

RELIABILITY OF STAINLESS ALLOY EQUIPMENT IN CHLORINE DIOXIDE BLEACHING

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ABSTRACT

The reliability of bleach plant equipment has been considerably improved over the last decade thanks to better process control and introduction of advanced alloys for corrosive service conditions. The paper briefly describes modern material selection practice for bleach plant applications. Nevertheless, failures of stainless alloy parts still occur, robbing the industry of valuable production time. Specifying higher alloy composition for a given part is often not sufficient in order to improve its performance, if appropriate changes and safeguards are not included into the purchase orders or repair contracts. The users of equipment must be aware of the necessary changes and the need to transfer the important information from the new equipment supplier to the local contractor or the repair shop.

INTRODUCTION

The reliability of a pulp mill, i.e. its ability to sustain uninterrupted production is one of the key objectives of the modern mill operation. High initial capital cost of production equipment, ever growing price of raw materials and increased world wide competition drive down the profit per ton of pulp. This intensifies the need for maximising production in the time available between regular shutdowns, while each unscheduled interruption due to the failure of equipment deals a serious blow to the profitability of pulp production in Canada and the US.

As was emphasised in our previous publication [1], pulp mill is being run as a conveyor line, so that failure of a stage would virtually stop the overall production process. Nowhere it is felt stronger than in the chlorinating bleaching stages (otherwise known as D-stages, thanks to the use of chlorine dioxide as a sole source of active chlorine), having traditionally the most corrosive environment in the chemical pulp mill. Over the last 2 decades, substantial investments were made in many pulp mills in order to replace 300-series stainless steels as a main material of construction with higher alloys, plastics or titanium. Especially successful was the introduction of superaustenitic alloys (6-7 % Mo) due to their high resistance to corrosion, facile fabrication and good availability from several reliable sources. On the other hand, there were many cases encountered and described, where new installations showed early signs of corrosion due to the unexpected new corrosion mechanisms (for example, trans-passive dissolution of high-Ni alloys [2,3,4]), poor microstructure, or improper fabrication methods. A good example of the latter problem is given by a plant study of field welded stainless alloy pipes conducting chlorinating

stage filtrates [5] – butt-welding of the pipe from outside only, is likely to lead to the corrosion of unmixed zone from inside.

It is generally understood that higher corrosion resistance and strength of advanced materials may come together with higher sensitivity to fabrication and handling mistakes. In other words, in order to get a full value from a more expensive new material one has to pay attention to metal supplier specifications, and information transfer to fabricators, installers and repair shops. A few examples from our practice will illustrate the point. But first, let us go over service conditions and common material selection rules.

D-stage elements and corrosion conditions

The D₁ and D₂ -stages in a modern pulp mill are usually run at medium consistency (MC), 100 % ClO₂ substitution (D) and pH over 3.5. Acid is still added to the pulp (at least in the case of D₁-stage) in order to lower its pH from preceding alkaline stage, down to neutral (pH=7) or slightly acidic (pH~5). The acid can be added in the form of a concentrated sulphuric acid, and/ or as a recycled D-stage filtrate. In the latter case, it would contain a considerable amount of chloride (Cl⁻), and, possibly, some active chlorine residuals. The acid is added using a simple pipe injectors or “tees” in the pulp conduit before steam and ClO₂ addition. Further decrease in pulp pH takes place upon addition of moderately acidic ClO₂.

The operating temperature of these stages is usually high, 70°C and higher, which is achieved by adding live steam to the pulp, usually by using mechanical mixer (**peg or high-shear mixer**). Heated pulp is then mixed with concentrated ClO₂, right before the retention vessel, using **titanium high shear mixer** of some kind, available from many suppliers.

In an up-flow tower arrangement, chlorinated pulp would enter at the bottom of the tower, passing through a large diameter **drain pipe**, **shut-off valve**, and a **nozzle**, all of which have to stand up to a highly corrosive, concentrated ClO₂. In this case, Titanium and fiberglass are the competing choices, although 6-Mo superaustenitic alloys are sometimes being used as well. The tower is often tiled or fiberglass lined. At the bottom of the tower, a **side-entry agitator** (marine-style impeller) is placed to resist channeling. These devices work under harsh conditions of high flow and concentrated ClO₂. On top of the tower, metal **rake** is placed to discharge the pulp. Noticeable ClO₂ residuals and high temperature make this piece as well as the downstream **bleach washer**, vulnerable to corrosion. Both the rake and bleach washer are routinely ordered from 6-Mo superaustenitic alloy (such as 254 SMO material, or Al6XN brands). After the washer, pulp is transported via a large diameter stainless pipe type-304L or 316L, which is not expected to corrode from inside, instead it could often be a subject to an external stress-corrosion cracking under insulation.

