CAUSTIC EMBRITTLEMENT IN THE BAYER INDUSTRY

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Abstract

Caustic embrittlement continues to occur in Bayer plants even though various safeguards and procedures are followed. QAL, Alcan-Gove and Alcoa World Alumina have collaborated to share information on failures, conduct work through studies at Monash University and with in-plant testing. The focus is to better define conditions that cause caustic embrittlement, standardise and publish procedures for welding and stress relieving to minimise the potential of caustic embrittlement, and to identify those materials that are particularly susceptible to caustic embrittlement. The paper will discuss: caustic embrittlement in terms of the Bayer industry, those areas of plant where caustic embrittlement has the most potential to occur, materials that have a proven track record of being particularly susceptible to failure and the joint research that has been sponsored at the Centre of Advanced Materials Technology, Monash University.

1. Introduction

Caustic embrittlement is both a well known and much maligned term in the Bayer industry. When major failures occur caustic embrittlement is frequently the suspect, but in detailed investigations it has rarely been the cause, especially in pressure vessels. However, there has, and continues to be, many instances of caustic embrittlement resulting in cracking and subsequent leakage of liquor. Champion (1957), in his excellent summary of plant experience with caustic embrittlement, gives many examples but also points out that many areas of plant seeing similar, or even more aggressive liquor or temperature conditions have not shown signs of caustic embrittlement. Such seemingly random variations in areas of plant suffering caustic embrittlement still occur today. Also there are many instances where caustic embrittlement in equipment has only been noted by chance, by routine inspections or through the evidence of leaks that indicate a crack has penetrated full thickness, rather than by planned inspections for its presence.

There is a great deal of confusion and differences of opinion as to:

- what are safe and unsafe liquor concentrations and temperatures,
- when and where stress relieving is required,
- the actual stress relieving conditions, and
- the susceptibility of various materials with often the quite erroneous belief that some materials are more resistant to stress corrosion cracking than mild steel (eg stainless steels).

Many papers have been written on caustic embrittlement and the Bayer industry (eg Chaubal, 1984) yet there are no overall, and agreed to, Industry guidelines for the design engineer, maintenance personnel and process personnel. The Industry is always pushing for higher caustic concentrations in process and caustic cleaning liquors for increased productivity and such increases are known to increase the risk of caustic embrittlement. Such increases can only be sanctioned if it can be demonstrated that no reduction in safety will occur.

The Bayer industry is not alone in suffering from caustic embrittlement. The Paper and Pulp industry uses similar liquors (excepting the alumina in the liquor) and temperatures and has issues with caustic embrittlement. Much of the excellent research work over the last twenty years has been undertaken by, or sponsored by, that industry. Also many other industries that utilise alkaline environments such as ammonia/ammonium carbonate are similarly faced with alkaline embrittlement of mild steel.

2. Caustic Embrittlement

Caustic embrittlement is the common terminology for stress corrosion cracking of steels in a caustic soda solution. Some typical examples of caustic embrittlement cracks are shown in Figure 1. In caustic embrittlement the metal loses strength because cracks propagate along grain boundaries. As these intergranular cracks grow, the available load-bearing cross-sectional area is reduced and failure may result by tensile overload or penetration of the cracks through the walls of containment vessels. The mechanism is still much in debate, the most widely accepted theories being that caustic embrittlement is a form of hydrogen embrittlement or results from anodic dissolution. What is clear is that after a time cracks initiate in the embrittled metal and propagate in an intergranular manner (Figure 2) with the grains effectively becoming unglued from each other. There is not a single crack tip but extensive branching with multiple crack paths; the metal is embrittled often many millimetres in front of the crack tip. Simply heating of the metal results in the cracks extending and opening up in this embrittled area. Attempts to repair the crack by welding can result in further crack propagation. Because of the branching and the intergranular nature of the cracks, prediction of the effect of the crack on the structural strength of the material is difficult and standard crack propagation models are not applicable.

2.1 *Factors affecting caustic embrittlement*

The four major factors that affect caustic embrittlement are:

1) Contact of the caustic solution and the metal surface
2) Stress state of the material
3) The environmental conditions, primarily liquor concentration and temperature
4) The type of material

For stress corrosion cracking of any material to occur there must be sufficient time of contact between the metal

KEY WORDS: caustic, embrittlement, Bayer, stress, corrosion, cracking

and the liquor. By definition this implies that the metal surface must be clean of scale.

