked item has been less than 75°C. There is no obvious factor linking plants which have experienced cracking.

In late 1969 we experienced leakages at welds in piping carrying lean liquor from the stripper to the lean solution cooler on one of our Vetrocoke units. The unit was commissioned in 1964. Inspection of the non-stress relieved stripper revealed extensive cracking of main shell welds in the stripper base. Radiography of many piping welds showed that cracking continued up to but not beyond the cooler. The absorber (also non-SR) has recently been inspected and no stress corrosion cracks found although more cracking has been found higher up the stripper.

The affected welds in the stripper were ground out and rewelded. A stress relief at 450°C for 24 hours was carried out. Recent inspection has shown the repair welds to be uncracked. Cracked piping was replaced.

This instance of cracking coincided with reports of SCC in the absorbers of two other Vetrocoke units. We therefore

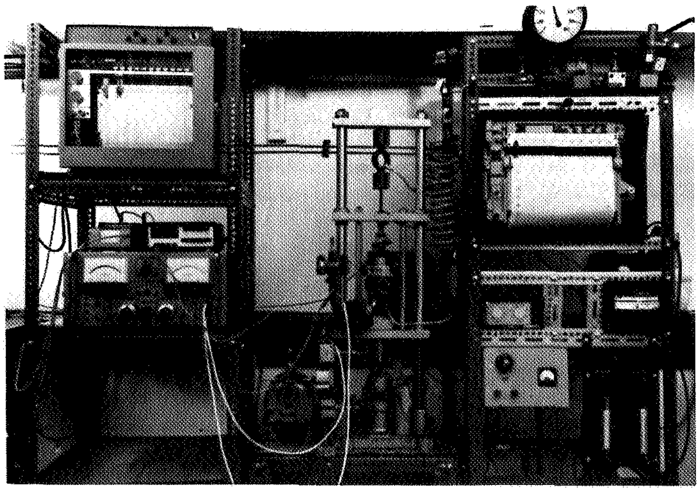

Figure 1. Experimental apparatus for SCC testing.

became concerned that a major problem was emerging with our other four Vetrocoke units at risk. A research programme was set up to define the conditions for SCC in Vetrocoke liquor and what, other than stress relief, could be done in prevention.

Research program and results

Research into nitrate and caustic cracking of carbon steel had shown that SCC only took place when the electrochemical potential of the steel in contact with the solution lay within a well-defined range of values.

We therefore sought to define the critical range of values for Vetrocoke solution by laboratory tests and, by measuring the potentials of Vetrocoke equipment under varying operating conditions, to define the circumstances necessary for cracking to take place given the necessary stress conditions in the steel.

We started off using 30% potassium carbonate solution containing no arsenite but with varying degrees of carbonation and established that this solution caused SCC of carbon steel within a clearly defined potential range. However, in all cases the cracks were intercrystalline whereas cracking of Vetrocoke units had been transcrystalline.

The main test method used was the constant strain rate test where a tensile test specimen of the steel, surrounded by the liquor under test, is very slowly stretched at a constant rate (10^{-6} to 10^{-7} ins/sec). The specimen either breaks by simple ductile rupture or prematurely due to the presence of stress corrosion cracks normal to the tension axis. Some U-bend tests were carried out initially to confirm the validity of the test method.

Tests were arried out at atmospheric pressure and boiling point but also under the pressure, temperature, and gas composition conditions typical of those in both absorber and stripper. The experimental set-up for the latter is shown in Figure 1.

Using a 30% w/w K_2CO_3 base solution tests were carried out over the complete range of As_2O_3 additions from 0.2% to 10.0% w/w. Pure grade chemicals were used. All of these solutions produce SCC at carbonation indices ranging from 0.8 to 1.7. Cracking is particularly virulent at concentrations from 0.2 to 1.0% As_2O_3 and we now understand why, several years ago, we had SCC of a hot-pot unit using 0.3%

Figure 2. Transcrystalline cracking produced in Vetrocoke solution at 130°C.

As_2O_3 as inhibitor.