A continuous or pulsating movement of highly viscous pulp through the pipes is effected either by modern MC pumps, or traditional thick stock pumps placed up-stream of steam and ClO₂ addition, while fairly corrosive washing filtrate is recycled by centrifugal pumps. The corrosion of the latter has been a subject to a special investigation presented a few years ago [6], which related severity of corrosion to the ferrite content of a given “austenitic” casting. The problem of high ferrite has been addressed by the newly issued TAPPI TIP [7]. In the case of traditional, predominantly austenitic alloy castings, controlling the balance between main alloying elements content is of a critical importance. However, a simpler solution is offered by the available duplex stainless casting construction (type 2205 or higher), which has been a standard practice for years in Scandinavian countries and elsewhere.

As was mentioned before, the concrete cases must include more careful analysis of local conditions and additional specifications and precautions, in order to get what one bargains for by installing new or rebuilt equipment.

THE RESISTANCE OF MATERIALS

There is plenty of information on the metal coupon behavior in bleach washers in ClO_2 service [8,9]. Some of the authors venture into predicting “safe” intervals of parameters, which in most cases are too conservative for a practical application [10]. Our experience shows that a well fabricated 6-Mo superaustenitic washer can survive through periods of very high ClO_2 residuals in the hundreds of ppm of total active chlorine and $\text{pH} < 2$ [11]. When we are talking about metal parts, one should discriminate between wrought alloy (plate, sheet or welded pipe), weld metal, and castings. In the case of titanium, the difference is relatively small, while in the case of stainless steels and alloys, it could be dramatic. For example, welds in 6-Mo alloy equipment (such as longitudinal seam weld in shower pipes) are often a subject to a preferential corrosion attack by wet ClO_2 gas, as shown in **Figure 1**.

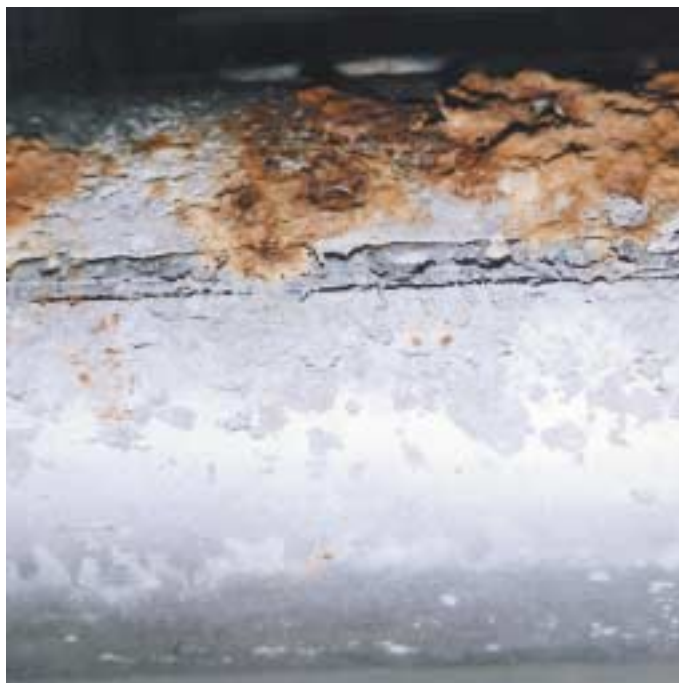


Figure 1. A 6-Mo shower pipe in ClO_2 washer .

The over-alloying of the weld metal used so successfully in the past for welding conventional austenitic stainless steels may have lost its effectiveness in the case of higher alloy materials. In fact, scaling down the nickel content in welds joining 6-Mo superaustenitic alloys to the level approaching the base metal has been suggested for ClO_2 service [12] equipment.