For stress corrosion cracking the material generally must have been stressed close to, or in excess of its yield point such as can occur with welding stresses or by machining such as in thread cutting. Operational stresses are normally insufficient to cause such stress corrosion cracking.

The environmental conditions need to be sufficiently benign so that there is no rapid corrosion. Indeed the surface of embrittled material often shows little signs of corrosion or general attack yet the material can have cracks penetrating full thickness. Caustic embrittlement is sensitive to the corrosion potential and there are distinct potential ranges in which cracking occurs. Aeration and other methods that can affect the environment at the metal surface and thus the corrosion potential can have a significant effect on the susceptibility to cracking. In conducting tests related to caustic embrittlement it is critical that such work be undertaken under defined corrosion potential conditions.

The type of material, and specifically its microstructure, can have a significant effect on stress corrosion cracking. Low carbon steels with a predominantly ferrite structure appear to be most prone to caustic embrittlement. Improved general corrosion resistance is not necessarily an indication of improved resistance to stress corrosion cracking. For Bayer liquors, nickel is the only metal that has proved to be both completely corrosion resistant and to not suffer from stress corrosion cracking.

There have been numerous laboratory studies on the mechanism of caustic embrittlement. Most have been related to the effect of liquor concentration, various additives, temperature and material type on the propagation of a developed crack (normally produced by fatigue). Generally their purpose has been to elucidate the mechanism of caustic embrittlement and extrapolation of the results to obtain life time assessment of Bayer equipment is not necessarily valid. For example, if such laboratory data were extrapolated then a life span of less than 10 years prior to major failure would be predicted for most equipment and piping that had not been stress relieved. Clearly this is in complete contrast to what is observed in practice in virtually all areas of a Bayer refinery.

A major difference between many of the laboratory studies and the refinery scenario is that there are two parts to caustic cracking: crack initiation and crack propagation. The time frame for crack initiation can be very slow and be many years. Crack propagation is more rapid. Crack initiation is much more difficult to study and is still relatively unpredictable. Most laboratory studies have concentrated on crack propagation. Solely using such data to assess caustic embrittlement potential could therefore be quite misleading. The fact that refineries have been in operation for so long with relatively few instances of caustic embrittlement, especially in pressure vessels and associated piping, suggests that there may be other factors that influence the onset of caustic embrittlement.

2.2 *General Guidelines for Caustic Embrittlement*

In order to get a better understanding of the magnitude and the variability of caustic cracking NACE undertook a survey of processes using caustic solutions including the Bayer industry and produced their seminal paper (NACE, 1951). Further reviews on caustic embrittlement have been undertaken for NACE (eg Parkins, 1977). The NACE survey found that caustic cracking was particularly prevalent at liquor concentrations above 15% NaOH and close to the boiling point, Figure 3. Variants of this Figure have been used for many years as a guide for stress relieving. A similar diagram is used for stainless steels (eg Schillmoller, 1996). There have been further studies that have incorporated more data and further refined these diagrams to cover a broader set of conditions more relevant to the Bayer Industry.

Complicating the situation is that the NACE survey data indicated that under seemingly identical conditions failures had occurred in some equipment and not in others. Consequently it was hard to define a specific set of criteria for the Industry. People within the Bayer Industry have tended to have their own views as to what was safe or not, and when stress relieving was required. This has been based on experience within their own refineries together

Figure 1 — Examples of stress corrosion cracks in a 50% caustic pipe, a caustic cleaning tank and from a precipitator.

