Corrosion of metallic and nonmetallic piping for bleach plant *D stage* filtrate

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Corrosion of metallic and nonmetallic piping for bleach plant *D stage* filtrate

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ABSTRACT

The condition of six inch diameter by two foot long spools of PVDF and PTFE lined steel, welded titanium, Alloy G, and type 317L steel after approximately 10 years exposure in a D stage filtrate line is reported. Weld and heat affected zone performance are described. Environmental conditions included pH 5.8 (NaOH added), temperatures 60 - 66 °C (140-150 °F), with low residuals and chlorides. This report is part of TAPPI Metals Subcommittee CA4924 Bleach Plant Pipe Test Program. Type 317L provided marginal service. Alloy G and titanium were reasonably resistant over this long exposure time. Improvements in butt welding practice are needed to improve the relative corrosion resistance of those welds.

INTRODUCTION

Corrosion resistant stainless steels or non-metallic materials are required for construction of chlorine dioxide bleach plant equipment. Service conditions have become progressively more demanding as increasing recirculation has increased temperatures and residual levels. Experience with materials for use in these bleaching processes has indicated a need to move to higher alloys to obtain the desired performance.

Early investigations of corrosion behavior in chlorine dioxide were made by Passinen and Ahlers (1). They found that ClO_2 alone could not corrode stainless steel, but that chloride also had to be present. They found that austenitic alloys with 4.3 % Mo were resistant to pitting up to 50 °C. The rate of attack in lower Mo alloys was increased with temperature and the content of chloride and ClO_2 in the filtrate. In the range from pH 3 to 5, corrosion rates were decreased only for stainless steel with at least 4.3 % Mo.

A review of Scandinavian experience (2) indicated that most corrosion problems occurred in the acid bleach stages in which chlorine or chlorine and ClO_2 were used. Alloys with the highest molybdenum contents were the most resistant. Few cases of corrosion of titanium or glass-fiber-reinforced polyester were reported.

Mueller (3) noted that ClO_2 caused the flow of cathodic depolarizing current proportional to its concentration and was essential to the corrosion. Mueller also pointed out the influence of chloride ion concentration on pitting, and thought that increase in the pH above 3 might prove effective in reducing corrosion. Cathodic protection and alternative materials such as titanium and fiberglass were proposed.

In a discussion of the environmental factors which cause corrosion, Garner (4) noted that recycling of filtrates can compound corrosion problems, for example recycling of D2 stage filtrate to the D1 stage washer showers. He recommended that recycling of the D1- or D2- stage filtrate to the C-stage washer should be avoided completely, since the more acidic C-stage filtrate (pH 2) regenerates ClO_2 from chlorite ions, making the shower water more corrosive to stainless steels. He described how rust deposits form on austenitic stainless steel when there is ClO_2 residual. These deposits are insoluble above pH 3.5, and their presence exacerbates corrosion. To minimize formation of these deposits, Garner ecommended that the pH be raised above 5.5 (target pH 7) with NaOH and the residual ClO_2 held to less than 25 ppm. He summarized a number of options for minimizing concentrations of residuals. It was concluded that 317L is not a satisfactory material for C- and D-stage washers.

In the TAPPI Bleach Plant Materials Study, candidate bleach plant alloys were exposed on test racks and exposed in duplicate in a number of bleach plant washers. In the first phase of this program, unwelded specimens were used; in the second phase, the coupons were welded. The results of the Phase I testing were summarized by Rushton et al. (5) and Tuthill (6). Phase II demonstrated the good resistance of austenitic materials with higher nickel contents (7). The Phase II data also indicated that the most

aggressive D stage conditions occurred in mills that did not add antichlor or NaOH between the tower and vat (8). Beetham (9), in a review of the TAPPI Phase II results, noted that mills which experienced corrosion of Hastelloy G had high levels of residuals in C-D/C stages. In D stages, corrosion for 317L and Hastelloy G was worse in mills with lower pH and higher chloride.

