CORROSION BEHAVIOUR OF STAINLESS STEEL NICKEL BASE ALLOY AND TITANIUM WELDMENTS IN CHLORINATION AND CHLORINE DIOXIDE BLEACHING

ARTHUR H. TUTHILL,
RICHARD E. AVERY
AND ANDREW GARNER

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Arthur H. Tuthill*
Tuthill Associates, Inc.
Blacksburg, VA
U.S.A.

Richard E. Avery*
Avery Consulting Associates, Inc.
Londonderry, N.H.
U.S.A.

Andrew Garner
Director of the Vancouver Laboratory
The Pulp & Paper Research Institute of Canada
Vancouver, B.C.
Canada

*Consultants to the Nickel Development Institute

ABSTRACT

An overview is presented of a decade-long series of programs which exposed welded coupon and full diameter pipe in chlorination and chlorine dioxide bleaching equipment. Findings have guided procedures for the fabrication and post fabrication cleanup of over 75 6% Mo stainless steel washers. Findings are also applicable to 6% Mo, nickel base alloy, clad nickel base alloy, titanium and plastic-lined piping for bleach plants. Guidelines for procurement and fabrication of piping materials are included. Applicability to mixer-to-tower, tower-to-vat and filtrate piping sections is reported.

KEYWORDS

CORROSION, CORROSION RESISTANCE, CORROSION TESTS, STAINLESS STEEL, BLEACH PLANTS, WASHERS, CHLORINE, CHLORIDES, PITTING, CREVICE CORROSION, TEMPERATURE, OXIDANTS, CONCENTRATION, WELDING, ALLOY, COUPONS, ELECTRODES, MOLYBDENUM, NICKEL, TITANIUM, PH, WELDED JOINTS, NICKEL BASE, CLAD, FILTRATE PIPES, WELD PROCEDURE, POST WELD CLEANING, PICKLING, GRINDING, GLASS BEAD BLASTING.

BACKGROUND

Increasing corrosion of type 317L and 904L stainless steel (SS) washers in chlorination (C) and chlorine dioxide (D) bleaching during the 1970's prompted several extensive coupon exposure programs in the United States, Canada and the Nordic countries (1-7). These programs produced similar results and led to the widespread use of 6% Mo SS washers welded with Alloy 625 or other higher Mo austenitic filler metal.

The initial U.S. programs, organized by the Metals Subcommittee of TAPPI's Corrosion and Materials Engineering Committee, led to a further series of full diameter alloy pipe test programs (8-11). The pipe programs were targeted to determine the suitability of the 6% Mo SS and nickel base alloy piping as produced by experienced SS pipe producers and fabricators. Bleach plant piping service includes tower-to-vat and filtrate piping where conditions are similar to those of the washer, as well as mixer-to-tower piping where residual oxidizers are greater and vibration is a concern.

The results of the basic welded coupon exposure program are presented first (5,6) followed by the results of three full diameter pipe tests (8-11) and discussion of post fabrication cleanup. Procurement specifications and welding procedure guidelines follow. A final section summarizes the results of the piping evaluation programs for the three different sections of C and D stage piping.

WELDED TEST COUPONS

Welded coupons of 24 different alloys were exposed in 19 different bleach plant washers most of which were C and D stage (5,6). Details of these coupons and their exposures are given in Appendix I. The significant findings are summarized as follows:

(a) **Austenitic stainless steels.** 6% Mo SS generally performed well compared with steels with lesser amounts of Mo. The tests also demonstrated the advantage of using enriched filler metal to avoid preferential weld metal pitting (Table 1, Figure 1). These tests and laboratory pitting tests in $FeCl_3$ (4) confirmed that welds without filler suffer preferential attack because of weld metal microsegregation (12,13). Localized areas of autogenous weld metal have lower chromium and molybdenum contents and are more readily attacked. Based on these results it has become standard practice to weld austenitic SS containing 4 to 6% Mo with enriched fillers such as Alloy 625, C-276, or C-22. More than 75 6% Mo SS bleach plant washers have been fabricated since 1982 with these enriched filler metals.

