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High-Performance Austenitic Stainless Steels in the Pulp and Paper Industry

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ABSTRACT

The corrosion resistance of recently developed stainless steels is reviewed with reference to their performance in pulp mill bleach plants. Field and laboratory test data are used to compare the merits of different alloys, and the background to alloy formulation is outlined. How to avoid preferential corrosion of welds is also covered.

INTRODUCTION

Pulp mill bleach plants have traditionally employed austenitic stainless steels because of their combination of good corrosion resistance and weldability. AISI Type 317L (18% Cr 14% Ni 3.5% Mo) has been the typical bleach plant alloy for oxidizing acid chloride environments.

Bleach plants, however, have become more corrosive over the past 20 years as mills have closed-up wash-water systems and reduced effluent volumes. In modern closed bleach plants, Type 317L is no longer adequate for long-term service,(1) and many mills have turned to higher alloy stainless steels, nickel-base alloys, and titanium for better corrosion resistance.

Metals are chosen over nonmetals for moving equipment (e.g., washers). They are stronger, tougher, have better fatigue properties and, if they have sufficient corrosion resistance, require virtually no maintenance. The more corrosion-resistant alloys, however, are more costly and the trick is to choose an alloy with just enough resistance to avoid corrosion problems, *Figure 1.*

A wide choice is now available in alloys for bleach plant applications. The list includes three families of stainless steels — austenitic, ferritic and duplex — whose differing merits are outlined in *Table 1.*

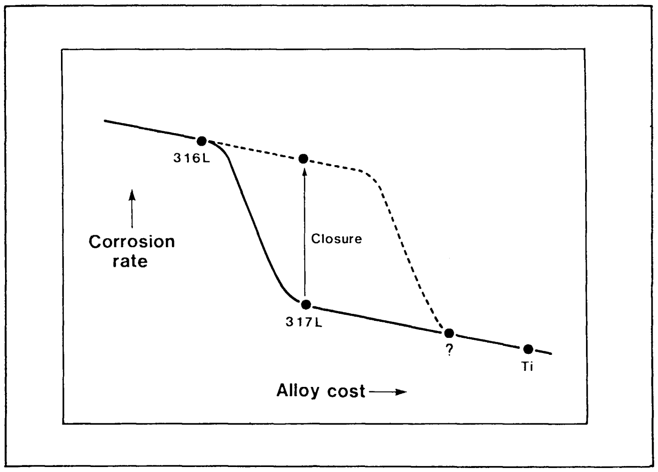

Figure 1 Filtrate recycling increases 317L corrosion rates; higher-cost alloys can resist the new conditions

Table II lists most of the commercially available candidate alloys, and their chemical compositions;

Table III outlines the influence of each alloy component on bleach plant corrosion resistance.

Austenitic stainless steels, including the AISI 300 series and enriched developments of these steels, are tough,

TABLE 1

CHARACTERISTICS OF THREE FAMILIES OF STAINLESS STEELS FOR BLEACH PLANT SERVICE

Family	Examples	Characteristics	Comments
Austenitics	316L 317L 904L 254 SMO	Tough, ductile, readily welded without loss of corrosion resistance. Corrosion resistance related to alloy content.	Bleach plant steels traditionally chosen from this group.
	Nitronic 50	As above, with better pitting resistance than 317L	Manganese-substituted austenitic, may be better value than 317L; not common at present.
Ferritics (low interstitial type)	29-4-2 29-4	Not as tough as austenitics, particularly after welding thicker sections. Special precautions needed for welding to avoid N_2 pick-up. Corrosion resistance, related to alloy content, can be very good.	Higher alloys have remarkable corrosion resistance. Thin-section (<3mm) may find applications as corrugated deck or tubing; not common at present. (C + N) <0.025%.
(Ti-stabilized type)	29-4C Nyby Monit SC-1	0.03% C versions.	Cheaper 0.03% C version of low interstitial ferritics, for thin section weldments. (<0.045 inch).
Duplex	2205 Ferralium 255	Tough, ductile, should be weldable without significant loss in corrosion resistance.	Combines toughness and corrosion resistance of austenitics and ferritics.

easily welded, with corrosion resistance ranging from fair to excellent, depending on the alloy content, *Table I.*

Ferritic stainless steels in the 400 series are not used in bleach plants because of their poor corrosion resistance, particularly after welding, but there is a new generation of extra-low carbon and nitrogen (low interstitial) grades that now retain post-welding corrosion resistance. As with austenitics, the corrosion resistance of these ferritics ranges from fair to excellent, depending on alloy content. Steels like 29-4, however, have not been used in the bleach plant because of problems with embrittling precipitation in thicker sections (3 mm and over) and the special precautions that are required to avoid nitrogen contamination on welding.