Titanium in all forms is considered to be completely immune to corrosion in ClO₂ service at all operating pH, with the exception of some ClO₂ generator elements (where the attack is due to the presence of concentrated sulphuric acid). The weak point of titanium is its vulnerability to mechanical fatigue. In order to suppress the latter, proper design thickness, full penetration welding, and adequate suppression of vibration must be engineered into a given component. Anyhow, the mixers, injectors, piping and valves between ClO₂ addition and the tower can be reliably made from the Ti, Grade-2 alloy.

Fiberglass is quite resistant to the “neutral” ClO₂ in the absence of abrasion or high flow. The resin rich corrosion barrier on the inside surface of a fiberglass pipe, is being gradually softened by the ClO₂, so that it is subject to wear and thinning in a high flow / high ClO₂ region. Therefore, all fiberglass installations at this location ought to be considered as of limited service time and be checked and replaced on a regular basis in order to avoid interruptions in production due to catastrophic failure. It is also common to install a Ti section (cone) between the high shear mixer exit and the rest of the drainpipe, if the latter is made from FRP. Inherent brittleness of FRP requires provisions to reduce vibration and control of bolt tightening to avoid flange-cracking [13].

6-Mo superaustenitic alloys can be used successfully under relatively harsh conditions, including those, before the tower entrance. However, the resistance to concentrated ClO₂ is marginal, especially in the case of fabricated pieces. The main culprit of such construction is a potential attack on welds by two distinct mechanisms:

- If the weld is made from outside only, the inevitable unmixed zone, where solidified weld metal has not been mixed adequately with the base is a subject of fast local corrosion attack [5]. Welding 6-Mo material for ClO₂ service must be done either on the process side, or on both sides of the welded plate. Castings might be a preferred choice when welding on the process side is impossible.
- Any stainless alloy with nickel content above 50 % is a subject to ClO₂ –specific general corrosion attack. Due to a fairly high nickel content of 6-Mo alloys (between 18 % in UNS 31254 and 25 % in UNS N08926), heavy welds made using alloy 625 Ni-base electrode (65 % Ni), can have areas with nickel in excess of 50 %. In order to reduce the chance for weld metal corrosion by ClO₂, one may prefer using C-276 (57 % Ni), or even G-30 (42% Ni) electrodes. In order to assure good mixing of the weld metal with the base, downhill welding on the process side should be avoided. General supervision of the welder by mill representative may be required to ensure the correct welding technique.

Cast 6-Mo parts must be solution annealed at 1150 °C minimum, followed by water quenching [14]. Request heat treatment chart to be enclosed with the part. The advantage of using properly made cast 6-Mo products, is the absence of high nickel spots even at a relatively high average Ni content, such as alloy UNS N06030 (G-30).

Lower alloy stainless steels such as 316L stainless, have been widely used in the approach piping and equipment, since the pulp entering D1 and D2 stages, comes from the caustic extraction washing, where conditions are quite mild. However, the addition of acid and/ or recycled chlorination filtrate to the pulp may require an upgrade to type-317L or type-2205 duplex stainless steel. Duplex alloys are believed to be more vulnerable to oxidation of unprotected root during welding than austenitic alloys such as type-317L. Accordingly, TIG

welding without argon backing of the root should not be used. In fact, stick welding, using AWS E2209 electrodes is a preferred technique for a duplex root pass in the field.

EXAMPLES

The following examples have been chosen to demonstrate the importance of detailed specification, control of materials, information transfer, and continued research for a successful application of advanced alloys in a new service environment.

The 6-Mo alloy pipe after ClO₂ mixer. The unmixed zone attack on a superaustenitic alloy weld from the process side caused failures of 2 ClO₂-tower drainpipes after 2 years in service. **Figure 2** shows a badly corroded weld seen on the process side of the pipe, while the base metal is clean. This is why the plant management agreed to upgrade welding specifications from the usual outside-only welding to double-side welded fabrication for the new 6-Mo alloy pipe when the stage was converted from low to medium consistency operation (**Figure 3**). Although initial fabrication cost had been higher for the double side welding, the pipe has been in service for 5 years by now with no sign of a localized corrosion attack on the inside surface as was recently verified by inspection through the exit nozzle of the ClO₂ mixer.