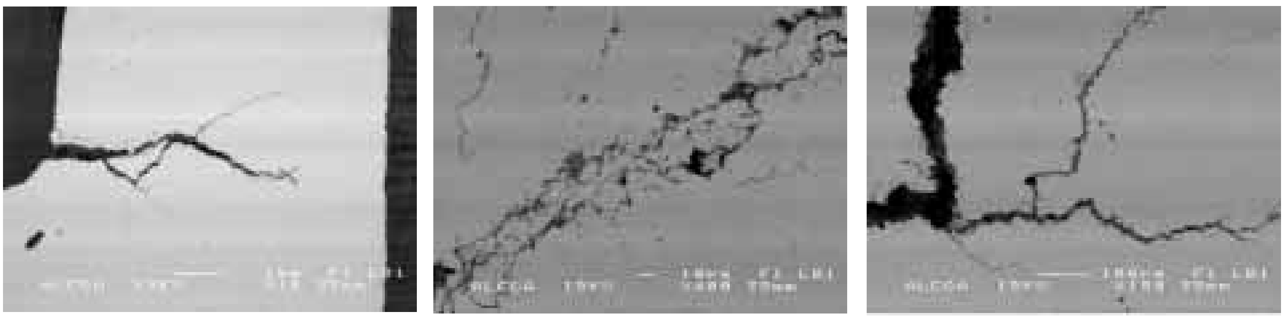

Figure 2 — Branching and intergranular nature of caustic embrittlement crack at a weld.

with the reported literature data. This has inevitably led to some confusion, especially for design engineers who are now often working on design for several refineries that have different criteria for when stress relieving is required. Further, once cracks are observed there are no specific guidelines as to how best to repair them, or whether they can be considered 'safe' for a certain period prior to the repair of the specific equipment. Cracking in equipment, even in pressure vessels, is common in many industries including the power industry. Such cracks are regularly monitored and equipment taken out of service and repaired once the safety limit related to such cracks is obtained. In the Bayer industry, once a crack is noted the normal approach is for immediate repair. This is in part because a cost analysis often shows that it is best to do the repair rather than live with a defect that requires continual management to monitor and evaluate. If there were clear guidelines related to crack propagation and the reduced integrity of the material (as is the case with other forms of cracking), then a policy of on-going management of with cracks may be more cost effective. Sizing of branching intergranular embrittlement cracks is no simple task (Liu and Walker, 1996). Also there are no validated crack propagation models for intergranular stress corrosion cracks and thus the policy is to remove cracks once detected.

For most equipment in Bayer refineries there is not the concept of a specific design life as there is for boilers. Many refineries are now well over forty years old and are expected to continue to operate for many years to come. Setting design life as "forever" is not helpful; economic considerations can be more fruitfully applied if design life is better understood and evaluated. This is widely practised in the power industry where remnant life assessment is used to ensure maximum usage of equipment after its original design life. In a similar vein the application of thermal stress relief to vessels is a conservative approach and can often be easily justified because it can help achieve nominated asset life expectations.

The authors of this paper are frequently asked to approve increased liquor concentrations, nominate stress-relieving requirements or make specific materials selection decisions based on their own experience. There is often little back up available from published material and no universal standards. Indeed most literature, as indicated previously, would predict that equipment would not last past 10 years in direct contrast to the 30 years plus that is achieved. Clearly, from both an industry safety perspective and from other perspectives it is essential that the laboratory data and actual plant experience are in unison. This includes the effect of factors such as liquor concentration, temperature and preventive treatments. What is required is a damage model that incorporates the laboratory data and is validated by plant experience that can be readily used by design engineers.

In practice the life span of equipment such as pressure vessels is determined based on regular inspections. Inspection times are normally based on descale frequency. Non-pressure vessels are equally susceptible and many failures have occurred in such vessels. Inspection procedures for such non-pressure vessels are often less frequent.

3. The Consortium

There has been an informal network of metallurgists and engineers at different alumina organisations who have discussed caustic embrittlement issues, especially when failures have arisen. Such discussions have focused very much on the safety requirement. It became clear that there was a need to better understand the phenomenon as it related to the Bayer industry and to agree on common standards for the Industry overall. The Bayer industry in general has been supportive of research and has been self-reliant in understanding and addressing problem areas with many individual companies sponsoring research. Previous attempts over the years to get industry groups together in Australia to discuss and sponsor joint research in the area of caustic embrittlement had proven to be unsuccessful. This was in part because the primary interest of the Industry was not well aligned with that of external researchers who were generally interested in the specific mechanism of caustic embrittlement failure. It became clear that there was a need for both joint research in specific areas, and for greater sharing of individual experience and knowledge between companies to better leverage their combined knowledge of caustic embrittlement. Consequently a Consortium approach with three major goals was adopted.

1. To have agreed industry guidelines related to caustic embrittlement to ensure that refineries operated as safely as possible.
2. To share information related to caustic embrittlement failures to minimise the risk of possible failures.
3. To undertake joint research work on caustic embrittlement aimed at better understanding the effect of the major controllable parameters. An outcome of that work would be an improved set of guidelines.