In contrast to the ferritic grades, properties of austenitic and duplex stainless steels are enhanced by nitrogen and, as a result, duplex stainless steels such as 2205 and Ferralium 255 have recently been developed with improved corrosion resistance.

Laboratory Assessment

The relative corrosion resistance of stainless steels and nickel-base alloys can be assessed with the $FeCl_3$ test, which was recently shown to be an appropriate assessment of bleach plant performance.(1) Thus the relative resistance to pitting corrosion of a range of commercial stainless steels can be seen in *Figure 2.*

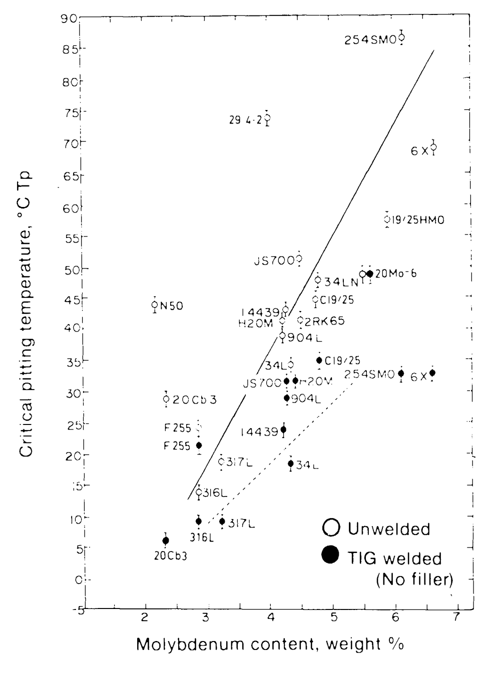

Figure 2 The relative pitting resistance of commercial stainless steels is shown by their $FeCl_3$ critical pitting temperature: more resistant steels have higher critical pitting temperatures

TABLE 2

TYPICAL CHEMICAL ANALYSES (WT %) OF COMMERCIALLY AVAILABLE BLEACH PLANT ALLOYS

Alloy	Cr	Ni	Mn	C	N	Si	P	S	Mo	Fe
Austenitic stainless steels										
316L	16	13	1.6	0.03	—	0.1	0.021	0.012	2.8	Bal
317L	18	14	1.9	0.02	—	0.5	0.029	0.009	3.2	Bal
Eastern SS 317LM	18	14	1.2	0.02	0.07	0.7	0.029	0.008	4.0	Bal
Uddeholm 34L	17	15	1.7	0.03	—	0.6	0.033	0.010	4.3	Bal
Uddeholm 34LN	18	14	1.4	0.03	0.15	0.6	—	—	4.7	Bal
1.4439	18	14	1.5	0.03	0.13	0.5	—	—	4.3	Bal
Nitronic 50	21	14	6.2	0.05	0.22	0.3	0.022	0.011	2.2	Bal (1)
Carpenter 20 Cb-3	20	33	0.3	0.04	—	0.04	0.015	0.005	2.4	Bal (2)
Uddeholm 904L	20	25	1.8	0.02	—	0.04	0.025	0.004	4.2	Bal (3)
Sandvik 2RK65	20	25	1.8	0.02	—	0.05	0.020	0.005	4.5	Bal*
Jessop JS700	21	25	1.7	0.03	—	0.05	—	—	4.5	Bal (4)*
Haynes H20M	22	26	0.8	0.03	—	0.06	0.013	0.010	4.2	Bal (5)
VDM Cronifer 1925 LC	20	25	1.4	0.02	—	0.04	0.018	0.003	4.8	Bal (6)
AL-6X	20	24	1.7	0.02	—	0.03	0.021	0.001	6.6	Bal (7)
AL-6XN	20	24	1.7	0.02	0.2	0.3	0.21	0.001	6.0	Bal
Avesta 254 SMO	20	18	0.5	0.02	0.21	0.5	0.015	0.002	6.1	Bal (8)
VDM Cronifer 1925 HMO	21	25	1.3	0.02	0.14	0.3	0.018	0.010	5.9	Bal (9)
Ferritic stainless steels										
29-4	29	0	0.1	0.00	0.01	0.1	—	0.010	4.0	Bal
29-4-2	29	2	0.1	0.00	0.01	0.1	—	0.010	4.0	Bal
29-4C	29	—	—	0.03	0.3	0.1	—	0.010	4.0	Bal (10)
NYBY MONIT	25	4	0.3	0.02	0.01	0.2	—	—	4.0	Bal (11)
Crucible SC-1	26	2	0.3	0.03	0.03	0.3	—	—	3.0	Bal (12)
Duplex stainless steels										
2205	22	5.5	1.5	0.03	0.14	0.5	—	—	3.0	Bal
Ferralium 255	25	5	0.7	0.03	0.16	0.3	0.021	0.002	2.8	Bal (13)
Nickel-base alloys										
Carpenter 20 Mo-6	24	Bal	0.3	0.02	—	0.3	0.021	0.004	5.6	31 (14)
Incolloy 825	22	Bal	0.3	0.02	—	0.2	—	0.002	2.9	28.5 (15)
Hastelloy G	22	Bal	1.3	0.01	—	0.4	0.014	0.002	6.4	19.8 (16)
Hastelloy G-3	22	Bal	0.7	0.01	—	0.3	0.011	0.002	7.1	19.9 (17)
Inconel 625	22	Bal	0.1	0.01	—	0.2	0.010	0.007	9.5	3.9 (18)
Hastelloy C-276	16	Bal	0.5	0.01	—	0.1	0.011	0.002	5.6	5.6 (19)