In all cases cracking is transcrystalline, Figure 2, and we are now of the opinion that cracking in Vetrocoke liquor is not a form of carbonate SCC but hydrogen embrittlement due to the arsenite.

Using liquor of Vetrocoke strength (i.e. 10% w/w As_2O_3) we searched for suitable inhibitors of this cracking. By this means we hoped to avoid reliance on stress relief as the only means of preventing cracking. In fact two inhibitors have been identified which synergistically combine to prevent cracking. The patent position prevents us disclosing the full system but we can reveal that ferric ion (produced in practice by air injection at the absorber) is one component. The work also defined an electrochemical potential, dependent on solution carbonation index, which represented the boundary between cracking and non-cracking conditions.

Our practice is now to maintain the second inhibitor above a defined minimum level in the plant liquor. By varying the rate of air injection in response to a signal from a monitor continuously measuring the potential of the plant in several locations, the liquor is kept in a state that inhibits SCC. The control loop is thus established. Figure 3

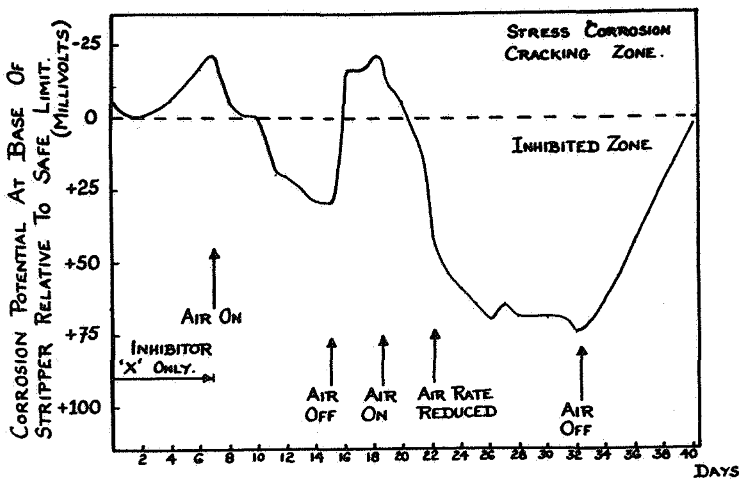

Figure 3. Effect of air addition on corrosion potential of Severnside 1A stripper base.

shows the influence of varying air addition rate, in the presence of the other inhibitor, on the potential of the regenerator base on the ICI plant which first experienced SCC. The correlation is striking.

Kellogg-built plants at Billingham

In May last year, a process operator saw a small plume of steam coming from an otherwise featureless area of lagging half way up the CO_2 Absorber of the second of our three plants. Closer inspection revealed a lot of solid material around the point where the steam was coming out, with stalactite-type growths characteristic of leaks from potassium carbonate scrubbing systems. When the lagging was removed, we found an apparently small vertical crack in the vessel shell. From this, issued a mixture of steam, synthesis gas and Vetrocoke liquor. The vessel had been delivered on site in two pieces, and the crack was on the weld made on site between them.

The area around the crack was cleaned up, and the entire site weld examined with ultrasonic crack detecting equipment. This showed a long circumferential crack on the inside surface, some 5 ft. 8 in. long, and about an inch deep—the vessel wall is about 1.65 in. thick. There were also several vertical cracks across this, and these did penetrate the vessel wall. In order to reduce the hazard from the leak, a pad was clamped over it with a chain around the vessel to hold it in place.

Calculations indicated that the circumferential crack was not the immediate cause for concern. The vertical crack however could not be allowed to grow very much before approaching unacceptably close to the critical length. The decision was taken to continue operating the plant, while monitoring the crack both ultrasonically and by measuring its length.

We examined externally one quadrant of the site weld on No. 1 Plant and 90% of that on No. 3 Plant, and found no evidence of defects. However, the weld on No. 1 was examined internally at the major plant overhaul in November last year and extensive cracking was found in the area not earlier examined. Slight leakage, with staining of the vessel shell on the outside, had also taken place. A major overhaul is due on No. 3 Plant in November this year, and we await this to inspect it internally. We believe it to be sound because the cracking later found on No. 2 Plant was exactly as predicted from the external ultrasonic survey.

