Evaluation of bleach plant piping materials

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Tests on fabricated pipes in the bleach plant show that further work is needed to establish an inside root pass procedure which avoids the formation of unmixed zones. Possible options include automatic gas tungsten arc welding, a greater root gap, or consumable inserts.

This test program was initiated by and is being conducted under the supervision of the Metal Subcommittee of TAPPI's Corrosion and Engineering Materials Committee. Its purpose is to evaluate candidate alloys in the form of production welded pipe in environments that earlier test programs had shown were among the most aggressive that are likely to be encountered in chlorine- and chlorine dioxide-stage bleaching.

Previous laboratory and field test programs (*1–6*) on welded coupons have established the credentials of candidate alloys, and guidelines for users have been well documented (*7*). However, this program is the first to test fabricated pipes in the bleach plant.

Experimental procedures

Longitudinal welding

Welding details, alloy selection, and test spool design have been reported (*8*). The pipe was formed on press brakes and rollers, and the longitudinal welds were made on a boom welder. As is common practice, the root pass was fused autogenously from the inside using a gas tungsten arc (TIG) welding head with argon shielding. The weld was completed from the outside using a second trailing TIG head and filler metal on the same boom. Twenty-foot-long (6.1 m) sections of pipe were seam welded in this manner.

Also following common practice, the stainless steel pipe with autogenous root pass was solution annealed, but the nickel-base alloy pipe was not. Nickel-base alloys do not require solution annealing after welding. All the straight lengths of welded pipe, except the C-276 clad, were pickled to remove heat tint, scale, and other surface contamination.

Circumferential welding

The straight pipe thus produced was then sent to the pipe fabricating shop and fabricated to the pipe drawings using close-to-typical 316L welding procedures. All butt welds were made from the outside of the pipe on a rotating table by manual TIG welding with hand-fed filler metal. For AL-6XN the filler was Alloy 625; matching fillers were used for nickel-base alloys. In general, the pipes were bevelled to give 1/32-in. (0.8 mm) land and positioned to give approximately 1/16-in. (1.6 mm) gap. Before welding, the inside of the pipes were filled with argon to avoid oxidation and to eliminate the need for post-weld cleanup. With this setup, experienced welders were able to achieve full penetration welds with few crevices and little excessive buildup on the inside diameter. Occasional lack of penetration was corrected with a wash pass from the inside to give crevice-free weldments.

Note that the common practice used by these welders for 316L butt welds differed only in that there would have been no gap for the inside diameter root pass and no filler.

For this program, lengths of 10-in.-diameter (250 mm) longitudinally welded pipe were cut circumferentially in half after the final pickling operation. These two halves were then butt-welded together and the face rings fillet welded on. The two halves were positioned so that, when the pipe was installed in a horizontal position, the longitudinal weld would be at the top of the pipe in one half of each length and at the bottom of the pipe in the other half.

Pipe assembly

The completed sections were assembled with gaskets and insulators around the bolts, checked with an ohmmeter to ensure electrical isolation between different materials, pressure tested, boxed, and shipped to the mill for installation. At the mill, the assembled test length was unboxed, lifted into place, and bolted into the FRP line, which had been cut and flanged to receive the assembly.

Mill exposure details

The 16-ft-long (4.9 m) assembled pipe was located in a horizontal run of piping in the D-stage filtrate line as