Garner (10) summarized results of tests of weldments in chlorination and chlorine-dioxide washers in bleach plants. Postweld cleaning by stainless steel wire brush led to pitting corrosion in austenitic and ferritic stainless steel weldments. Weld metal pitting in austenitic stainless steels with more than 3 % Mo could be avoided by the use of enriched filler metal. In the 317L samples welded with 317L filler, about half of the coupons showed evidence of preferential pitting of the weld metal, associated with weld metal microsegregation or dendritic coring. Weld metal pitting was independent of weld metal ferrite.

Garner (11-13), in studies of failures of welded joints in acid chloride solutions, found that pitting preferentially occurred in the Cr- and Mo-depleted austenitic dendrite centers, while the interdendritic ferrite remained.

Tuthill (14) presented data on the performance of weldments of austenitic stainless steels with 2-6 % Mo. For 9 alloys welded with matching composition filler metal there were multiple instances where the weld metal corroded when the base metal did not. For 5 alloys welded with higher Mo content filler metal, alloy 625, the weld metal was resistant. Tuthill and Garner (12) evaluated a number of bleach plant piping materials via exposure of pipe sections in a D2 washer seal tank. In high Mo alloy AL6XN, some unmixed zones of standard shop made butt welds suffered pitting. The HAZ of the longitudinal weld and the weld itself as well as the base metal were resistant. Hastelloy G30 experienced significant pitting attack some distance from the weld and HAZ. Alloy C22 and C276 and Inconel 625 experienced no localized corrosion.

Recently, Wensley et al. (15) measured high rates of general corrosion for nickel-base alloys (>50% Ni) in the hot, oxidizing, chloride-containing, near-neutral pH environment of the chlorine dioxide bleach washer. This behavior was attributed to possible transpassive dissolution of molybdenum oxide. Materials tested included C22, 625 and C276 in addition to high nickel and stainless steel alloys. High nickel (30-50% Ni) and stainless steels (<30% Ni) did not experience thinning but did suffer crevice corrosion attack.

As an alternative to stainless steels, non-metallic materials such as PTFE and PVDF have gained increasing acceptance due to their excellent chemical resistance and successful long-term performance (16,17).

The results of a long-term corrosion test of pipe spools in a D stage filtrate line are described here. Six pipe spools each 2 feet in length and 6 inch diameter were removed from the bleach plant at the mill in June 1989. They had been installed in a horizontal run, and were not isolated from each other. These were offered to the TAPPI bleach plant pipe test program, CA 4924. The pipe string had been installed about 1979 and had been in service about 10 years. One of the pipe spools was lined with polyvinylidene fluoride (PVDF) and another with polytetrafluoroethylene (PTFE). Two metallic pipe sections were constructed of 317L stainless steel, one of Alloy G and one titanium. Each section of unlined pipe contained a longitudinal weld and two butt welds where stub ends were attached. Markings indicated the pipe and stub ends were furnished by Alaskan Copper Co. Documentation was not available on welding. However, it is reasonable to assume that the longitudinal welds were made by Alaskan Copper using a boom welder which placed an autogenous weld on the inside and a filler bead on the outside. Butt welds appear to have been made in the field via TIG welding from the outside with filler.

The mill where the spools were installed employs a CEDED bleaching sequence. During the time of exposure of the pipe spools, the bleach plant was operated using hardwood. The pipe spools were located in the line from the D_1 stage filtrate tank to the E_1 stage showers. A schematic of the process flows is included in Figure 1. The pH of the filtrate is adjusted to 6 by the addition of NaOH. The level of residual is in the range of <0.01 g/L ClO_2. Temperature ranged from 60 - 66 °C (140 - 150 °F). The level of chlorides was low. Based on historical data, conditions during the test are assumed to be pH 5.8, 66 °C (150 °F), 800 mg/L Cl^- and 10-20 mg/L residual ClO_2. Short periods of residual as high as 25 mg/L ClO_2 may occur about twice per week. There was no significant vibration in the line. The line is shut down semiannually for approximately two days, but is not drained or flushed.