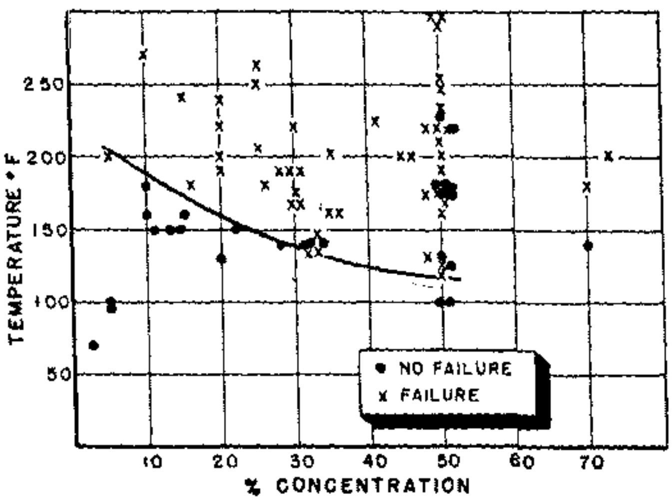

Figure 3 — The NACE chart for caustic embrittlement (NACE, 1951).

The Consortium has been meeting approximately twice a year and those discussions have led to useful sharing of information. Jointly funded research work has been undertaken at Monash University at the Centre for Advanced Materials Technology (CAMT) using a slow strain rate testing procedure, similar to that described by Breault and Simard (1991). The test procedure has been refined to reflect cracking characteristics that are observed at the refineries. In-plant testing of sample coupons is planned but has not yet started.

The information sharing has proven to be one of the major benefits of the Consortium. The other has been the joint focus on the research work that has ensured that the work has progressed in the desired direction and produced reliable and repeatable results. The latter requirement of repeatability has resulted in slower than hoped for data but the Consortium are adamant that information obtained must be self consistent and must advance our understanding of caustic embrittlement. In particular the results from the test rigs must be self-consistent with what is known within the industry rather than at total odds with industry experience as is the case with much of the literature data. To this end the test procedure is first being validated on solutions that are known within the Industry to either cause cracking or not. Similarly a suite of materials is being tested for their susceptibility to caustic embrittlement to check if a similar ranking is obtained to that found in practice. Welding and stress relieving will also be tested and backed up by in-plant testing of samples. In addition to obtaining a set of laboratory data which is consistent with plant experience, it is envisaged that the test will enable the effect of moving to higher caustic concentrations, or the susceptibility of new materials, to be predicted. These are ambitious goals but the Consortium members believe they are achievable and will help to make the industry environment a safer place.

The data from the CAMT work, and the in plant testing data will be published both at relevant alumina processing meetings and within the materials literature. Currently the CAMT work has focused on caustic cleaning solutions at temperatures below their boiling points. Such solutions are known to cause caustic embrittlement and alumina producers have different upper limits for such cleaning liquors (both temperature and caustic concentration). Also stress relieving requirements in such cleaning systems vary between alumina producers. Examples of the type of information from the work at CAMT for mild steel in a caustic cleaning liquor at a high and low temperature are shown in Figures 4 and 5. Industry experience has shown that caustic embrittlement can readily occur at the high temperature with the caustic concentration used but not at the low temperature. At the low temperature (Figure 4) the fracture is typical of a ductile failure. At the higher temperature the time for failure and %reduction in area were dramatically reduced and there was extensive cracking and embrittlement of the material (Figure 5). The initial part of the failure cross-section for this sample clearly indicates that there has been extensive intergranular cracking. These results are in line with industry experience.

4. General Materials Information from Consortium Discussions

The information below is that shared amongst consortium members and comes from first hand experience, reported data and interpretation of previous failures.

Significant necking of sample, failure is ductile in nature.

Fracture surface showing only one mode of failure, and typical of a ductile failure.

Micrograph of fracture surface showing typical ductile dimples.

Figure 4 — Sample tested in caustic cleaning solution at 80°C.

Extensive cracking and little reduction in area.

Fracture surface shows an outer brittle fracture and an internal ductile failure.

Micrograph of outer brittle fracture surface showing intergranular failure.

Figure 5 — Sample tested in caustic cleaning solution at 95°C.