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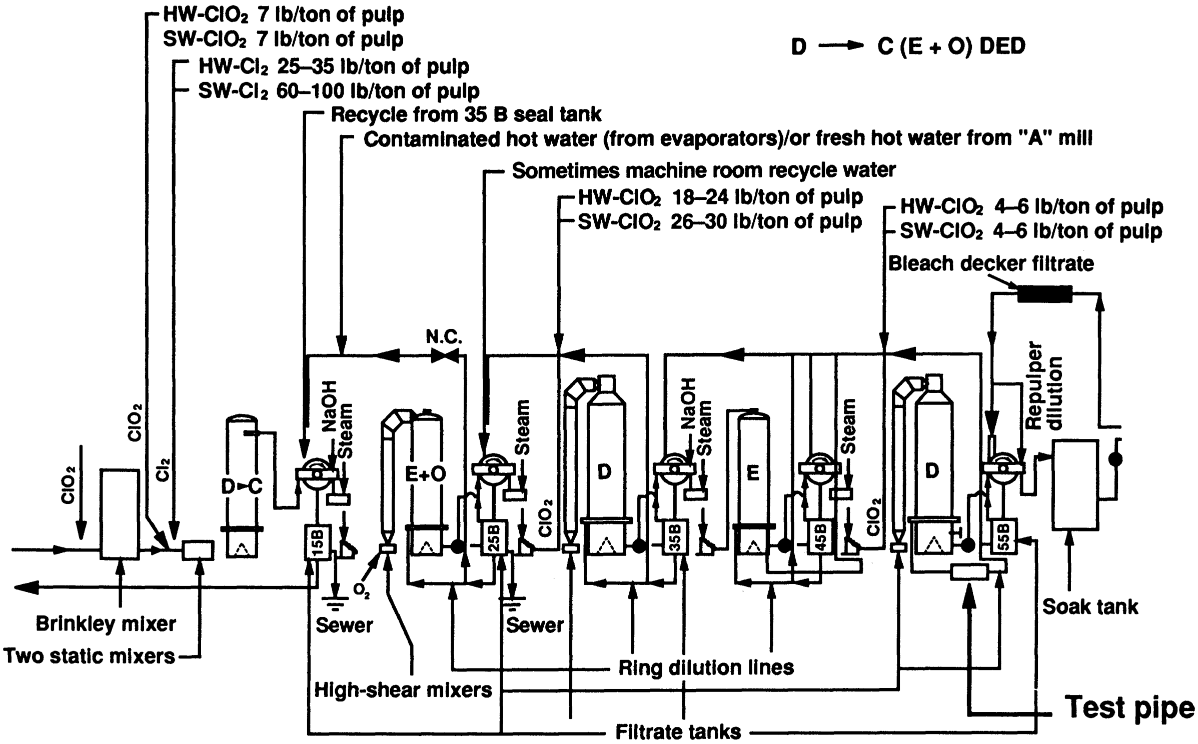
1. Bleach plant flow diagram showing position of test pipe



I. Daily exposure conditions during the alternating hardwood and softwood runs

		Period 1	*Period 2*
Hardwood	pH	3.8-4.2	3.0-3.5
	Residual ClO_2, mg/L	0.03-0.05	0.02-0.04
	Time, months	6.5	7
Softwood	pH	4.0-4.7	3.8-4.1
	Residual ClO_2, mg/L	0.04-0.6	0.03-0.05
	Time, months	8.5	5

indicated in **Fig. 1.** It was installed and put into service on April 17, 1987, and removed on June 5, 1988. Visual inspection from the ends indicated that the surfaces were clean and free of pulp, except in the vicinity of localized corrosion sites near the welds of some—but not all—sections. Mill practice was to flush and drain lines on shutdown. No other cleaning was done on the test assembly.

The mill operated on hardwood for 181 days and on softwood for 200 days. In this period, a total of 33 shutdown days occurred, comprising one one-day, four two-day, one 10-day, and one 14-day periods. The pipe was left full during one- and two-day shutdowns, flushed and drained during longer ones.

Exposure conditions

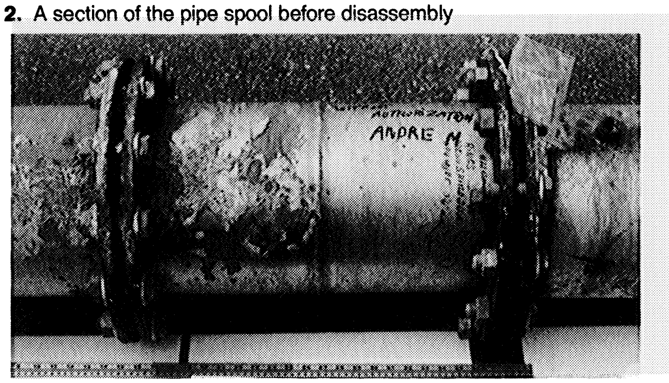
The range of the daily maximum residual chlorine dioxide levels and the range of the daily minimum pH (tower bottom) for the alternating hardwood and softwood runs are shown in **Table I.**

During the exposure period, bleach plant operators decided to adjust to somewhat lower pH with H_2SO_4, first on hardwood and later on softwood.