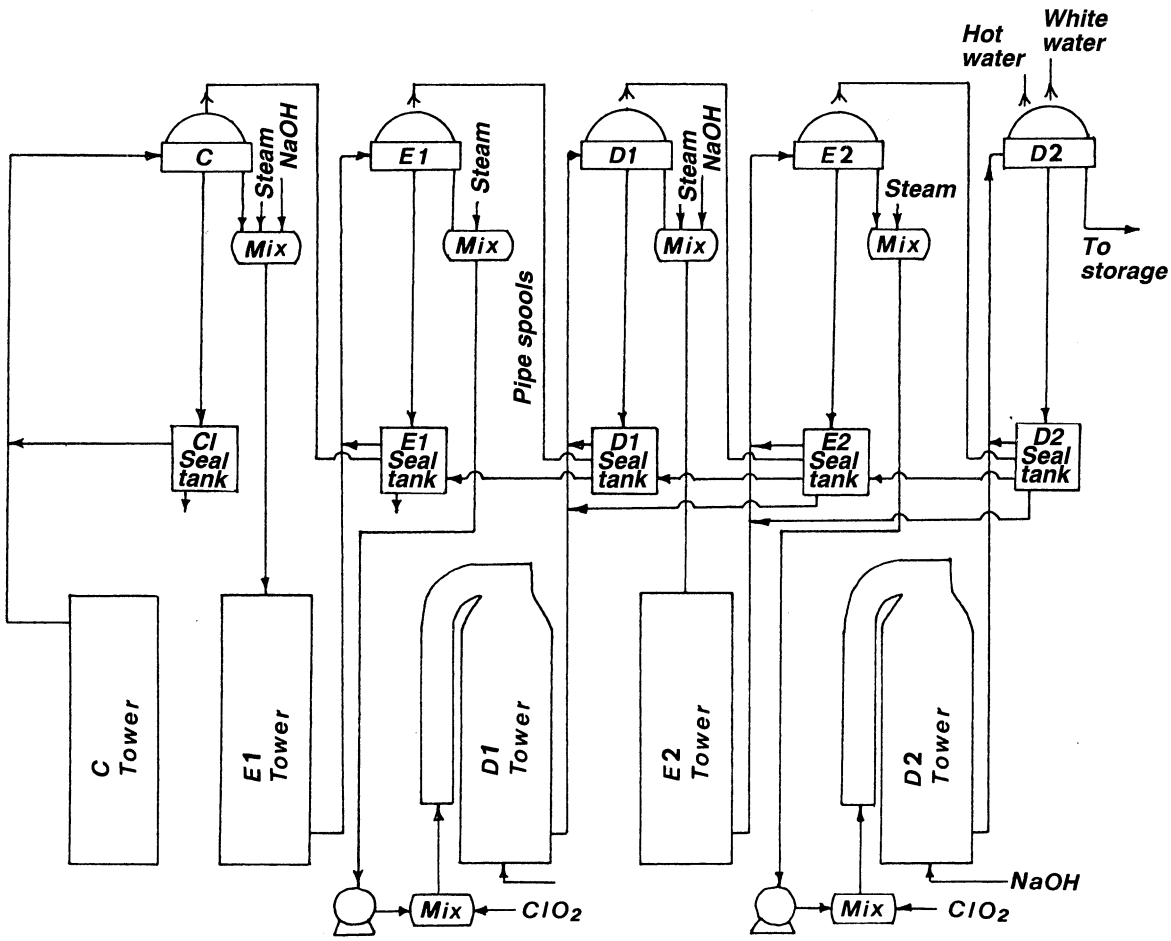

Fig. 1. Schematic diagram of the bleach plant showing the location of the pipe spools.

EXPERIMENTAL

Visual Observation

The pipe spools were cut in half lengthwise and photographed. One half of each length was cleaned by low pressure blasting with glass beads.

Compositional Analysis

The alloys were identified by X-ray fluorescence using a Texas Nuclear Alloy Analyzer. The composition of the weld metal was determined separately by chemical analysis. Matching composition filler welds had been used. The chemical analyses for the weld metal are summarized in Table 1. The concentrations of C and S were not measured.

TABLE 1
COMPOSITION OF WELD

	317L	317L	Titanium	Alloy G
Mn	1.35	1.34	0.01	1.38
P	0.003	0.003	-	0.009
Si	0.77	0.66	-	0.43
Cu	0.32	0.32	-	1.50
Ni	13.82	13.85	-	38.50
Cr	18.95	18.96	<0.01	20.69
Mo	3.51	3.54	<0.01	6.27
V	0.039	0.038	0.09	0.036
Ti	0.015	0.022	>99.	0.037
Al	-	-	<0.01	0.15
Nb	0.025	0.025	-	2.09
W	-	-	-	0.64
Co	-	-	-	2.11

Analysis of Scale

Scale from the inside of the 317L stainless steel spool was analyzed by X-ray dispersive spectroscopy to obtain an elemental analysis.