(1) 0.18V
(2) 3.4 Cu, 0.83 (Cb + Ta)
(3) 1.5 Cu
(4) 0.2 Cb
(5) 0.36 Ti
(6) 1.6 Cu
(7) 0.05 A1, 0.07 Ce
(8) 0.7 Cu
(9) 1.7 Cu
(10) Ti = 6x(C + N)
(11) 0.3 Cu 0.6 Ti
(12) 0.5 Ti
(13) 1.6 Cu
(14) 3.3 Cu, 0.05 (Cb + Ta)
(15) 2.2 Cu, 0.06 A1, 0.88 Ti
(16) 2.18 (Cb + Ta), 2.07 Co, 0.79 W)
(17) 0.5 (Cb + TA), 3.2 Co, 0.8 W)
(18) 0.12 A1, 0.24 Ti, 3.61 (Cb + Ta)
(19) 1.13 Co, 0.2 V, 3.49 W
*Nominal composition

A critical temperature has been measured for each alloy below which no pitting will occur in $FeCl_3$.(2,3) The higher the temperature, the more resistant is the steel to pitting. Steels like Types 316L and 317L, for example, have comparatively poor pitting resistance, 904L-type alloys with about 4.5% Mo are somewhat better, and the 6% Mo steels like 254 SMO are remarkably resistant.

Based on these results, we might predict that the duplex steel, Ferralium 255, and the manganese-substituted austenitic, Nitronic 50, should outperform 317L in the bleach plant.

Generally, similar conclusions can be drawn from crevice corrosion tests in $FeCl_3$ *(Figures 3, 4)*.(4,5)

Note that critical temperatures for crevice corrosion are lower than those for pitting, indicating that crevice corrosion is more readily initiated. If equipment is not designed to avoid crevice corrosion, then this will be the mode of

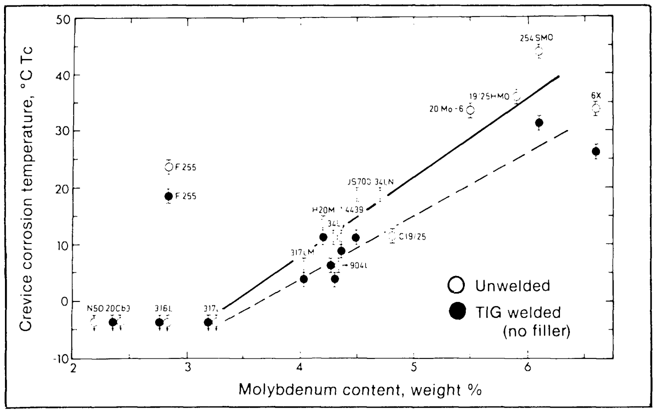

Figure 3 More resistant steels have higher crevice corrosion temperatures in the $FeC1_3$ test