No. 2 Plant continued to operate until February this year, with the cracks growing hardly at all. One of the vertical cracks then suddenly lengthened in a period of only 10 days by some 0.4 in., so the plant was shut down for repair of the vessel. Clearly we cannot be precisely certain about the accuracy of the measurement of the apparent extension, but we were not taking any chances.

Details of the cracking

No. 1 Plant: The surface was lightly ground to prepare it for Magnaflux crack detection. Numerous circumferential and angled cracks were found, together with areas crazed by fine cracks, Figure 4. All the damage was local to the weld made on site to assemble the two halves of the vessel, between strakes 6 & 7. A full width radial crack was also found on the weld between the semilean liquor inlet nozzle and the vessel shell. This had not leaked. It is still subject to close inspection, and a decision on the repair method is still to be taken.

No. 2 Plant: Ultrasonic crack detection with the plant on line had revealed a further six vertical cracks, as well as the leaking one, and a circumferential crack some 6 ft. long on the south side of the vessel. This was confirmed by internal inspection and once again, the cracking was local to the site weld between strakes 6 & 7.

Diagnosis

ICI has five ammonia plants using the Vetrocoke process, and they have been operating between 6 and 8 years. Yet only three exhibited the cracks, and of three nominally identical plants, run by the same operating team at Billingham, only two had suffered. If there was an explanation other than a purely statistical one, it had to be a difference in materials, fabrication, commissioning or very detailed operating technique.

The absorbers on the three Billingham Plants are made of fairly high strength material, 19 Mn 5, and are thus possibly more prone to stress corrosion cracking. Each half of the vessel brought on site had been stress relieved at the fabricators. They were welded together on site, and then this weld itself stress relieved. The quality of the stress relieving operation seems to be exceedingly critical. Those temperature record charts that are available for the vessels show that the stress relief of all three vessels was satisfactory, but there is some suspicion that the stress relief of the site weld may have been only partially effective. It also appears that the vessel on No. 3 Plant had its site weld stress relieved twice, but there is no evidence to suggest why this was done, if indeed it was done.

The five plants are operated in broadly similar ways, using the same raw materials and similar start up and shutdown procedure. They were commissioned in similar ways. There was no obvious difference in the operation of the Billingham units—indeed liquor is often transferred between the three units. Only the air addition policy is

Figure 4. Cracking of site weld on Billingham No. 1 Vetrocoke unit.

different, and that difference is consistent with the apparent pattern of failure. Air is added to the base of the absorber to keep the dissolved iron in the ferric, and thus soluble state; this was found to be particularly important at start up. During normal operation, the air was often shut off.

On No. 1 and No. 2 Billingham plants, air was added to maintain the pentavalent arsenic level between two arbitrarily set values. It was therefore often shut off for long periods. On No. 3 Plant, air was added all the time. The policy on the Severnside plant was like that of No. 1 and No. 2–and of course it too had suffered cracking. The policy at Immingham was similar, but the water makeup required by the water balance was of undeaerated water. This has been shown to carry enough oxygen dissolved in it to supply all that is required. This confirms that air injection is indeed critical in maintaining the liquor in a non-aggressive state.

Future operation

All the research showed that cracking only took place when the corrosion potential exceeded certain values depending on the carbonation index. We have therefore installed probes to measure this potential, and air is added to maintain it at a satisfactory value; there would seem to be a threshold level, above which the air holds its own and satisfactory inhibition is maintained, and below which the situation slowly deteriorates and the solution becomes aggressive. It is important to start adding the air as soon after establishing a gas flow as possible. The second inhibitor is maintained above a minimum specified value.

The siting of the corrosion probes is difficult because they must always be submerged, and should be at the site of the possible corrosion. This is not always practicable, and, for example, they are often positioned in pump suction lines. The probe itself has been developed to become a reliable plant instrument, but still with facility for isolating it in case it springs a leak. The potential measured is that developed by the metal in contact with liquor; one wire is attached to the plant and the other to an electrode in contact with the liquor through a salt bridge. The signal from the probe is amplified by a charge amplifier to prevent a current being drawn from it, and displayed on a chart recorder. This recorder is best fitted with an alarm because the signal can be so steady as to be ignored except during process changes.