Metallographic Examination

Cross-sections were taken from one of the butt welds in each section and from the longitudinal weld. The objective was to look for the unmixed zone and any associated pitting.

Critical Pitting Temperature

Pitting resistance of various alloys can be ranked by means of the critical pitting temperature test. The critical pitting temperature was determined in 10% $FeCl_3$ (pH 1) on duplicate samples of uncorroded base metal. These were polished to 120 grit with SiC paper. Temperature was increased by 2.5 °C each working day until pitting was observed. The test appears to be appropriate because it is likely that $FeCl_3$ itself may be formed in bleach plant corrosion deposits when ferrous salts are oxidized by ClO_2 ·

Testing of the Non-Metallics

Deterioration of mechanical properties of the PTFE and PVDF was evaluated by tensile testing. The test specimens were 2.54 cm x 15 cm (1 in. x 6 in.) strips cut from the liner in the longitudinal direction. The span distance was 10 cm (4 in.) and the crosshead speed was 5 cm/min.

RESULTS AND DISCUSSION

317L

There were black, adherent corrosion deposits on the inside of the 317L pipe spools, as shown in Figure 2. The scale was dense, quite adherent and similar to the scale usually observed on stainless steel specimens exposed in D-stage. The scale contained primarily Fe, Cr and Mo, constituents of the alloy, with some Si, Cl and Ca. Garner (18) noted that in D-stage exposures, ferrous oxide deposits are insoluble above a pH of about 3.5, which is consistent with their presence here at pH 5.8. However, deposits were thought to be less likely above pH 5.5 since ClO_2 becomes less corrosive toward steels and is transformed over time to chlorite, ClO_2^-. The present results suggest that the deposits may form at pH as high as 5.8, or that they are formed during periods of lower pH, but not removed at pH 5.8.

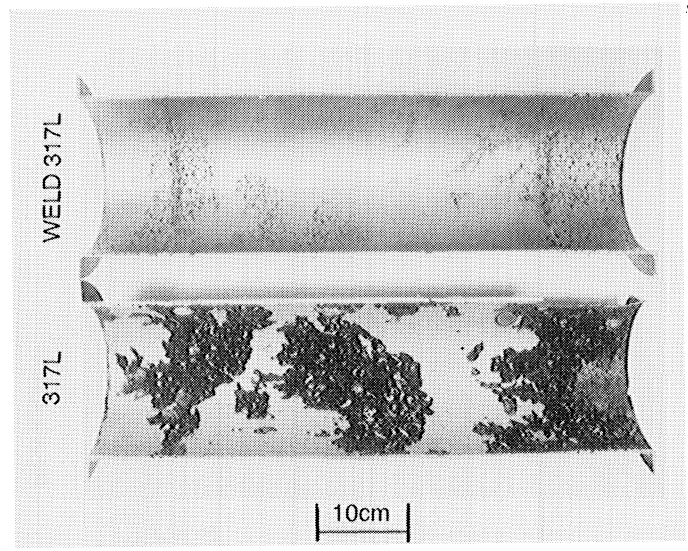

Fig. 2. Black adherent corrosion deposits had formed over pits inside the 317L stainless steel spools.

When the scale was removed, many pits were observed, as shown in Figure 3. On the outside, areas of through wall pit penetration were marked by dark patches of corrosion product. There was pitting on the outside surface of the pipe beneath the scale. Acidic corrosion products including $FeCl_3$ are believed responsible for spreading this underscale corrosion. Figure 3 illustrates how pitting was more prevalent near to welds but was not restricted to welds. Extensive pitting was found in the base metal, well away from the welds. Pitting at the welds may be related to the structure there such as Cr- and Mo-depleted austenitic dendrite centers. The pipe flange face suffered crevice corrosion, pitting and some stress corrosion cracking from the crevice sites, Figure 4. High stresses would be expected due to flaring of the flange material.