TABLE 3

EFFECT OF ALLOY COMPONENTS ON CORROSION OF STAINLESS STEELS IN BLEACH PLANT APPLICATIONS

Element	Effect	Comments
Beneficial alloy additions		
Cr	Enhances resistance to initiation of pitting and crevice corrosion.	Steel must have more than 12% Cr to exhibit *stainless* property.
Ni	Enhances resistance to propagation of pitting and crevice corrosion.	Higher levels of Ni enable partly corroded component to remain functional; little or no Ni in ferritic grades.
Mo	Enhances resistance to initiation and propagation of pitting and crevice corrosion.	About three times as effective as Cr against pitting and crevice attack, but has solubility limit of 7% in stainless steels.
N	Enhances pitting resistance, particularly in combination with Mo.	Used in austenitic and duplex grades only; increases strength of the steel.
Detrimental residual elements		
C	More than 0.03% can cause sensitization, making heat-affected zones of welds less corrosion resistant.	Oxidized out of steel during refining, down to limit set by simultaneous, costly, Cr-oxidation.
P	Can cause hot-cracking, i.e., cracks formed in weld metal on cooling. Hot-cracks are sites for crevice corrosion, which looks like pitting attack.	Can only be controlled by use of low-P charge materials. Less than 0.015% P is respectable.
S	As with P, can cause hot-cracking.	Can be controlled to very low levels (less than 0.005%) S) by good steelmaking practice. Less than 0.015% S is respectable. Less than 0.005% S is excellent.

Si, Mn and Cu are added for steelmaking reasons or sulphuric acid resistance (Cu)

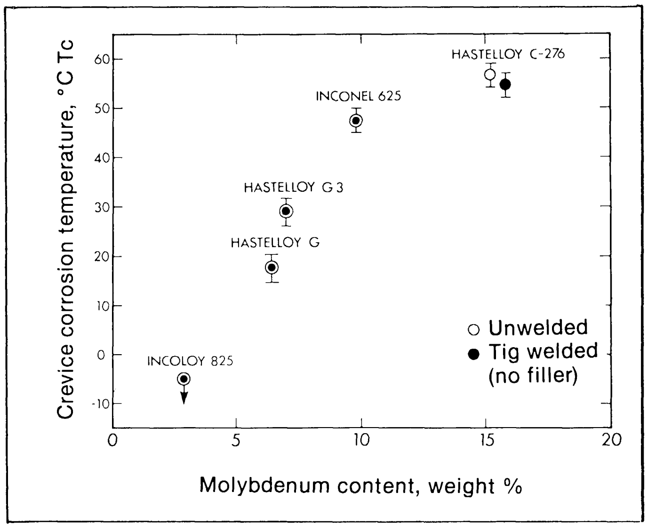

Figure 4 Ni-based alloys like Inconel 625 and Hastelloy C-276 have excellent crevice corrosion resistance (compare with *Figure 3*)

failure. An example of this form of attack is shown in *Figure 5,* a 317L corrugated deck from a C-stage washer which failed because of crevice corrosion.

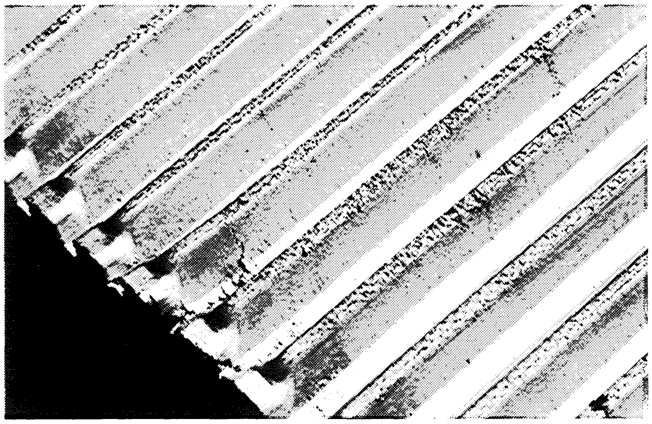

Figure 5 Failure of corrugated 317L washer-decking is commonly associated with crevice corrosion

Bleach Plant Environments

Environmental conditions in the chlorination-, chlorine dioxide-, and hypochlorite-stage washer exposure sites have been described elsewhere in detail.(1) Typical conditions are summarized in *Table 4.* In addition, typical redox potentials and washer corrosion potentials are listed in *Table 4* to show how oxidizing the conditions are in chlorination- and chlorine dioxide-stage washers.