(Photos and micrographs from the work of Dr. Raman Singh at CAMT, Monash University)

4.1 *Failure experience and scale*

When reviewing the failures over the many years of Bayer refinery experience accessible to the Consortium members a clear picture emerges. There have been very few instances of major failures with loss of equipment and major production losses; those that have occurred have not been in pressure vessels or associated piping. However, there have been instances of crack penetration through vessel walls and pipes with subsequent weeping of liquor, and detection of cracking within vessels and pipes. There have been failures in salting out evaporators and evaporators for liquor burners, non-pressure equipment such as precipitators, caustic cleaning equipment, and vessels that are caustic cleaned regularly (especially if direct steam heating is used). Cracking has invariably been associated with welds and in many instances those welds had not been stressed relieved, especially in general piping. For some pipelines cracking had occurred even where welds had been stress relieved. There have been failures where caustic has leaked at gaskets resulting in high local concentrations through evaporation (for example in heater heads).

From the observations above, the overriding factor in determining whether caustic embrittlement may possibly occur, irrespective of stress relieving, is whether the vessels were scaled or not. As indicated previously, caustic embrittlement requires metal/liquor contact. In reviewing many of the failures the scaling state of the equipment is frequently not noted. In digesters and evaporators a silica scale (DSP) readily forms within hours of returning equipment to service thus protecting the metal. For salting out evaporators and the recirculating type used in liquor burning, the concentrations frequently exceed the solubility limit for the silica scale so the liquor is no longer supersaturated with respect to DSP and thus it affords no protection. Similarly in caustic cleaning equipment there is virtually no silica in solution so again the metal surface is exposed to the liquor.

Hydrate scale can similarly act as a barrier between metal and liquor. Several failures have occurred in equipment where hydrate scale is present. The failures have been associated with the vessels being caustic cleaned (eg precipitators). In many of the failures steam lances were used to heat the caustic cleaning liquor. The failures occurred close to the steam lance where the hydrate scale would have been quickly removed and the metal exposed to high caustic concentrations and high temperatures; the failure did not result from exposure to normal operating conditions where the hydrate scale is present.

A good example of how the situation can change quickly and dramatically occurred at a refinery where contact heaters are used to mix the bauxite slurry, spent liquor and steam. The heaters would continually scale and thus were on an annual descale schedule. They had been in service for over 20 years with annual inspections and no observable cracking (all welds had been stress relieved). Following a change in the steam nozzle design a heater was found to be leaking from cracks close to a weld. On inspection massive cracking was found in several areas of the heaters; the cracks had not been evident 12 months before. The change in the nozzle design had directed steam close to the wall of the heaters and not only prevented scaling but would also have increased the local temperature in those areas. Wear plates had been attached via welding without stress relieving to overcome the erosion problems caused by the steam nozzle design. Major cracking had occurred in all areas of the welds attaching the wear plates. The cracking was so extensive the heater could not be repaired. Other heaters that had had the modification were also inspected and cracking was detected. Those heaters were repairable. The failure was a combination of the change in the steam nozzle design that prevented scale formation in localised areas, a local high temperature of the liquor at the metal surface in those areas and that stress relieving of welds fixing the wear plates had not been undertaken. The original, full thickness, welds of the pressure vessel that had been stress relieved had not cracked.

In some parts of the refinery the scale is more a settled type scale rather than a growth scale (Roach and Cornell, 1985) such that liquor contact between the metal surface and the liquor can be maintained and there is therefore no barrier to caustic embrittlement. Also, with fluctuations in temperature (through environmental/season changes or power failures) growth scale can detach from walls of vessels and enable liquor ingress. Consequently scaling is an ally in preventing caustic embrittlement but it is not safe to rely on that ally as the primary protection mechanism

4.2 *Effect of liquor conditions and temperature.*

The majority of failures have occurred and continue to occur in caustic cleaning systems. Each alumina producer has its own set of upper limits with respect to temperature and caustic concentration for caustic cleaning. Process tanks are normally not stress relieved because of the low free caustic concentration (and they have the benefit of having a scaled surface). The caustic cleaning tanks require stress relieving because of the higher free caustic concentration and the fact that they normally have no potentially protective scale coating. Failures had been common in such systems when the cleaning liquor was heated by direct steam injection because of the localised severe conditions as noted above. Where steam coils are used for heating, failure of bolts securing the flanged sections frequently occurs. At some refineries where the temperature of the cleaning liquor is well controlled by indirect heating of the cleaning liquor through shell and tube heat exchangers, the caustic concentration was not well monitored and the normal 20% sodium hydroxide limit was frequently exceeded. Cracks at welds in most of the pipework and in the non-stress-relieved cleaning vessel occurred and the whole system needed to be scrapped. This highlights that caustic cleaning conditions must be carefully controlled.