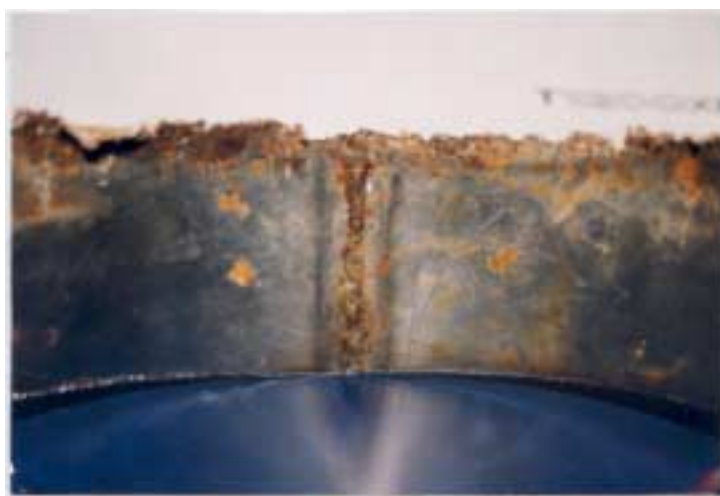


Figure 2. Corroded tower drain pipe.

The failure of 6-Mo gate-valve casing. Contrary to the previous example, another application of a fabricated superaustenitic part downstream of ClO₂ addition, resulted in a corrosion failure. The gate valve was fabricated from UNS NO8926 alloy, containing 20 % Cr, 6.2 % Mo and 26 % Ni. It failed by through-the-wall pitting from inside in less than 2 years of service. In addition to a clearly seen unmixed zone corrosion of the root pass (**Figure 4**), the metallographic cross-section of a plate shows pitting, preceded by the intergranular attack (**Figure 5**). The scanning electron microscopy demonstrated the presence of a large Mo peak in the intergranular space compared to the Mo content in the grain centre (**Figure 6**), indicating inter-metallic compounds (sigma-phase). Omitting or delaying the water quenching as the plate-finishing step at the rolling mill, leads to sigma with the associated loss of corrosion resistance.

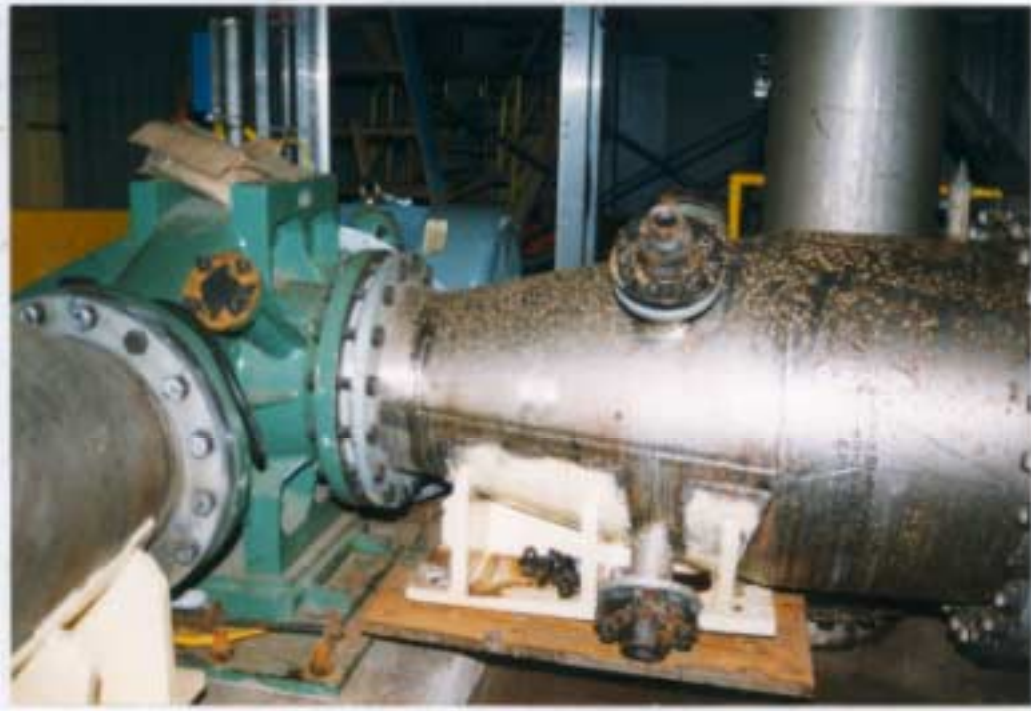


Figure 3. New double-welded 6-Mo pipe.