TABLE 4

TYPICAL ENVIRONMENTAL CONDITIONS

Washing Stage

	Chlorination	Chlorine dioxide	Hypochlorite
Oxidant	30 ppm C1$_2$	30 ppm C10$_2$	30 ppm Na0C1
pH	2	4	9
T (°C)	45	65	40
(Cl$^-$) (ppm)	1 500	1 000	2 000
Electrochemical potentials, mV$_s$ce			
(a) Redox	1 000	500	
(b) Washer	750	500	

Field Testing

Field testing of candidate alloys has been done by a number of workers.(1,6-9) An early study measured pitting attack on a range of welded alloys in comparatively benign Nordic bleach plants.(6) Pitting and crevice attack were later tested in more closed (more corrosive) Canadian bleach plants. This program focused on a few representative alloys, looked at the choice of welding electrodes, and compared gaseous and liquid exposure in C-and D-stage washers, *Figures 6, 7.*(1)

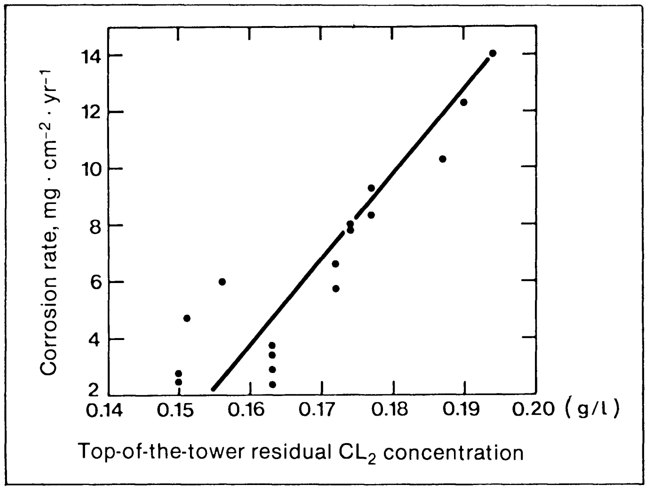

Figure 6 Residual chlorine increases corrosion rate measured by coupons in the C-stage washer

Two other exposure programs of note were carried out by the TAPPI corrosion and Materials Engineering Committee, in U.S. and Canadian mills; in the first(7) unwelded, and in the second(8,9) welded alloys were tested. This was probably the most ambitious alloy-assessment program ever undertaken, and the alloy range included almost all conceivable choices for bleach plant applications. Alloy development has been such an active field in recent years, however, that other promising steels (Ferralium 255, AL-6XN and 29-4C) have been commercialized since the comprehensive TAPPI exposure program.

Data from all these test rack programs can be interpreted as follows:

1 The premium bleach plant alloy of the future

It will probably be chosen from: Avesta 254 SMO, Hastelloy G-3, Sanicro 28 or Carpenter 20 Mo-6; VDM Cronifer 19/25 HMO, AL-6XN and 29-4C (thin section) were not tested, but they should also be competitive.

2 Attractive alloys close to the 317L cost level

Nitronic 50 and 1.4439 (317LMN) are promising alternatives to 317L. Ferralium 255 was not tested but should also be competitive.

3 Alloys with less competitive price or performance

Titanium, Hastelloy C-276, Inconel 625, 29-4-2, all performed exceptionally well, but are expensive; 904L and related alloys appear to perform slightly below the level required for a premium alloy.

Corrosion of Welds

Stainless steel washers occasionally fail because of weld-related corrosion, the principal causes of which are detailed in *Table 5* and outlined in reference (10).

Welding without filler metal creates a preferential attack site on austenitic stainless steel and should be avoided in washer construction. In choosing a suitable filler metal, it is important not to select one that gives a deposit less corrosion resistant than the base metal. For 316L the AWS standard filler(11) is adequate. For 317L and higher alloys, however, recent field and laboratory tests have shown that fillers with similar composition to base metal can have much lower pitting resistance.(1)

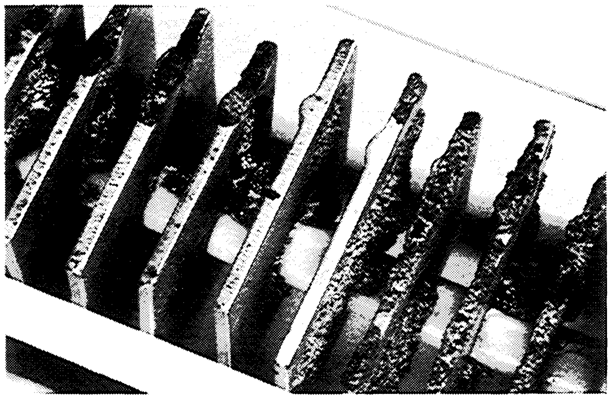

Figure 7 Stainless steel coupons 316L, 317L and 904L on a rack exposed below the incoming stock of the D-stage washer of mill D. Profuse ferrous oxide corrosion products cover the coupons

The best choice of weld metal for all 4.5% to 6% Mo austenitics is Inconel 112 or equivalent (e.g., Inconel 625 or Avesta P12). IN 112 is a good choice because:

☐It is metallurgically compatible with all austenitic stainless steels.