As previously mentioned, use of steam sparging is particularly likely to cause caustic embrittlement because of the localised high temperatures and poor temperature control of the bulk solution. As a cleaning practice, its use should be highly discouraged in the Industry.

In the NACE surveys it was noted that 50% caustic tanks failed in some industries, especially if not stressed relieved, whereas in other industries no failure had occurred. Within the Bayer industry some alumina refineries have stress relieved their caustic storage tanks whereas others have not. There have been few, if any, cases of cracking in such tanks in the Industry. This leads to the question as to whether such tanks should be stress relieved or not. The caustic tanks that have cracked have one common factor. They have been in climates where it has been necessary to steam trace the tank to maintain the caustic at sufficiently low viscosity to pump. Where steam tracing crosses welds, localised conditions occur that could lead to caustic embrittlement. In tropical climates the liquor temperature never drops to a level where steam heating is required and thus stress relieving is not required.

From the above discussion it is clear that caustic cleaning conditions can result in cracking. Increases in the severity of the caustic cleaning conditions such as an increase in the caustic concentration needs to be preceded with a large amount of good data to determine whether the new conditions are safe. If not, stress relieving of all welds including pipework, is required. There is a continual push to increase the caustic concentration in such liquor from process and technical personnel. This is primarily to reduce dilution and to maximise the amount of alumina cleaned per unit volume of liquor. This is particularly an issue in plants operating with low reactive silica bauxite as the amount of caustic make up is low and hence maximum usage of it for dissolving scale is required. The issue is complicated by the fact that caustic cleaning conditions often refer to the % sodium hydroxide in the liquor. The causticity of Bayer liquor is defined often as total caustic (TC) concentration which refers to the caustic concentration present as both free caustic and tied up as the aluminate ion. The question of whether free caustic (ie that not combined with alumina) or total causticity is the critical parameter is still unclear. This is one issue which needs to be resolved to ensure optimum cleaning liquor concentrations can be chosen to maximise process efficiency without compromising equipment integrity and safety.

4.3 *Materials*

What has become clear from Consortium discussions is that there are specific materials that appear to be very prone to caustic embrittlement. As a Group we have been continually asked whether one material is better than another. Unfortunately little direct comparison work has been undertaken under the specific conditions that apply to our industry. However, there is a clear picture emerging about some materials. For others there is a need to have a reliable test procedure to evaluate their propensity for embrittlement, especially in the welded state. Also it would be ideal to be able to determine whether a reduction in temperature of say caustic cleaning solutions, or the need for stress relieving, is a better economic solution than a change of materials.

It is well documented that low carbon steel and, in particular, ferritic structures, are particularly susceptible to caustic embrittlement. The specific reason for this is not known but the practical evidence is overwhelming that higher carbon content and more pearlitic materials are less susceptible. Microstructure rather than carbon content appears to be the dominating factor. A good example is that of malleable, spheroidal graphite or nodular cast irons. Such materials are high in carbon yet have a microstructure that is essentially ferritic but with large flakes or nodules of carbon. In that condition there has been many failures even in quite benign conditions. An example of a ball valve having failed at the thread is shown in Figure 6. The valve had been in place for several years in low temperature spent liquor and had literally fallen off in service. Both Alcoa and QAL have had similar failures with such materials and they are no longer used. Use of such materials for fittings and valves is frequently proposed because of their low cost; strict purchasing guidelines are required to prevent their ingress into the refinery. Information on the high susceptibility of this material to caustic embrittlement is not generally available across the Industry. The specific reason for this material being very susceptible is not known. There have been no specific laboratory studies. It is suspected that because the material essentially has a ferritic structure with large carbon nodules, significant localised potential differences accentuate the embrittlement process.

The major failure was on the right end of the sample, another crack is evident emanating from the last threaded section. The intergranular nature, and the carbon and ferritic microstructure are readily observed at the higher magnification.