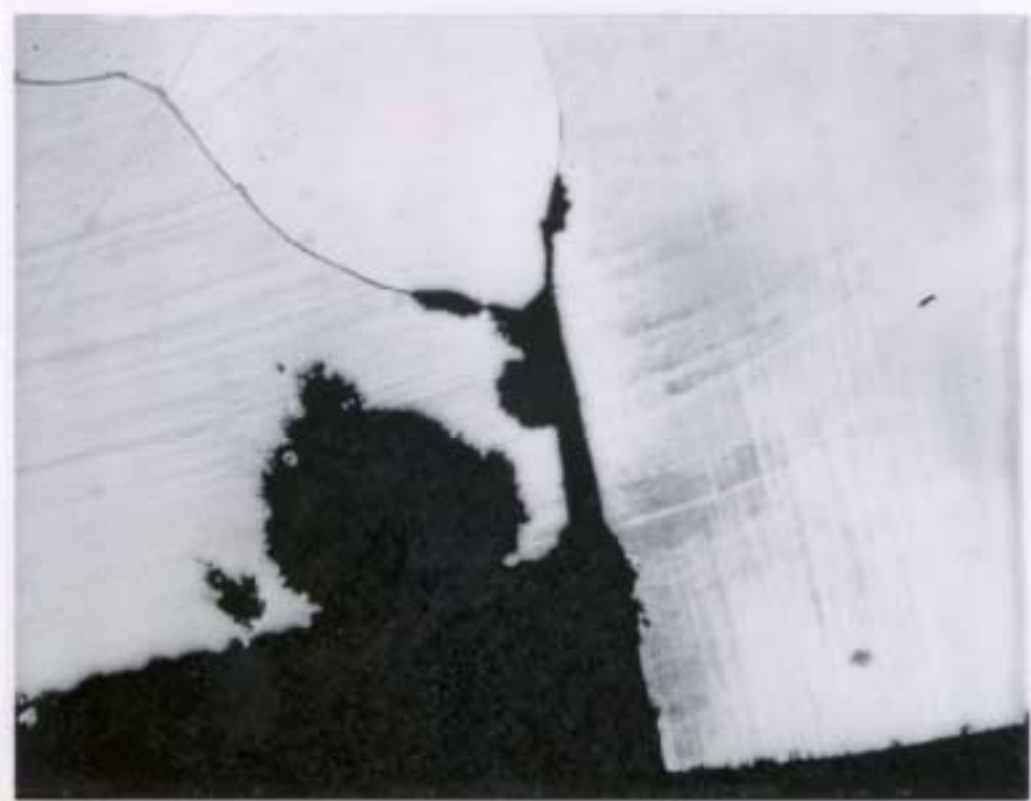


Figure 4. Unmixed zone corrosion of the root pass in 6-Mo valve.