(b) **Nickel base alloys and Titanium.** These alloys generally did well. The least resistant in this group, Alloy G and G-3 showed similar resistance to the 6% Mo SS. Weld metal microsegregation in nickel base alloys does not lower weld metal pitting resistance to any significant degree, although two cases of weld metal pitting on the G Alloys were noted (Table 1). For the highly resistant nickel base alloys and the two titanium alloys matching composition filler metal gave weld metal resistance equal to base metals in all 19 bleach plant environments. Subsequent work by Wensley et al (14) has shown that in the special case where caustic is added after chlorine dioxide bleaching prior to washing, nickel-based alloys can be subject to general corrosion, apparently related to their high molybdenum content.

PIPING TESTS

The Metals Subcommittee undertook three additional test programs designed to evaluate high alloy welded piping as produced in qualified pipe fabrication shops (8-11). One program included titanium and plastic-lined piping. The objective was to determine the suitability and behaviour of longitudinal and circumferential welds in more highly alloyed SS and nickel base alloy piping in C- and D-stage bleaching and to develop guidelines for procurement and welding of these materials.

Details of the fabrication procedures for pipes, and of their exposures are outlined in Appendix II. Figure 2 shows typical pipe sections after exposure.

Chlorination Stage Filtrate Line Results

11-month exposure. The relatively mild filtrate in this C-stage line (11) was easily handled by all alloys tested, namely AL-6XN, 20 Mo-6, 254 SMO, Polarit 778, Alloy G-30, Alloy C-22, Alloy C-276 Clad, and Alloy 625.

The filtrate was less corrosive probably because at this mill chlorination bleaching is done relatively hot at 140°F (60°C). Under these conditions bleaching is fully completed in the tower allowing little of the corrosive chlorine into the washer and filtrate. (Mill exposure conditions are given in Appendix 2).

This exposure was notable in that it demonstrated some fabrication problems to avoid. Some of the 6% Mo SS pipes were initially post-weld heat-treated at too low a temperature. They were successfully re-heat-treated at the required 2150°F (1175°C). Some superficial fabrication-related heat-affected zone cracks were found in some of the 6% Mo SS and attributed to surface contamination with copper during shop fabrication. None of these cracks corroded in subsequent service. Weld metal dilutions appeared normal and no pitting of the critical unheat-treated circumferential-welds was observed in this mild exposure.

Chlorine Dioxide Stage Filtrate Lines Results

(a) **14-month exposure.** This relatively aggressive filtrate (Appendix II) was survived by Alloy 625, Alloy C-22 and C-276 clad. However Alloy G-30 and the 6% Mo SS were close to their limit of resistance (8,9). G-30 showed some pitting independent of welds (Figure 3). The 6% Mo SS pitted along the circumferential welds in undiluted weld metal (Figure 4 and 5). Because the circumferential welds are not post-weld heat-treated, the procedure for making the root pass from outside the pipe must minimize unmixed zones or areas with lack of mixing. The subsequent section on weld procedures addresses this problem.

Parallel laboratory testing confirmed that $FeCl_3$ is particularly appropriate for predicting corrosion performance in the bleach plant.

(b) **10-year exposure.** A second somewhat less aggressive but much longer exposure in another mill (Appendix II) yielded some interesting comparisons (10). In this case, 317L was badly pitted but still serviceable, Alloy G survived, and the titanium pipe was uncorroded despite poor welding. Pipes lined with PTFE and PVDF also survived this decade-long exposure without failure and with only minor strength loss.

POST WELD CLEANING

(a) **Stainless Steels.** It has long been known that post weld cleaning of stainless steel weldments is necessary for the best performance of any grade of stainless steel, but there is very little good data in the literature to substantiate "what everyone knows". Differences of opinion have arisen on the cost and usefulness of pickling and other post weld cleaning in the past. Some recent work done by VDM-KRUPP provides definite information on post weld cleaning (15). Figure 6 shows that nitric-hydrofluoric acid pickling provides a modest improvement in the corrosion resistance of surfaces that are untreated, light-ground, or glass bead blasted after welding. The data in Figure 6 provides a good yardstick for those that need to know just how much improvement in corrosion resistance nitric-hydrofluoric pickling provides.