Over-enthusiastic air addition is to be discouraged, because it can lead to a greater corrosion rate and iron buildup in the liquor and to an increasing pentavalent arsenic level. This last is troublesome on plants with good housekeeping where there is little purge from the system to hold the arsenate level down. Arsenate can build up, and ultimately it will raise the crystallization temperature by its presence, if all the other solution concentrations are kept up for efficient scrubbing.

We believe that we can prevent further serious stress corrosion cracking by maintaining the right environment in the plant, and by monitoring the factors found to be necessary.

Repair of the damaged vessels

On both No. 1 and No. 2 Plants the repair has been carried out by welding an external band of steel plate over the defective weld around the full circumference of the tower. Alternative methods of repair considered involved either cutting out the original weld and re-welding, or cutting out a section of the tower including the defective weld and welding in a new section.

The reduction of stress concentrations to a minimum is obviously a major objective in a potentially stress corrosive environment and the evidence indicates that the problem has not arisen in the shell of the vessel under the normal design stresses, nor where the weld has been shop welded and shop stress-relieved. The natural conclusion is to lay particular emphasis on effective stress relief after welding and this has been given particularly careful attention during the repairs carried out on Nos. 1 and 2 Plants. However, it is known that in some other plants where repairs have been carried out by welding sections or "windows" into the shell, cracking has subsequently recurred even though careful stress relief has been carried out. The precise conditions for welding and stress relief to ensure that stress corrosion cracking will not occur are not accurately known and it is for this reason that the method of repair utilizing an external band where the new welds are not in contact with the solution has been technically preferred. Further important advantages of this method are that the time required for the repair is significantly reduced and that toxicity hazards arising from welding on contaminated surfaces inside the absorber are avoided. In order to reduce the possibility of Vetrocoke solution getting to the root of the fillet welds in the repaired sections on both plants, the annulus between the shell and band has been filled with epoxy resin. Though it was also recommended that the shell inner surface should be protected over the cracked area by epoxy resin backed by a support ring, this proved to be impossible in the time available and was not carried out.

It was decided that the steel band should be capable of taking the hoop and the longitudinal stresses, so that although the cracked weld might get worse, the strength of the tower was unimpaired. The details of the system in the two plants differed as can be seen from the sketches, Figure 5. On No. 1, which was the first to be tackled, a band made from 1½ in. thick plate to BS 1501-151 28A in nine pieces 14 inches deep, was welded to the shell with 1 inch fillet welds using Fortrex 31 electrodes. ¼ inch BSP tapped holes were provided in each piece to enable epoxy resin to be pumped into the interspace to prevent leakage from the crack which penetrates the shell coming into contact with the fillet and butt welds attaching the strap to the shell. In the event of complete failure of the vessel's circumferential weld the stresses in the strap and in the attaching 1 inch fillet welds are well within the acceptable figures for the materials involved.

One disadvantage of the external band method of repair is that local discontinuity stresses are produced in the shell at the top and bottom of the reinforcing band again, Figure 5. An opportunity arose of measuring the change in stresses at various points during the pressurizing of No. 1 Plant in