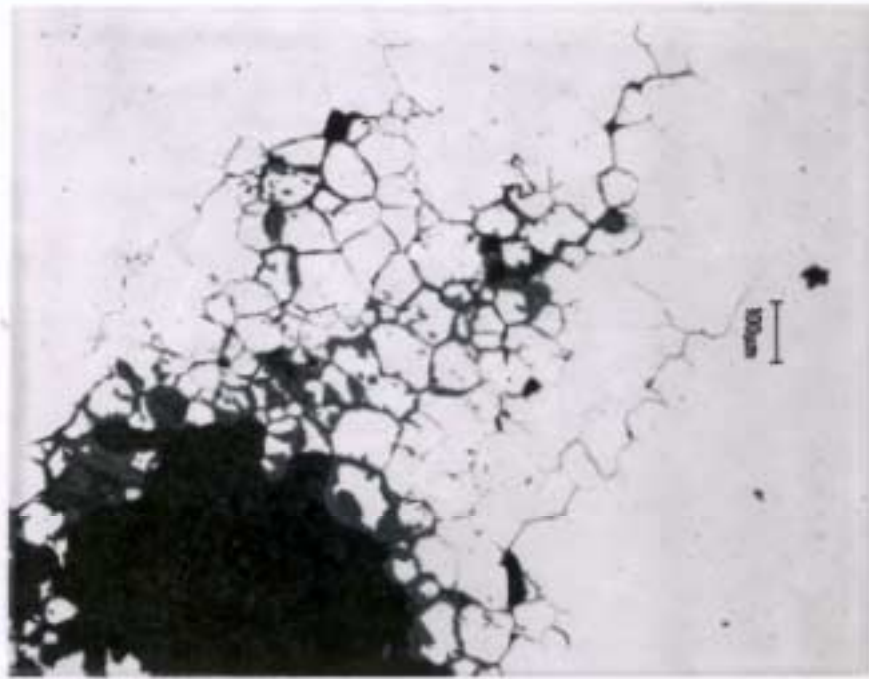


Figure 5. Intergranular attack on 9-Mo alloy.

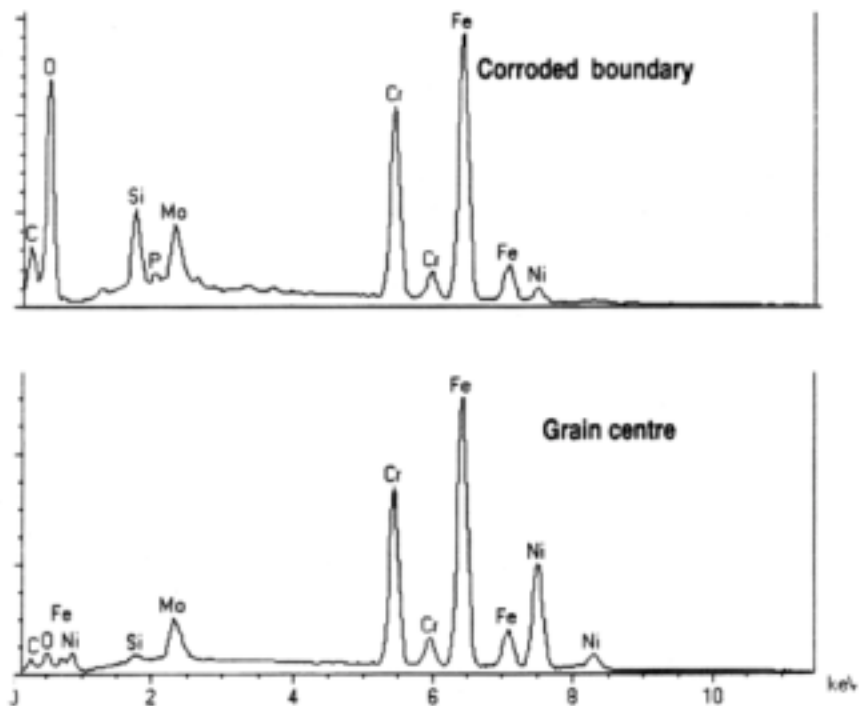


Figure 6. Composition of the corroded boundary versus grain centre.

Rebuilding cast duplex rotor for a thick stock pump. The wear and rebuilding of thick stock pump rotors is a routine operation conducted by the original suppliers or local shops. In the past, a typical problem associated with such a rebuild, was sensitization of the original part (typically an alloy CF-8M or CG-8M casting), followed by fast pitting and cracking in subsequent service.

Recently, many such rotors have been replaced with duplex castings of 22 %Cr- 5 % Ni or higher composition, which increased pump throughput and resistance to corrosion. Surprisingly, a freshly rebuilt duplex rotor failed in service in a few weeks after returning from the shop. A cross-section of the failed piece was electro-etched in NaOH solution to reveal duplex microstructure in the middle and a 100 % austenite on the outside surface. Apparently, the duplex rotor has been rebuilt by using austenitic alloy electrode at a local shop, unaware of the change in the rotor alloy composition. The piece failed due to stress-corrosion cracking of the austenite surface layer, followed by a crack propagation inside the duplex core, running parallel to the elongated austenite grains as seen from the photograph in **Figure 7**. Similar propagation features for SCC in duplex stainless steel has been reported in ref. 15.