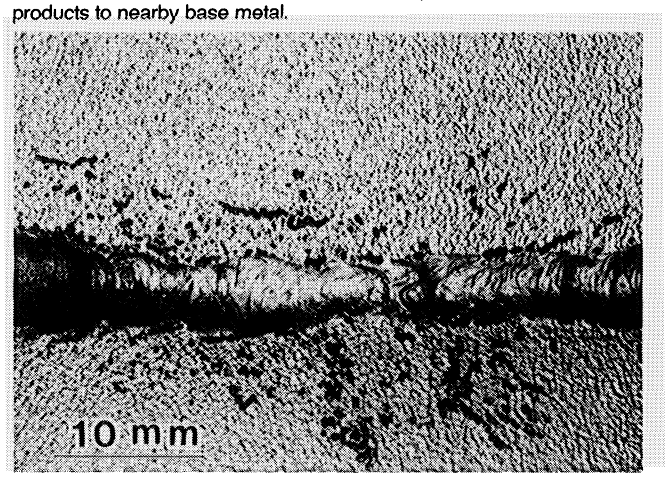
The seal tank filtrate temperature, as seen by the test pipe, was 155-165°F (68-74°C), and the chloride level was about 5600 ppm Cl^-, unusually high by industry standards. A previous test-rack program showed the environment to be over twice as corrosive as an average D-stage filtrate (*4*).

At the laboratory, the assembly was photographed (**Fig. 2**), unbolted, flanges removed, and each length was cut in half longitudinally for visual inspection. One half of each length was cleaned by sand blasting. Samples were cut for metallography and for immersion testing in ferric chloride solution. Critical pitting temperatures were determined on the upper face of duplicate samples of uncorroded base metal in 10% $FeCl_3$ at a constant temperature, which was increased by 2.5°C each working day.

2. A section of the pipe spool before disassembly



3. A cleaned circumferential weld of AL-6XN showing pitting. Pits initiated in unmixed zones of weld metal and spread under the corrosion products to nearby base metal.



Results

Observations from exposed pipe sections are summarized for each alloy as follows.

AL-6XN

The base metal and longitudinal (solution annealed) welds were unattacked. However, the circumferential butt-weld was pitted over about 60% of its length to depths up to 0.197 in. (5 mm) (**Figs. 3 and 4**). Metallography revealed that the manual TIG welding procedure had produced weld metal with substantial unmixed zones, i.e., zones in which remelted base metal was not mixed with the alloy 625 filler metal (**Fig. 5**).

These observations were confirmed using energy dispersive X-ray analysis on a scanning electron microscope. Weld metal unmixed zones contained about 50% iron, as did the base metal; light-etching weld metal contained about 5% iron, i.e., as alloy 625 filler. In 6%-molybdenum austenitic stainless steels, such autogenous areas are well known to have pitting resistance much inferior to parent base-metal (*9, 10*). Dendrite coring or microsegregation leaves areas of microstructure depleted in molybdenum and chromium, areas through which pits can more easily propagate (Fig. 5).

As was found in previous field tests, the corrosion deposits themselves led to additional under-deposit pitting adjacent to the welds (**Figs.** 3, 4, **6, and 7**). As will be discussed later, these ferric deposits create crevices under which active corrosion can occur readily at these temperatures.

Hastelloy alloy G-30

After superficial brown deposit was removed, substantial pitting was evident to a depth of 0.075 in. (1.91 mm) (Fig. 7). About 100 individual pits were visible to the naked eye on cleaned base metal, weld metal, heat-affected zones, and occasionally on a scratch, without any discernible pattern.