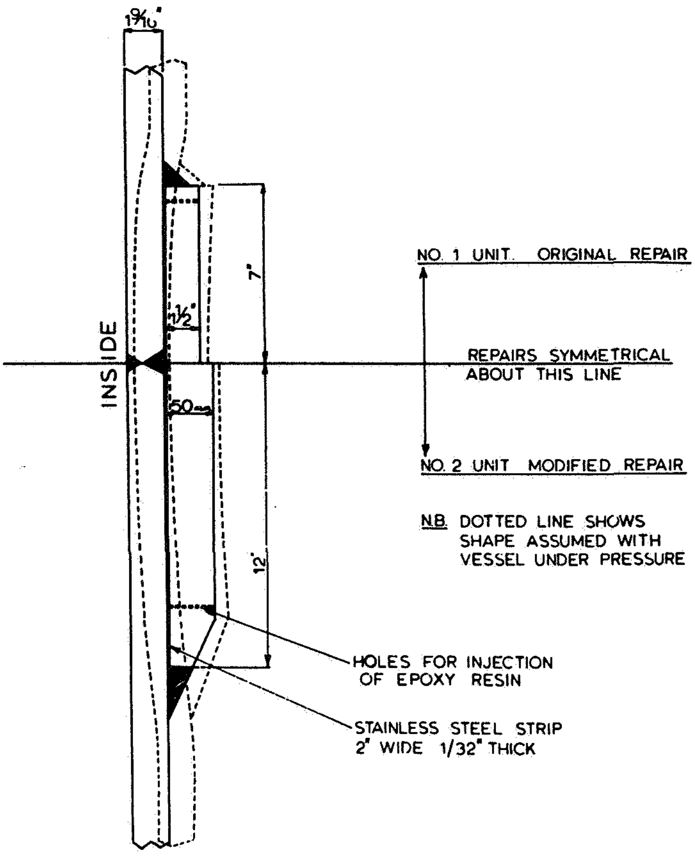

Figure 5. Methods of repair and stress distribution.

February, 1973, which indicated a change in bending stresses in the main shell plate in the vicinity of the fillet weld of some 24,000/lb./sq. in. because of the discontinuity between the shell and strap. Although the UTS of the material from which the towers were made is specified at 45,000/lb./sq. in. and is actually about 10-15% higher than this it is felt that the stresses under working conditions might be in a range to render the material vulnerable to stress corrosion cracking.

For the subsequent repair on No. 2 Plant, the reinforcing band and upper and lower fillet welds were tapered off at 30°. This has the effect of reducing the maximum stress in the shell arising from the discontinuity to a lower value than the hoop stress which has already been shown to be acceptable in the Vetrocoke environment. The steel band was made 24-in. wide. The change of thickness to 50 mm was determined by availability of suitable material and for no other reason. All the stresses involved are obviously less than those in No. 1 Plant.

Another modification in the attachment to No. 2 Plant absorber was to attach a 1/32nd of an inch thick strip around each plate in order to improve the chances of 100% gap between the strap and the shell to ensure a 100% homogenous filling by epoxy resin since the tolerance on the shell circularity is sufficient to cause considerable variations in this gap.

For both vessels the post weld heat treatment was the same. The hot zone in each case extended 2 ft. 6 in. each side of the welded edge of the strap. Temperatures on the whole of the strap were maintained between 580°C and 620°C for four hours with the temperature grading off to 300°C at the 2 ft.-6 in. distance away from the weld. Temperature gradients through the thickness of the shell and strap were no more than 10°C at the points where the internal thermocouples were attached and temperature gradients outside the weld, i.e. in the parent plate, along the axis of the towers reached a figure of 100°C per ft.

Using modified grease guns and as soon as the temperature after stress relief had fallen to 50C, Epoxy resin, Araldite type GX250 with hardener HY830 and accelerator DY830 was injected into the space between the strap and the shell wall until all the air was displaced. The operation was completed before the temperature fell to 40 C. The injection and vent holes were then sealed off with plugs. Both towers were tested hydraulically with the shell at a minimum temperature of 40 C.

The area of the main shell material just outside the fillet weld may be susceptible to stress corrosion cracking on the inside and regular monitoring of this area by ultrasonics from the outside, not more often than once a month unless anything abnormal is detected, is being carried out. Inspection of the fillet welds attaching the pad to the shell is also to be done within six months and then at normal vessel inspection periods. This will be a magnetic particle crack detecting technique. Reduction of the bending stress due to the discontinuity could be achieved by welding a 6 inch wide strap ¾ inch thick above and below the existing strap. This of course would be a major operation requiring stress relief and pressure testing and can hardly be justified unless any abnormal signs are found in the area concerned.