Heat tint is frequently removed mechanically. The authors' experience indicates that light grinding with clean aluminum oxide abrasive discs or flapper wheels, and glass bead blasting are effective methods of removing heat tint. However, even these lightly cleaned surfaces are improved by nitric-HF pickling as Figure 6 shows.

Wire brushing with stainless steel wire brushes is also a common method of cleanup after welding. In the coupon tests outlined in a previous section, corrosion initiated on several stainless steel coupons in the area which had been power wire brushed with a clean stainless wire brush, Figure 7 (16). The attack may have been due to inadequate heat-tint removal, the use of low alloy stainless steel brushes like Type 410 or 304, or due to redeposition of abraded metal and oxides. Pickling would be expected to remove any such metal transferred by stainless steel wire brushing and remove other foreign surface deposits. Pickling may be done by immersion, spray or pickle paste.

The authors have found that heavy grinding with grinding wheels degrades the corrosion resistance to a greater depth than can be restored by pickling. Blasting with steel grit and steel shot also degrade the corrosion resistance beyond the ability of pickling to fully restore. Grinding wheels and grit blasting are useful for carbon steel fabrications but not for stainless steel. Grinding with grinding wheels should be limited to removal of weld reinforcement where removal is required for other reasons.

(b) **Nickel Base Alloys.** The question of whether heat tint is as detrimental to the corrosion resistance of the inherently more corrosion resistant nickel base alloys was investigated by Silence and Flashe (17). While not conclusive, this work indicated heat tint removal did not appear to give the same incremental increase in corrosion resistance that heat tint removal does for stainless steels. This may be due to the greater inherent corrosion resistance of the base metal or to other factors yet to be determined.

PROCUREMENT OF HIGH ALLOY PIPE AND FITTINGS

Bleach plant piping is normally purchased to ASTM A778 (as welded) in the larger diameters and to ASTM A312 (annealed) in the smaller diameters which are widely stocked in warehouses. One of the 6% Mo alloys can be purchased to ASTM A312, however, others must be purchased to different specifications. These are shown in Table 2 and the comparable specifications for fittings in Table 3.

Users would be well advised to review with 6% Mo alloy supplier and the pipe producer, 1) The need for higher Mo content filler metal addition as required under B804 but not under the other four specifications; 2) The solution annealing temperature that the alloy producer recommends be reached in order to keep second phases in solution; 3) The ability of the pipe producer to pickle or otherwise remove oxide scale developed during welding in a satisfactory manner; 4) The extent of weld repair that is to be permitted; and 5) Post weld repair annealing practice.

The pipe test program showed post-weld anneal of 2150°F (1175°C) minimum is needed for 6% Mo SS.

The ASTM specifications for nickel base alloy and titanium pipe are listed in Table 4 and for fittings in Table 3. The specifications for the nickel base alloys instruct the user to consult the alloy supplier for the proper solution annealing temperature which is usually even higher than for the 6% Mo alloys.

There are no ASTM specifications for nickel base alloys clad pipe. These must be developed with the clad pipe and fitting supplier. Critical points are changes in the usual shop procedure for making the longitudinal welds and for post weld cleanup. These changes were readily accomplished in producing the clad pipe test spools, but should be reviewed with the pipe producer.

Circumferential Or Butt Welds In Pipe

ASTM offers no specifications for the butt welds needed to fabricate piping systems. Users must develop their own specifications covering butt welds. These are general guidelines:

1. Full penetration butt welds.
2. Smooth ID with no more than 1/16" root bead crown.
3. Meet general requirements of ASME B31.3 for Chemical Plant and Petroleum Refinery Piping.
4. Joint preparation per Figure 8.
5. Prefer shop welds. Minimize or prohibit field welds. Most alloy producers have developed excellent guidelines for making quality butt welds in 6% Mo pipe stimulated, in part, by the problem with insufficient mixing in the root bead of 6% Mo pipe discussed earlier. One investigation has been published (18) and is summarized in the next paragraph.