There has long been the view that slight differences in the microstructure/chemical composition might increase the susceptibility to caustic embrittlement as discussed by Champion (1957). As more refined testing procedures are developed, information is starting to emerge supporting this view, eg Liu et. al. (1994). High tensile materials appear to be more susceptible to caustic embrittlement. For example, there have been failures of high tensile chains whereas normal steel chains have not failed, Figure 7.

More and more cracking is being found in heat treated and tempered steels with a martensitic structure. Such materials are used in high erosion areas because of their hardness and thus invariably the metal surface is free of scale. Initially cracks observed were assumed to occur from welding this hardened material to the base metal. However on closer examination it became clear that much of the cracking was from embrittlement and as more and more material has been inspected, it is clear that this is a quite common occurrence. Such cracking appears also to be occurring in hard-facing materials. The body of evidence, slowly being accumulated through this Consortium and published data is pointing very strongly to the fact that both the temperature limit, and caustic limit, for low alloy steels is less than that for mild steel. Cracking in the long term in such materials probably cannot be avoided even if high tempering temperatures are used (there is a temperature limit for tempering such materials otherwise the desired properties of the alloying are not obtained).

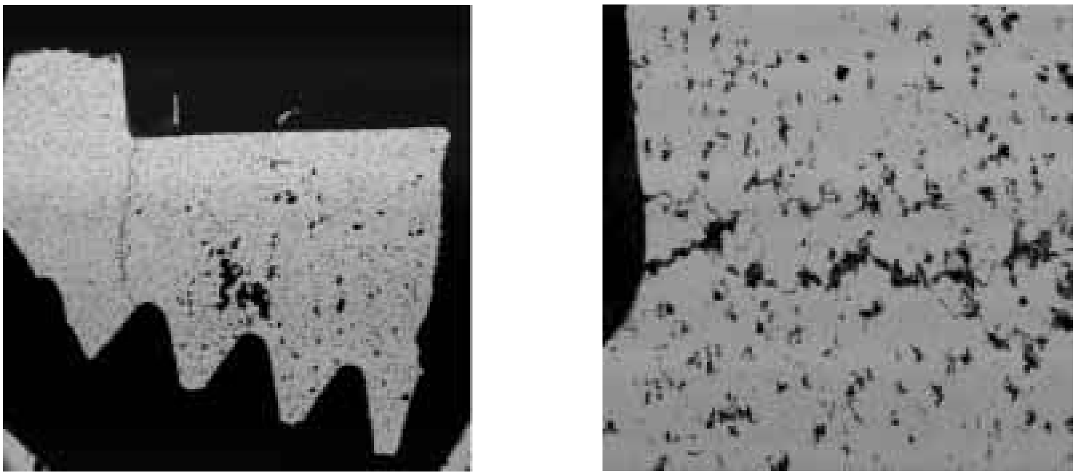

Figure 6 — Caustic Embrittlement in a malleable cast iron fitting.