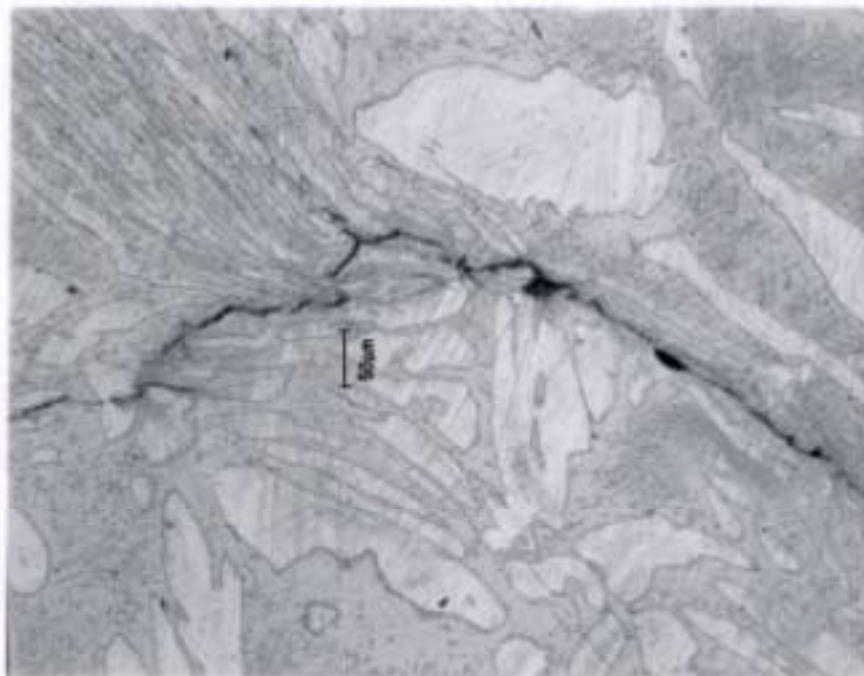


Figure 7. Cracking of duplex casting.

Stress-corrosion cracking (SCC) of 6-Mo alloy parts in ClO₂ service. This case relates to one of the most severe corrosion conditions in the bleach plant, i.e. corrosion under stagnant wet chlorinated pulp. The rake arms and backside of the flights in the up-flow tower rakes are subject to extensive pitting under the wet pulp deposits as compared to the clean, corrosion-free faces of the same flights. Corrosion under ClO₂-impregnated pulp is presently a subject of an active research project in Finland [16]. Recently, we noticed an extensive cracking in addition to pitting of the welded crossbars. The cracks display characteristic features of a trans-granular SCC (**Figure 8**). The literature describes cases of chloride SCC of UNS3124 but only at temperatures above 100 °C [17], while the rake operating temperature did not exceed 70°C at any time. On the other hand, the cracking of cast and welded 6-Mo impellers in the side-entry agitators working in ClO₂ towers, were seen before (**Figure 9**). A SEM analyses of a small sample from the cracked area, revealed the presence of a secondary phase (**Figure 10**) with much higher Mo to Cr peak ratio than in the matrix material. Once again, inappropriate thermal history (missing or ineffective quenching) of the casting was likely to cause poor performance.