☐As-welded IN 112 is highly resistant to pitting and crevice corrosion.

☐There is no significant galvanic effect between IN 112 and austenitic stainless steels in bleach plant liquors.

TABLE 5

WHY AUSTENITIC STAINLESS STEEL WELDMENTS CORRODE

Attack site and mode	Reason for attack	When is it a problem?	How to avoid
Weld metal			
Pitting	1 Welding with no filler.	All Mo-containing austenitics*	Use appropriate filler.
	2. Welding with under-alloyed filler	3 to 6% Mo austenitics*	Use appropriate filler, e.g., 1N 112.
Crevice corrosion	3 Microfissures in weld metal create sites for crevice corrosion (looks like pitting).	In ferrite-free stainless steel weld metal, e.g., fillers commonly recommended for 904L*	Use 1N 112 electrode for 4% to 6% Mo austenitics.
	4 Lack of penetration.	In one-side or stitched butt-weld joints.	Ensure full penetration and do not use stitchwelds on process side.
	5 Entrapped welding flux.	Stick (SMA) welded joints.	Use electrode with good flux detachment.
Heat Affected Zone	1 Precipitation of carbides during welding.	When steel has 0.03% C.	Use steel with 0.03% C max.
Fusion Line	1 Unmixed zone formed at fusion line.	With high-alloy steels close to their corrosion limits.	Use lower heat input on final pass.
	2 Precipitation of carbides at fusion line.	In Nb- or Ti-stabilized steels.	At very rare problem Nb- and Ti-stabilized steels not common.

☐ If microfissures or hot-cracks occur in the weld metal, they will be preferentially attacked by crevice corrosion. (This is a particular problem for most ferrite-free stainless steel fillers).

Microfissuring or hot-cracking is a phenomenon associated with thermal stresses during welding. These stresses usually cause small cracks to form in the weld metal or heat-affected zone of a stainless steel or nickel-base alloy weldment.

Higher nickel-content alloys, which have a greater coefficent of thermal expansion, are more susceptible to hot cracking. Cracking is exacerbated by higher phosphorous (i.e., over 0.015% P) and sulphur (over 0.015% S) in the alloy, or contamination of the weld area. It is most commonly seen in the heat-affected zone in the previous pass of a multipass weld. Hot cracking rarely has a detrimental effect on the mechanical properties or structural integrity of a fabrication. It can be very detrimental to the corrosion properties of a weldment, however. Microfissures form crevice corrosion sites which are attacked with ease.

Recent laboratory tests have shown that other fillers can be used for 904L, such as Sanicro 27.31.4L CuR, Smitweld NiCro 31/27 and Thermanit 30/40 E. These fillers would be appropriate for microfissure-free shop construction; however, contaminated weldments are best repaired with IN 112 or equivalent filler.

Another common problem with stainless steel weldments — sensitization in the heat-affected-zone — is avoided in bleach plants by use of low-carbon steels (i.e., 0.03% C for austenitics). Similarly, fusion-line attack (sometimes called knifeline attack) due to precipitation of carbides at the fusion line in Nb- and Ti-stabilization steels is rarely seen, since these steels have been made obsolescent by new steelmaking technology.

Attack at the fusion-line is possible, however, when over-alloyed fillers like IN 112 are used with high heat-input welding. Such welding can create zones of melted base metal, unmixed with weld filler — called unmixed zones (UMZ) — at the fusion line and occasional instances of UMZ corrosion have been observed in the bleach plant. In practice this can be minimized by use of lower heat-input on the final weld passes.

Summary

Bleach plant closure has led to increased incidence of corrosion attack on 317L stainless steel, principally because of higher levels of residual oxidants in acidic process streams. Corrosion control under these new conditions can be attained by using properly welded and more resistant stainless steels. A number of cost-effective, premium-quality stainless steels are now available for corrosion-free use in bleach plant washers.

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