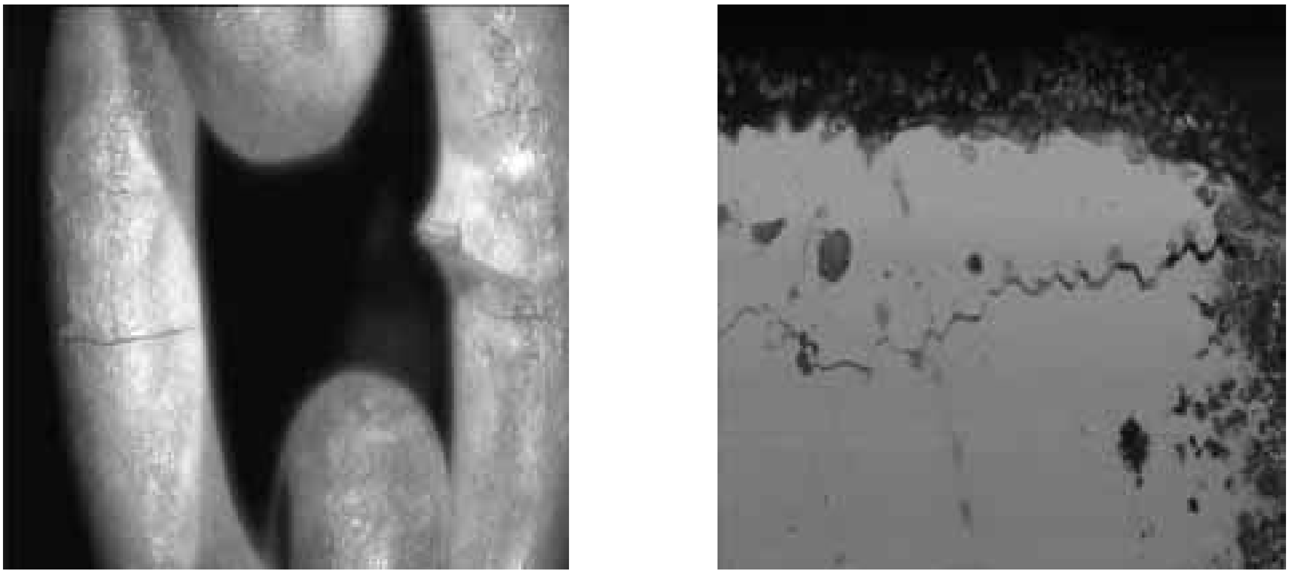

Figure 7 — Caustic embrittlement of a chain, several cracks are evident. The higher magnification shows the fracture area and a crack, intergranular in nature, is evident close to that fracture surface.

Stainless steels are not immune to caustic embrittlement. Such criteria as liquor temperature and caustic concentration limits must be set and applied if austenitic stainless steels are to be used safely and cost-effectively.

Part of the work in progress at CAMT is aimed at testing a variety of materials to determine how sensitive they are to caustic embrittlement under a range of test conditions. Such work will be backed up by in plant testing at the refineries of Consortium members.

General evidence from The Consortium discussions is that:

- High nickel alloys such as Incoloy 825, Hasteloy C and Monel are relatively non-susceptible.
- Duplex stainless steels like SAF 2507, SAF2304 and SAF 2205 are valuable in tubing applications where welding is not required. Fabrication must be approached with caution and is not recommended, ie not only the material, but the specific application needs to be considered.
- Austenitic stainless steels like 904L, 316 and 304 are known to crack and must be used only within specific temperature limits and caustic concentration limits

With regard to microstructure:

- Massed ferrite has the highest susceptibility to cracking in mild steels and non-heat treatable irons, and propensity tends to drop as carbon content is increased.
- It is probable that long term susceptibility cannot be removed in heat treated low alloy steels,
- Experience with high alloy heat treated steels is poorly documented and understood. It is suspected that, like low alloy steels, susceptibility will increase as strength is increased.

4.4 *Welding procedures*

Welds are by far the largest enabler for caustic embrittlement. Welding procedures aim to standardise the means to produce a quality weld. Several of the essential variables that appear in a weld procedure can significantly influence caustic embrittlement susceptibility as follows:

- Joint configuration — this affects residual stress
- Welding sequence and the probable benefits of temper-bead treatments to refine microstructure.
- Welding method and consumable in terms of how the weld metal matches the parent plate with regard to corrosion potential.

There is still great debate as to whether the change in microstructure or the stress state is the most important factor for welds. The bulk of evidence points to the fact that removal of the in situ stress by stress relieving is the primary factor for preventing caustic embrittlement even though the microstructure may not be altered. It has proven to be very effective. However, there are conditions where stress relieving by itself has not been sufficient to remove the potential for caustic embrittlement. Whether this is indicating that microstructure changes are required or that, under certain conditions, such intergranular corrosion will occur irrespective of stress state is not known. Normalising has the benefit that it improves homogeneity between weld and parent plate and probably alters the differences in corrosion potential. Such normalising is specified under certain operational conditions.

5. Conclusions

Caustic embrittlement is still a major failure mechanism within the Bayer industry There are no universal Industry guidelines to assist engineers and process personnel to ensure that optimal design, environmental conditions or materials are chosen in order to maximise efficiency without compromising safety. Utilising the experience of the industry through a collaborative forum such as the Consortium has increased our knowledge base on caustic embrittlement. Further information sharing, combined with the joint research testing currently being undertaken (and planned for the future) and data from the planned in plant testing, it is expected that general guidelines on caustic embrittlement can be formulated. These guidelines will ensure occurrences of caustic embrittlement are further minimised or hopefully eliminated and process efficiency is maximised.

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