The longitudinal welds in the 317L material were well made and did not appear to be the site of preferred pitting. The butt welds showed lack of penetration and there was an apparent pit at the root of an incompletely fused butt weld, Figure 5.

Titanium

Some attack of the titanium sections was observed adjacent to a poorly made butt weld, Figure 6, where there was evidence of improper cut off practice having been employed. One of the stub ends which had been attached to the roughly cut end of the pipe spool had a site of localized corrosion. There was a lot of fine weld spatter adjacent to the roughly cut end. Some rough spots on the inside

of the pipe appeared to be due to scraping, perhaps during manufacture. There was no evidence of corrosion at these scraped areas. Generally, the titanium was in excellent condition.

The longitudinal weld in the titanium was well made, but the butt weld was of poor quality. Penetration was incomplete and a fine crack was observed to run from the location of lack of penetration into the material as shown in Figure 7; this may have been an incompletely fused section of the original joint.

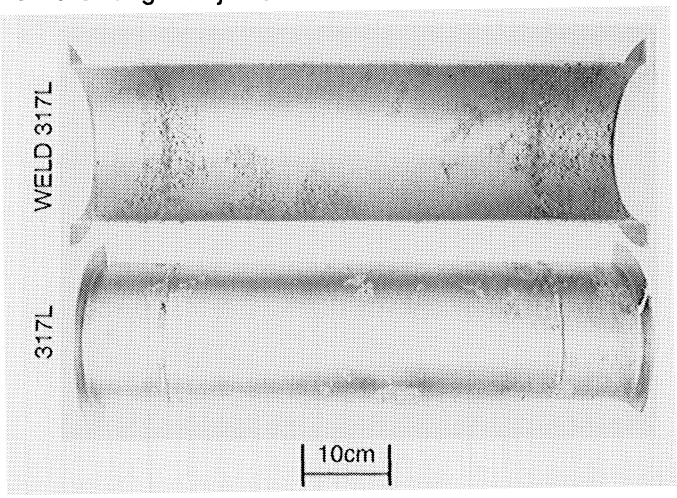

Fig. 3. Pitting of the 317L was more prevalent near the butt welds.

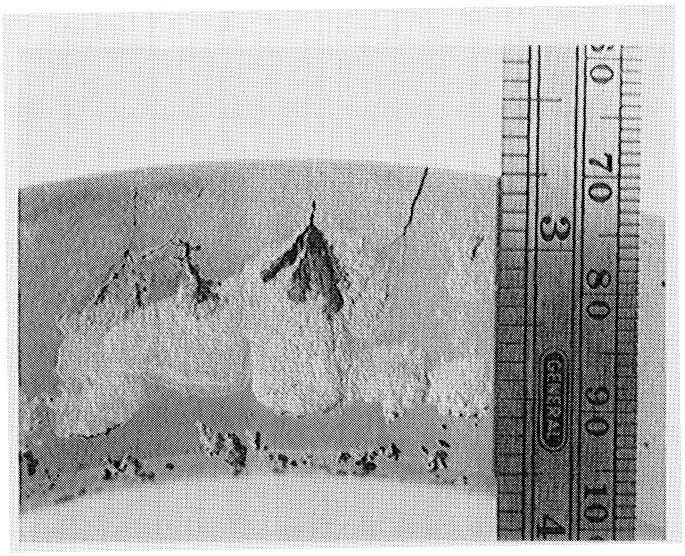

Fig. 4. The 317L flange face suffered crevice corrosion and cracking.

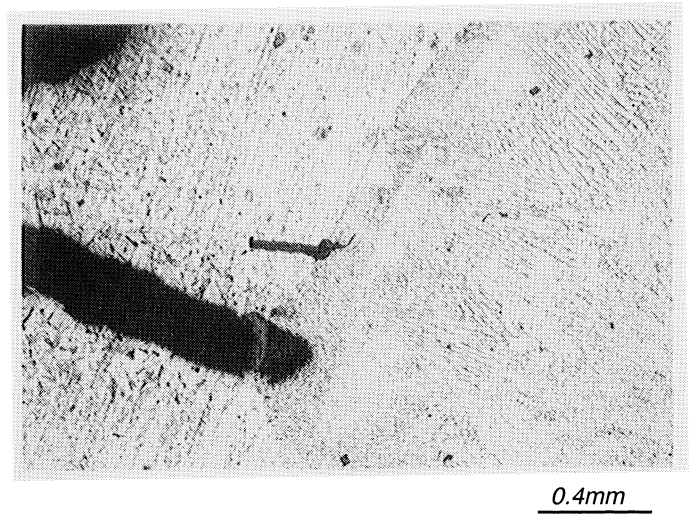

Fig. 5. There was incomplete fusion at butt welds in the 317L.