This was an investigation of a number of GTAW root pass variables to determine the effect on weld metal mixing and weld metal corrosion resistance to ASTM G-48A and G-48B ($FeCl_3$) was undertaken. The root pass variables included:

- filler metals, Alloys 625 and C-276 with some reference welds made without filler metal addition
- consumable inserts of Alloys 625 and C-276
- no inserts, hand fed filler metal with
  - key-hole technique
  - non key-hole technique
- heat input variation
  - high heat input - low current, low travel speed
  - low heat input - high current, high travel speed

The investigation found that by using a broad range of welding techniques and over-matched filler metals, excellent welds were produced having corrosion resistance equivalent to the base metal. There was no attack related to unmixed zones in the weld with the G-48A test. Unmixed zones cannot be totally eliminated but the size and/or width can be minimized by filler selection and proper technique.

The following guidelines can be useful in developing GTAW root pass welds with corrosion resistance closely approaching that of the base metal.

1. Specify Alloy 625, C-276 or C-22 filler metal and/or consumable insert ring.
2. Limit misalignment to 1/16" mismatch.
3. Select from the following welding procedures listed in order of preference:
   a) Orbital welding with ring insert
   b) GTAW welding in 1G position, pipe rotated, consumable insert ring
   c) GTAW welding in 1G position, pipe rotated using hand fed filler metal with a gap to permit generous filler metal addition.

Circumferential Or Butt Welds In Nickel Base Alloys And Titanium

1. Specify matching composition filler metal.
2. Limit misalignment to 1/16" mismatch
3. Select from the following welding procedures listed in order of preference:
   a) Orbital welding with ring insert
   b) GTAW welding in 1G position, pipe rotated, consumable insert ring
   c) GTAW welding in 1G position, pipe rotated using hand fed filler metal with a gap to permit generous filler metal addition.
4. In welding titanium use a dry box to the extent possible. For welds made outside of a dry box, use a trailing shield in a draft free enclosure to prevent oxygen and nitrogen pickup from the atmosphere.

Circumferential Or Butt Welds In Clad Nickel Base Alloy Materials

Excellent quality butt welds were made in clad C-276 pipe spools in these test programs with little modification in standard fabricating practice. However, users need to develop in consultation with clad alloy and pipe suppliers specifications for butt welds in clad pipe.

BLEACH PLANT PIPING EVALUATION SUMMARY

Table 5 summarizes the likely candidate piping alloys for the three sections of bleach plant piping, based on the data developed in these programs. The mixer-to-tower service is the most severe from the standpoint of both corrosion and vibration. Alloy C-276 and related alloys have met good success after chlorination though not after chlorine dioxide injection (19) where titanium has been the material of choice. When titanium is used, vibration must be properly controlled, and contact with alkaline peroxide or dry chlorine avoided. The clad nickel base alloy is shown first for the chlorination mixer-to-tower environment as the heavier section of clad piping is an advantage where vibration is concerned.

The data herein reported was developed in the vat or filtrate piping and is not directly applicable to the more corrosive mixer to tower environment. 6% Mo SS appeared to be the leading candidate for these sections.

Solid or clad nickel base alloy piping appear to be excellent candidate piping materials for the tower-to-vat section. 6 months coupon exposure tests are suggested before use in chlorine dioxide service in those mills adding caustic to neutralize the tower effluent, where significant general corrosion rates can be experienced (14).

6% Mo and nickel base alloys appear to be excellent candidates for filtrate piping.

CONCLUSIONS

1. 6% Mo stainless steels welded with Alloy 625 or higher Mo content filler metal are excellent candidates for many bleach plant applications. Over 75 washers have been placed in service since 1982 with few reports of problems.
2. Welding 6% Mo stainless steels with Alloys 625, C-276 or C-22 compensates for the molybdenum segregation that occurs in the cast weld metal and can maintain base plate corrosion resistance.
3. Excellent quality longitudinal and butt welds can readily be made in nickel base alloy and clad nickel base alloy piping with only minor adjustments in standard practices employed by experienced stainless steel pipe producers.
4. 6% Mo alloy piping, properly fabricated to maintain root bead corrosion resistance, as outlined herein, is a leading candidate for 4 of the 6 C and D stage piping environments.
5. Solid or clad nickel base alloy piping is a good candidate for the mixer-to-tower environment after chlorine bleaching, though not after chlorine dioxide, where titanium can be used with success.