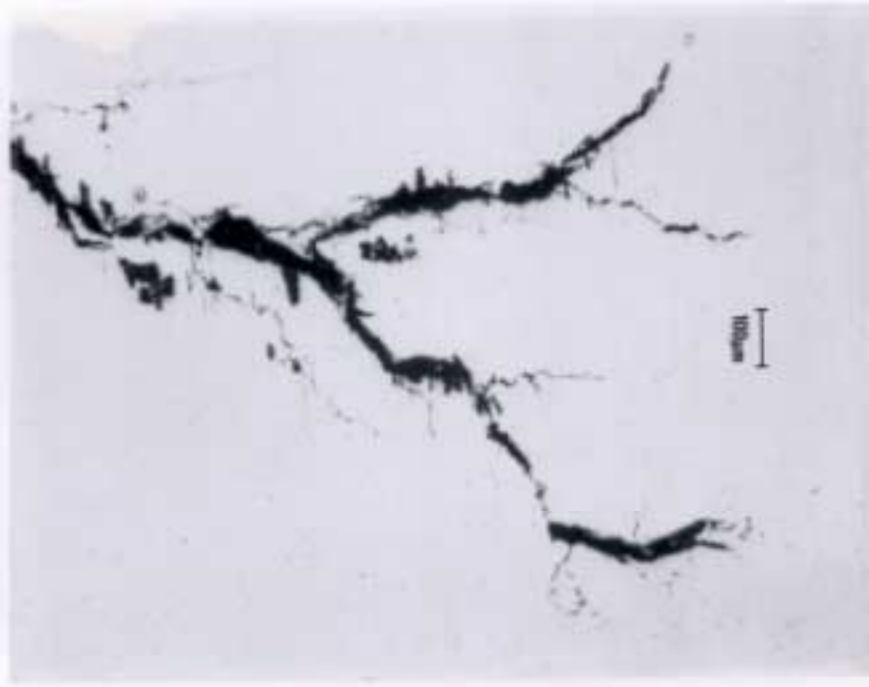


Figure 8. SCC of 6-Mo bar from ClO₂ tower rake.



Figure 9. Cracks in 6-Mo side-entry agitator.

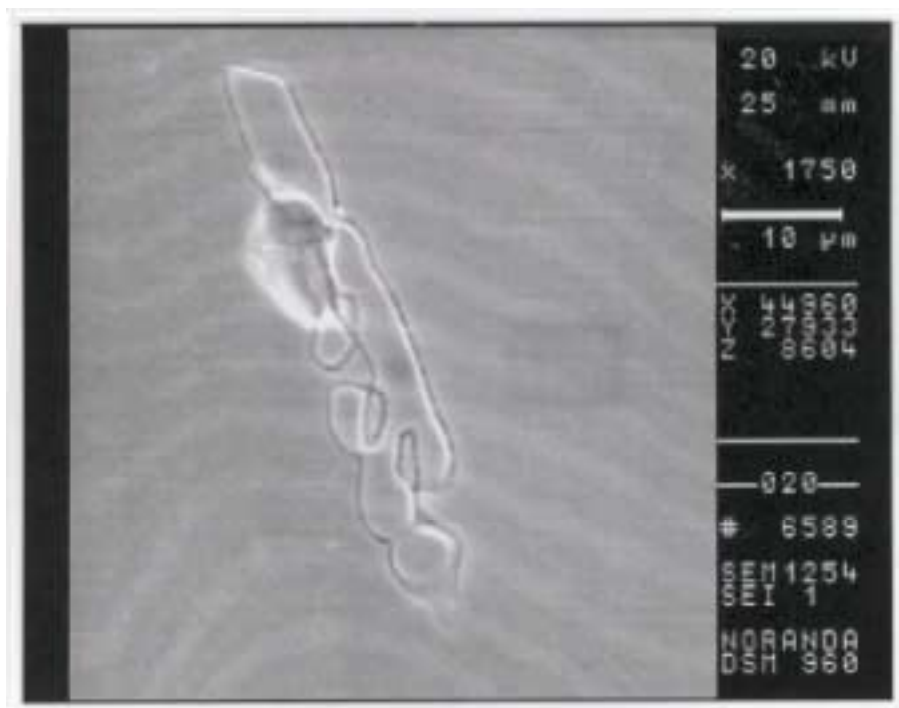


Figure 10. Secondary phase in 6-Mo casting.

CONCLUSIONS

Switching to a higher alloy fabrication is not sufficient in order to increase reliability of pulp mill equipment. Matching fabrication procedures and a serious quality assurance program are the necessary and often missing components.

Modern materials used in fabrication of new equipment require special attention to fabrication procedures and welding consumables. It is important to transfer information between supplier and client and between client and local contractor.

Overmatching of the base metal composition with higher alloy welding consumable is not always beneficial and should be minimised in the case of 6-Mo superaustenitic alloys in ClO₂ service.

Welding on the process side is essential for long-term survival of fabricated stainless parts in the presence of ClO₂ residuals.

Solution anneal in the proper time and temperature intervals followed by a rapid water quenching are critically important both for castings and wrought alloy plates used in ClO₂ service.

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