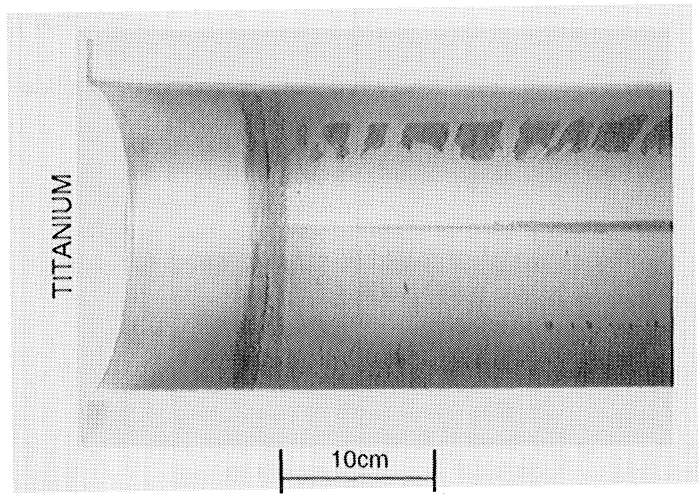

Fig. 6. Some pitting was observed on the edge of a stub end adjacent to the poorly made butt weld of this titanium spool.

Hardness measurements made across the butt weld showed the weld to be 349 Hv, the heat affected zone 469 Hv and the bulk material 173 Hv. The increase of hardness at the weld is indicative of uptake of nitrogen and oxygen.

Alloy G

Some minor crevice corrosion was observed on the Alloy G flange face, illustrated in Figure 8. The inside surface of the pipe was lightly etched. There was distinct but superficial pitting in the HAZ of butt welds and to a lesser extent at the longitudinal welds. The zone of pitting extended for approximately 5 mm on each side of the joint,

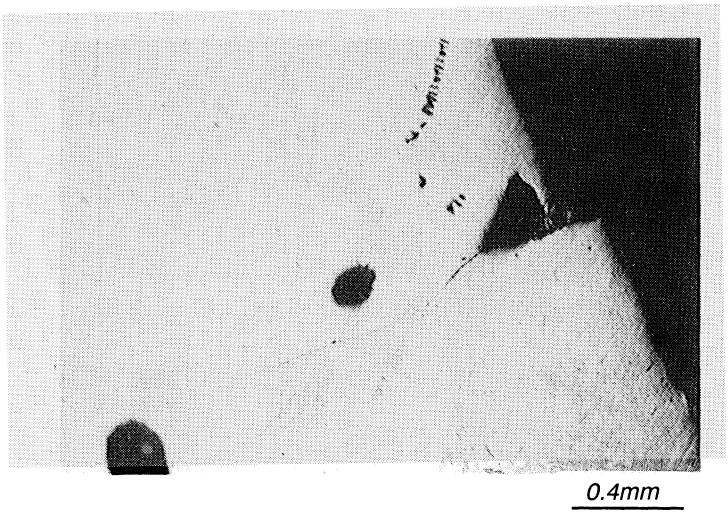

Fig. 7. At titanium butt welds showing incomplete fusion, a crack was observed.

Comparison of Longitudinal and Butt Welds

Comparison of the longitudinal and butt weld quality shows that there is a basic need to upgrade the quality of butt welds.

	Longitudinal	Butt
317L	Uniform structure No evidence of localized corrosion	Incomplete fusion Possible pit emanating from root pass. Pitting more prevalent near welds.
Alloy G	Uniform structure	Incomplete fusion Pit emanating from root pass. Superficial pitting HAZ butt weld; less near longitudinal weld.
Ti	Small grain size Uniform structure	Incomplete fusion Possible crack from root pass.