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APPENDIX I

Welded Coupon Tests

Experimental procedures and environments. Welded coupons of 24 stainless steels and nickel base plus two titanium alloys were exposed in 19 different bleach plant environments. The coupons were 2 x 3 in. (50x75mm) with the weld usually across the 2 in. dimension (1). Base metal compositions are given in Table A1 and filler metal compositions in Table A2. Producing companies of the alloys used in the coupon exposure program are shown in Table A3. Corrosivity, as estimated from total weight loss of all specimens exposed, varied by two orders of magnitude from the least to the most corrosive environment. Except for the most resistant alloys this wide variation in corrosivity resulted in exposure to three general types of environments 1) mild environments where the base metal, weld metal (WM) and heat affected zone (HAZ) were resistant; 2) moderately aggressive environments where the base metal was resistant but WM or HAZ or both pitted; 3) severe environments where base metal, WM and HAZ all were pitted. Titanium, Alloys C-276 and 625 were so resistant that there were no environments where WM and HAZ were pitted. While it is not possible to identify the way in which 26 alloys performed in 19 different environments in a single table, there were multiple examples of each alloy within each of the three classes of environments as illustrated in Table A4.

The actual environments, shown in Table A5, define the range of temperature, pH, chlorides and residual oxidizers such as chlorine in the C&D/C stage, ClO_2 in D stage and hypochlorite in H stage.

The welds were made by each producer following standard procedures and using producer selected filler metal. Nickel base Alloys 625, C-276, G-3 and G-30, the ferritic alloys and the two titanium alloys were welded with matching composition filler metal. The austenitic stainless steels were welded with either a matching composition filler metal or Alloy 625 as the producer supplying the specimens elected. The one duplex alloy, Uddeholm 44LN, was welded with a 2.6% higher Ni and 1.3% higher Mo content filler metal as compared to the base metal.

APPENDIX II

Pipe Tests

Pipe fabrication (Chlorination and 14-month chlorine dioxide filtrate tests). Typical procedures for pipe production and fabrication were replicated as closely as possible.

Longitudinal welds: Welding details for the longitudinal weld, which were described in an earlier report (8) are summarized briefly below. Sheet material of around 3/16" (5 mm) thickness was sheared to size and roll-formed into short (12" to 24") lengths of 10", 12" and 24" pipe. The eight alloys used in the C-stage exposure, are shown, along with their compositions, in Table A6. Edges were cleaned by power wire brushing with Type 304 wires, tacked with a tungsten spot welding gun, welded on a boom welder, and reshaped for concentricity (Table A7). As is common practice for production of large diameter stainless steel welded pipe of over 1/8" (3 mm) wall thickness, the root pass was fused autogenously from the inside using a gas tungsten arc welding (GTAW) head with argon gas shielding. The weld was completed from the outside using a second trailing GTAW head on the same boom and adding filler metal. Alloy 625 filler material was used for the 6% Mo SS and matching composition filler metal was used for the nickel base alloys.

The C-276 clad pipe was welded differently. The inside (alloy side) weld was made with a GTAW head in the down hand position using C-276 filler metal. The pipe was then rotated 180 degrees and the weld completed from the outside using a GTAW head and adding filler metal. Two passes of the welding boom were required for the C-276 clad weld as compared to one pass for the other alloys.

Following the reshaping operation, the stainless steel lengths were solution annealed as described below. Nickel-base alloys do not require solution annealing after welding and were not solution annealed.

All 6% Mo alloy pipe sections, except AL-6XN, which had been welded and solution annealed in a separate shop, were placed in a RA 333 bar rack and introduced into a gas fired furnace that had been heated to about 2200°F (1200°C). Separate thermocouples in the spool pieces at the front and back of the furnace were used to insure the work itself reached the desired 2150°F (1175°C) temperature. The work was held after reaching 2150°F (1175°C) as read on the thermocouples for 24 minutes before the door was opened and the charge quenched in water. Time from door opening to quench was 23 seconds.