Inconel alloy 625, Hastelloy alloy C-22, and Hastelloy alloy C-276 clad

These alloys suffered no localized corrosion anywhere on the weldments. Thickness measurements showed that general corrosion rates were insignificant.

Ferric chloride testing

Base metal critical pitting temperatures (CPT) in 10% $FeCl_3$ are shown in **Table II**. Alloys with a CPT over 70°C also resisted pitting in this 70°C chlorine dioxide bleach plant test. Note that $FeCl_3$ itself can be formed in bleach plant corrosion deposits when ferrous salts are oxidized by ClO_2. For this reason, $FeCl_3$ may be a particularly appropriate laboratory test medium: it gives conservative predictions of temperature limits for corrosion-free operation in chlorine dioxide service.

Discussion

In planning this work, we assumed that the procedures used to weld 304L and 316L pipe could be used, with minor alterations, to weld 6%-molybdenum stainless steels. However, we found that, even with fully qualified and experienced stainless steel pipe welders, these procedures can result in unsatisfactory welds for 6%-molybdenum stainless steels. Although unmixed zone corrosion had been noted in previous coupon test programs (*10*), its importance had been difficult to gauge without more careful replication of pipe weld procedures. This program was carried out to address this kind of shortcoming. It has shown that further work is needed to establish an inside root pass procedure which avoids the formation of unmixed zones. Possible options include automatic TIG, a greater root gap, or consumable inserts.

Summary

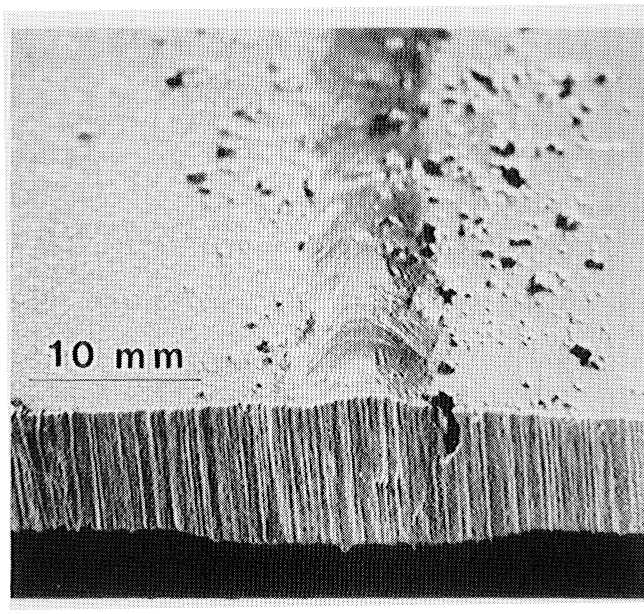
After 14 months exposure in this particularly corrosive ClO_2-stage environment, we found that:

1. For the 6%-molybdenum stainless steel AL-6XN, no pitting occurred in the base metal or longitudinal weld. However, circumferential weld procedures involving manual TIG and hand-fed filler metal produced unmixed zones which pitted readily.
2. The nickel-base Hastelloy alloy G-30 suffered significant pitting attack, independent of welding.
3. Nickel-base Inconel Alloy 625, Hastelloy Alloy C-22, and Hastelloy Alloy C-276 clad were uncorroded.
4. Laboratory test results in 10% $FeCl_3$ correlated with critical pitting temperatures for this chlorine dioxide service.
5. Unmixed zone corrosion had not been highlighted by previous field tests of 6%-molybdenum stainless steel welded coupons because coupon preparation did not replicate root pass welding.□