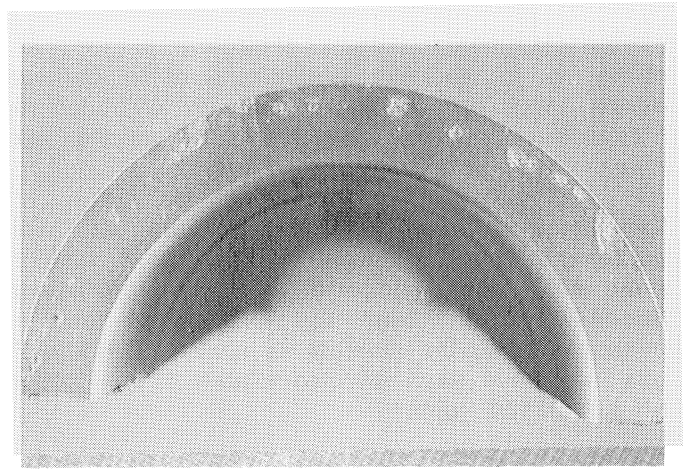

Fig. 8. Minor crevice corrosion on the flange face of the Alloy G spool.

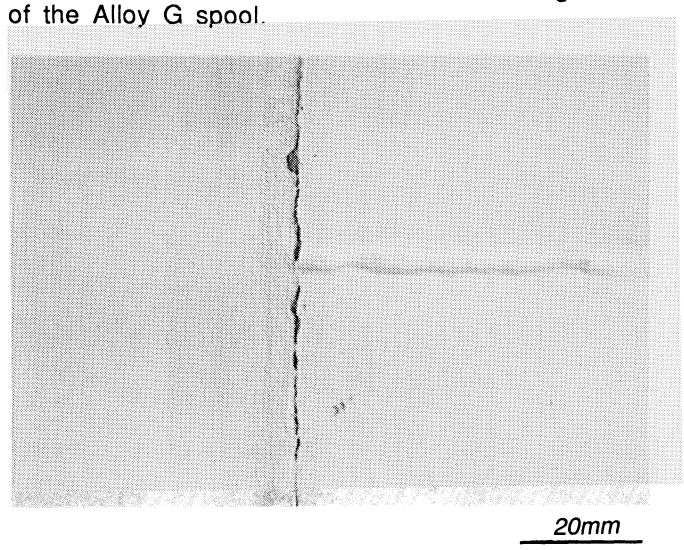

Fig. 9. Shallow pitting in the HAZ adjacent to the butt weld in Alloy G.

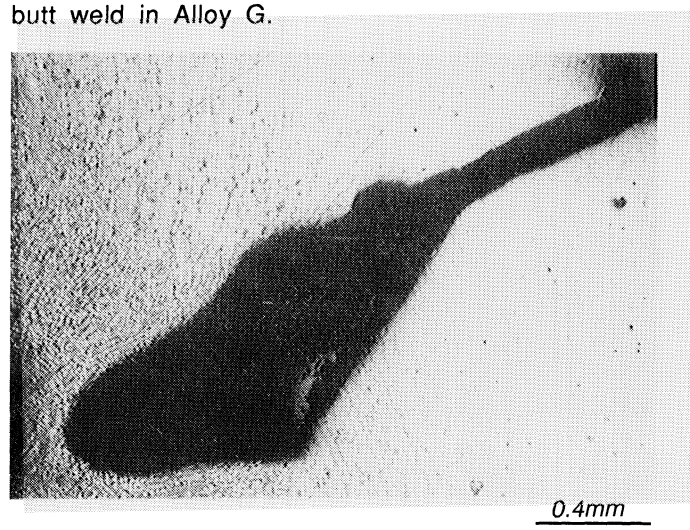

Fig. 10. Apparently a pit formed at the bottom of the incompletely fused Alloy G butt weld.

PTFE and PVDF

The PTFE and PVDF liners showed no evidence of blistering which would be caused by permeation. There was no evidence of check cracking where the liner is flared out to cover the flange and where the stress is at its maximum. The inside surfaces of the liners were smooth and clean, showing no evidence of deterioration or attack. The excellent performance of the PVDF confirms previously published accounts of its resistance (16,17). The excellent resistance of the PTFE was also as expected.