The 254 SMO and Polarit 778 specimens used in the chlorination stage test had been previously solution annealed at a lower temperature which had allowed undesirable second phases to precipitate at the grain boundaries. The 20Mo-6 specimen was remade from new material. For both the re-heat-treated and new material, the microstructure after the 2150°F (1175°C) solution anneal was clean and free of deleterious grain boundary precipitates indicative of normal good quality 6% Mo material. After heat treatment, the pipe sections were resized for concentricity and pickled to remove heat treating scale.

Circumferential butt welds: The straight pipe lengths thus produced were cut circumferentially in half on a band saw and rotated 180° before circumferential welding as previously described (8). Pipe edges were bevelled with a clean abrasive disc grinding wheel to give a 1/32" (0.8 mm) land and positioned to give an approximately 1/16" (1.6 mm) gap, somewhat wider than the 1/32" (0.8 mm) gap commonly used on 304L and 316L pipe. Tacks were made by GTAW to hold the alignment.

In an attempt to partially imitate field welding practice, all circumferential (butt) welds were made from the outside of the pipe on a rotating table by manual GTAW with hand fed filler metal. For the steels, the filler metal was Alloy 625; for the nickel base alloys matching composition filler metal was used. When the root pass has a rough profile, the welder is trained to reach inside and smooth the rough spot with a wash pass. Experienced welders routinely make quality circumferential welds in stainless steel pipe in pipe fabricating shops in this manner.

Pipe-assembly: Lengths of 12" (300 mm) diameter pipe thus produced were assembled into longer lengths with gaskets and insulators around the bolts, checked with an ohmmeter to insure electrical isolation between adjacent sections, pressure tested, boxed and shipped to the mill for installation. At the mill the assembled test pipe spools were unboxed, and the lengths were lifted and bolted into place. In the C-stage test the mill found it necessary to remove one section from one of the two lengths as the space available could not accommodate a full 8 foot section. This length was not exposed. It was later determined that the unexposed length was Cronifer 1925 hMo.

Mill exposure conditions:

Chlorination stage filtrate line: Eight pipe sections made from 6% Mo austenitic stainless steels (AL-6XN, 20Mo-6, 254 SMO and Polarit 778) and nickel base alloys (Alloys G-30, C-22, 625 and C-276 clad) were tested for about 11 months in horizontal runs of C-stage filtrate piping. Mill practice is to flush and drain lines on shutdown. No other cleaning was done on the piping. After removal the test sections were boxed and shipped for disassembly and evaluation.

This mill operates a C_D-E_O-H-D_1-E_2-D_2 bleach sequence. Chlorine dioxide (ClO_2) substitution in the chlorination (C_D) stage was between 5-10% during the period of exposure. Tower and vat conditions were pH 0.8-1.0, temperature 60°C, residual chlorine - trace, and chlorides 3000 ppm. Shower water is taken from E_2, with pH 8.5 to 9 and temperature 70°C. Filtrate conditions are not as severe as in the vat but approximate conditions in many C_D stage bleach plants: the pipe was exposed to filtrate at pH about 1.8-2.0 and temperature 62°C.

Chlorine dioxide stage filtrate lines:

(a) **14-month exposure:** The 16-ft-long (4.9m) assembly of pipe spools was located in a horizontal run of piping in the D-stage filtrate line. 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 1 one-day, 4 two-day, 1 ten-day, and 1 fourteen-day periods. The pipe was left full during one- and two-day shutdowns, flushed and drained during longer ones.

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 A8.

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 (68-75°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). The pH and temperature of the shower water approximated that of the vat. No caustic or SO_2 additions to the tower effluent are made at this mill.

At the laboratory, the assembly was photographed (Figure 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 (Table A9).

(b) **10-year exposure:** Five two foot long spools of type 317L, Alloy G, titanium, polyvinylidene fluoride (PVDF) lined and polytetraflourethylene (PTFE) lined pipe had been installed in the D-stage filtrate line 10 years earlier at one mill. These were offered by the mill for inclusion in the Metals Subcommittee evaluation program (10). Despite the fact that the original records of fabrication had been lost, some useful information was obtained from examination of these spools.