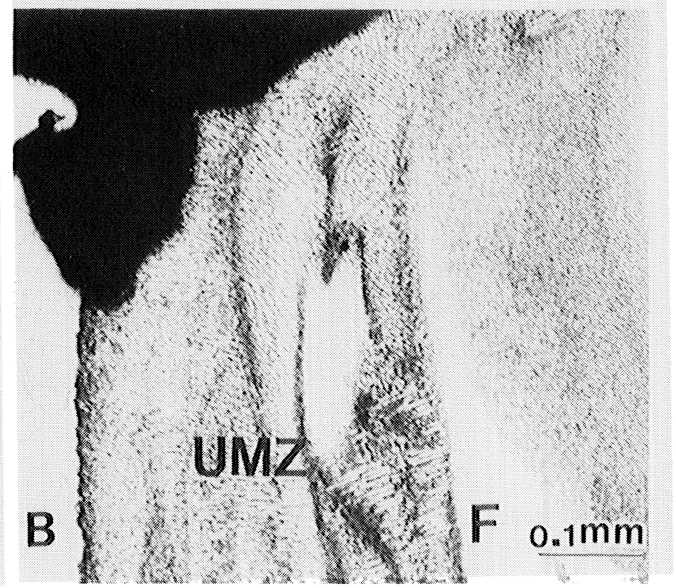
II. Critical pitting temperatures in 10% $FeCl_3$

Base metal	*Temperature, °C*
AL-6XN	72.5
G-30	60
625	90
C-22	>100
C-276	>100

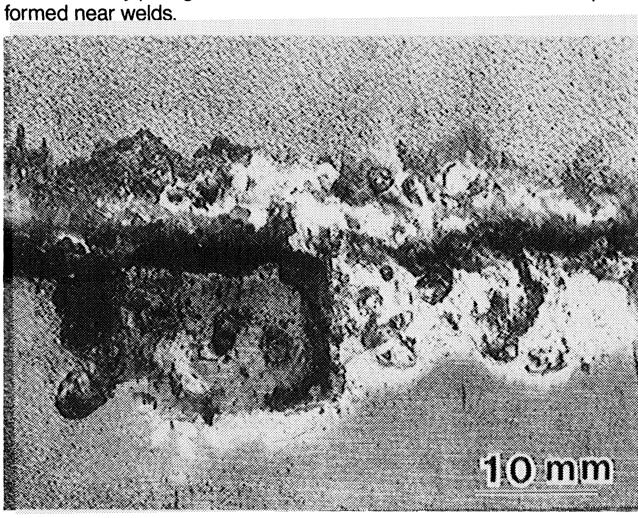
4. Cleaned and sectioned circumferential weld in AL-6XN. Deep pitting followed weld metal unmixed zone.



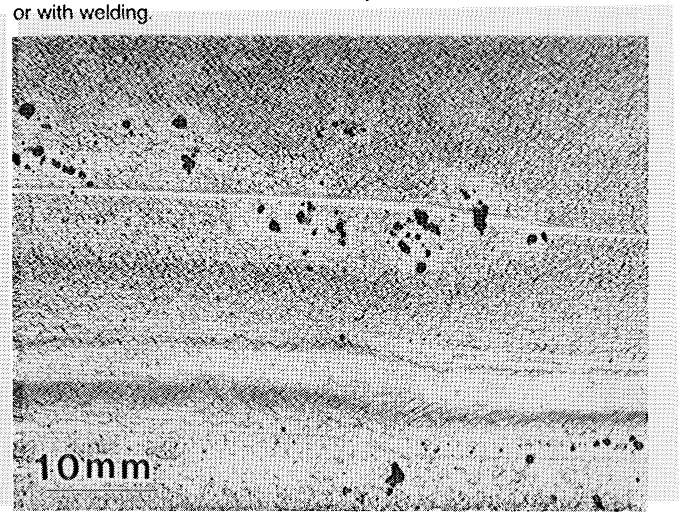
5. Metallographic section of pit in the circumferential weld in AL-6XN. Dark etching unmixed zones (UMZ) are susceptible to pitting. Base metal (B) and light-etching undiluted Alloy 625 filler metal (F) resisted pitting in this aggressive bleach plant environment (Etch = 40 mL HCl + 10 mL H_2O + 10 mL HNO_3).



6. Secondary pitting and crevice corrosion occurs under ferric deposits formed near welds.



7. Pits in G-30 sometimes, but not always, are associated with a scratch or with welding.



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