Mechanical testing results are summarized in Table 2. The value of tensile strength for the PTFE was below the 3000 psi minimum spec according to ASTM F423, but was not tested identically to the specification. The elongation was better than the minimum of 250% required. The PVDF was better than the minimums required by ASTM F491 (5000 psi and 8 % elongation).

TABLE 2
TENSILE TEST RESULTS FOR NON-METALLICS

	Tensile Strength, psi	% Elong.
PTFE	2430	390
PVDF	7920	23

Ferric Chloride Testing

Results of ferric chloride testing are summarized in Table 3.

TABLE 3
CRITICAL PITTING TEMPERATURES

Alloy	T_p, °C
317L	25
Alloy G	67.5
Ti	>80

Laboratory test results in 10% $FeCl_3$ correlated with critical pitting temperatures for this ClO_2 service at 66 °C. From the ferric chloride test, it would be expected that the 317L would pit badly, that the Hastelloy would pit slightly, and the titanium would resist pitting, as was observed.

CONCLUSIONS

Results of the 10 year exposure indicate that:

1. Type 317L stainless steel piping would provide marginal to poor service for D-stage filtrate service.

2. Titanium and Alloy G were resistant to corrosion and would be good candidate materials for these conditions in D stage filtrate even if fabrication practice is poor.

3. Butt welds were poor quality. Improved techniques for welding are required to improve their corrosion resistance relative to the base material and longitudinal welds.

4. PTFE and PVDF lined pipe were shown to be resistant to this D-stage environment and good candidates for piping.

REFERENCES

1. K. Passinen and P.E. Ahlers, Corrosion of Acid Proof Steel in ClO_2 Solution, Paperi ja Puu, 48(9): 549-552, 554-560 (1966).

2. S. Henrikson, Corrosion in Bleach Plant Filter Washers - Extent, Causes and Countermeasures, Report 1982:2, Swedish Corrosion Institute, Stockholm (1983).

3. W.A. Mueller, Corrosion by Kraft Liquors and Bleaching Solutions, Trend No.14: 9-13 (1969).

4. A. Garner, pp. 95-105, Proceedings 1984 TAPPI Maintenance Conf., Tappi, Atlanta (1984).

5. J.D. Rushton, A.H. Tuthill, J.J. Geissler, R.H. Heasley, and L.L. Edwards, Corrosion Resistance of Alloys to Bleach Plant Environment, Tappi Press Report, Atlanta (1980).

6. A.H. Tuthill, Progress Report: Corrosion Test Results - Phase I Bleach Plant C, D and H Stages, Corrosion Resistance of Alloys to Bleach Plant Environment, Tappi Press Report, Atlanta (1980).

7. A.H. Tuthill, Mat.Perf. 24(9): 43-49 (1985).

8. A.H. Tuthill, pp.171-177, Proceedings 1987 TAPPI Engineering Conference, Tappi, Atlanta (1987).

9. M.P. Beetham, pp. 665-681, Proceedings 1986 TAPPI Engineering Conf., Tappi, Atlanta (1986).

10. A. Garner, pp.45-53, Proceedings 1985 TAPPI Engineering Conference, Tappi, Atlanta (1985).

11. A. Garner, PulpPap.Ind.Corr.Prob. 2: 87-93 (1977).

12. A.H. Tuthill and A. Garner, PulpPap.Ind.Corr.Prob. 6B: 273-285 (1989).

13. A.Garner, Corrosion 35(3): 108-114 (1979).

14. A.H. Tuthill, pp.683-689, Proceedings TAPPI 1986 Engineering Conference, Tappi, Atlanta (1986).

15. D.A. Wensley, D.C. Reid and H. Dykstra, to be presented at Corrosion90, NACE, Houston (1990).

16. A.A. Dukert, Tappi 58(4): 152-154 (1975).

17. T.J. Holmes, M. Sikich and M.H. Coulombe, PulpPap.Can. 90(6): T212-T215 (1989).

18. A. Garner, Pulp Pap.Can. 82(12): 414-425 (1981).

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