Environmental conditions in the D stage filtrate line, which had not been changed significantly during the 10-year exposure period follow:

pH 5.8 (Mill adds NaOH between tower and vat)
Temp. 140-150°F (60-66°C)
Chlorine residual - low
Chloride - low

The metallic pipe spools had been fabricated using a short length of welded pipe and two stub ends. This resulted in two butt welds in each metallic spool. Chemicals analysis of the base metal and the weld metal showed composition to be in the normal range and that welds had been made with matching composition filler metal. Longitudinal welds were of good quality. Incomplete fusion and severe crevices were present in all circumferential welds.

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19. A. NADEZHDIN and C.B. THOMPSON, "The corrosion resistance of nickel alloys in C/D mixer environments. *Corrosion/92*, Paper 320. National Association of Corrosion Engineers, Houston, TX (1992).

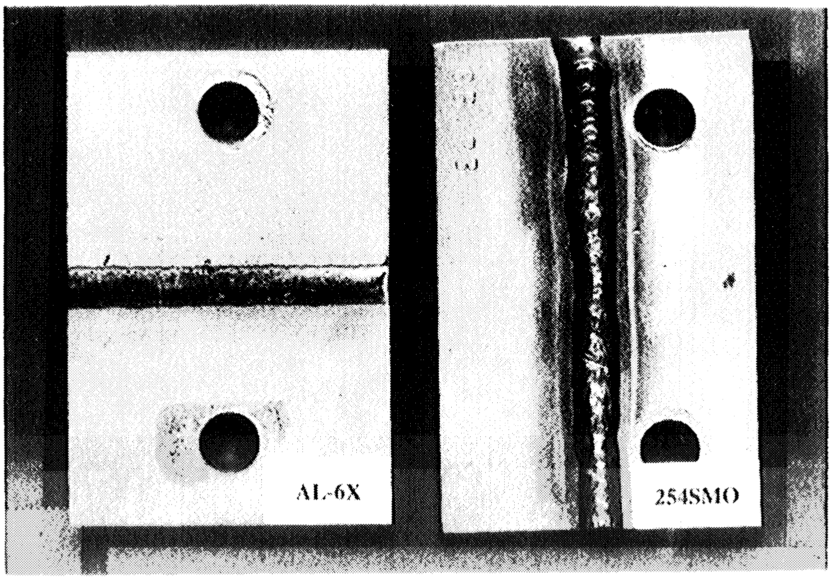

Figure 1. Typical coupons of 6% Mo Stainless Steels after exposure in a chlorine-dioxide-stage washer. Weld metal pitting on the autogenous (no filler) weld (*left*) was avoided when Alloy 625-type enriched filler was used (*right*)

Figure 2. Typical pipe sections after chlorine dioxide filtrate service. Each section contained longitudinal and circumferential welds.