Future inspection

No. 1 Plant: At the first available opportunity the site weld, the inner surface of the shell opposite the upper and lower edges of the external bend and the inlet nozzle at semi-lean level will be inspected internally to see if the cracking has extended.

Because of the 14 in. wide external band, no meaningful external ultrasonic examination of the site weld can be done, but the fillet welds of the band will be examlined visually and, should the vessel be available off-line, preferably by crack detection. Weekly monitoring for leakage into the space between the shell and compensating plate at the semi-lean inlet will also be continued.

No. 2 Plant: This plant is scheduled to run for about 18 months from March, 1973, and if there is no unforeseen major shutdown in that period it will not be possible to examine the site weld internally. However, should the opportunity arise, an internal inspection of this weld will be carried out.

For the reasons stated above, it will not be possible to carry out meaningful external ultrasonic examination of the site weld but visual and, if possible, crack detection examination of the band fillet welds will be carried out.

In general the same remarks apply as to No. 1, for even though the strap width and design should here be sufficient to reduce the stress concentration, a change in stress has been imposed on the shell and the area will be checked periodically from the outside (or inside if available) by ultrasonics.

In the strap, ¼-inch tapped holes have been drilled about

3/8 inch from the fillet weld, one at the top and one at the bottom of each plate. They have been fitted with Klinger cocks so that the atmosphere of the space beneath the pad can be monitored for hydrogen and/or Vetrocoke solution.

No. 3 Plant: This plant is due for a planned shutdown in November, 1973, and then we will look at the site weld internally, and as many as possible of the remaining welds to which internal access is possible without removal of further packing. In addition, between now and November, 1973, regular monitoring of the external circumference of the site weld will be carried out, visually and by ultrasonics.

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DISCUSSION

P.A. RUZISKA, Exxon Chemical: We have one Vetrocoke unit in service for about seven years. No stress corrosion cracking has been experienced. But, we use continuous air injection. I wonder if your studies have shown what sort of minimum air rate would prevent a stress corrosion cracking potential, particularly without your unnamed second inhibitor?

FYFE: In fact, the investigation did show that inhibition was possible with only ferric ion present. However, the sort of concentration needed is pretty high and I think one would be dubious about the wisdom of, in fact, running with the sort of level I am talking about. Here we are talking of above 500 ppm ferric ion but if you have that then that might explain the absence of cracking in your plant.

However, since these were laboratory results, one must be cautious about using the precise figures to predict plant operation. The real test is to put a monitor in the plant and that will tell you if you have enough inhibitor. However, for the potentials measured to mean anything you must have done the necessary work to determine the potential values critical for cracking.

RUZISKA: In the Benfield and Catacarb systems, we use vanadium as the corrosion inhibitor. Have you done any work with the vanadium systems to see if a stress corrosion cracking potential is encountered in the presence of vanadium?

FYFE: Point one — as far as I know there is no in-service case of cracking in a vanadate inhibited carbonate solution CO_2 removal unit. This in itself suggests no problem exists.

Point two — we have done laboratory work on those solutions and confirmed, using the very severe slow strain rate test, that vanadate is an inhibitor of SCC as well as general corrosion. The potential values measured fit in with the physical result in each test, in that they are what we would classify as "safe" in Vetrocoke solution.

Q. I might have missed it but what was the reference electrode that you were reporting your potentials against and does your protective potential vary with temperature.

FYFE: If the liquor temperature is below 70°C then the potential adopted by the steel would put it in a safe region anyway. In addition, no cracking is found when testing in solutions at below 70°C. There appears to be some sort of corrosion activation at about 70°C, which, if there is no inhibitor present, pushes the potential into the danger zone. Between 70°C and 130°C, which is as high as we have gone, there is no difference in the critical potential which I showed in my graph. However, the critical value does vary with degree of liquor carbonation.

Q. What was the reference electrode?

FYFE: We started off using a simple tungsten wire but it proved to have an insufficiently stable reference voltage. On plant probes, we have used both the calomel and mercury/mercurous sulphate electrodes. The latter is better because it has a lower temperature coefficient, i.e., the reference voltage is less temperature sensitive. We therefore prefer it.