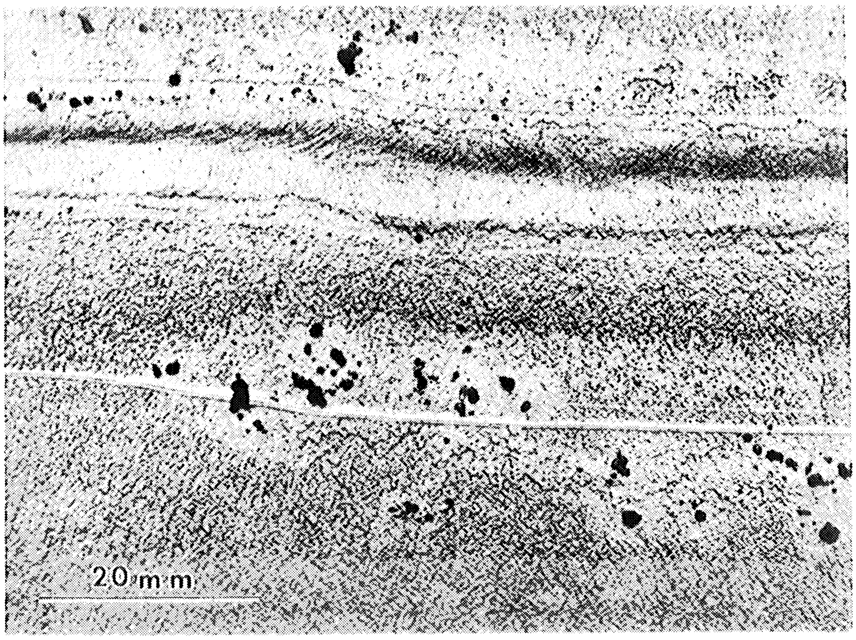

Figure 3. Pits in Alloy G-30 chlorine dioxide filtrate test-pipe were sometimes but not always associated with scratches or welding.

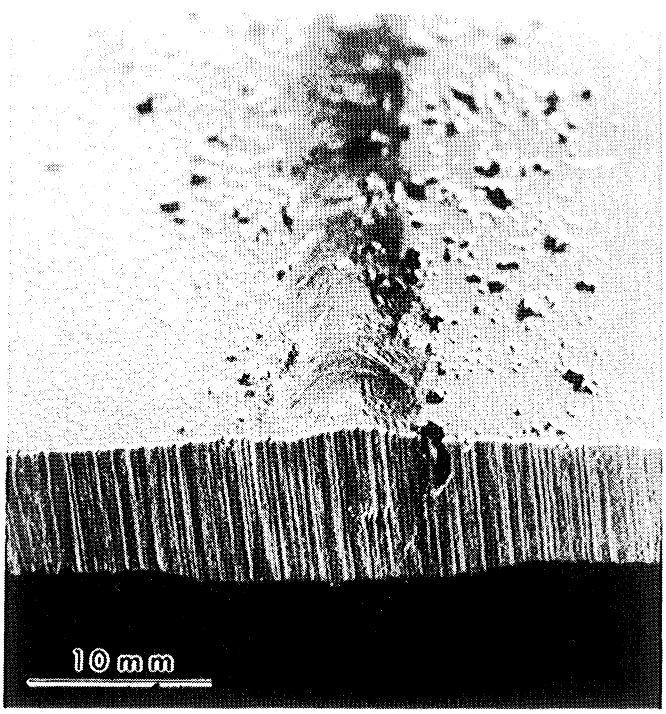

Figure 4. Cleaned and sectioned circumferential weld in AL-6XN. Lack of mixing weld filler metal resulted in deep pitting. Corrosion product deposits also caused secondary base metal pitting.

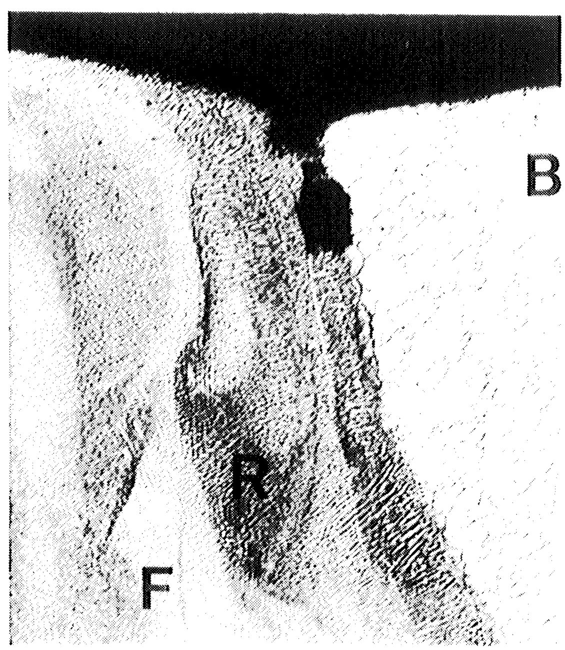

Figure 5. Metallographic section of pitting shown in Figure 4. Dark-etching (R) areas are remelted base metal unmixed with filler metal and are susceptible to pitting. Base metal (B) and light-etching undiluted Alloy 625 filler metal (F) resisted pitting.

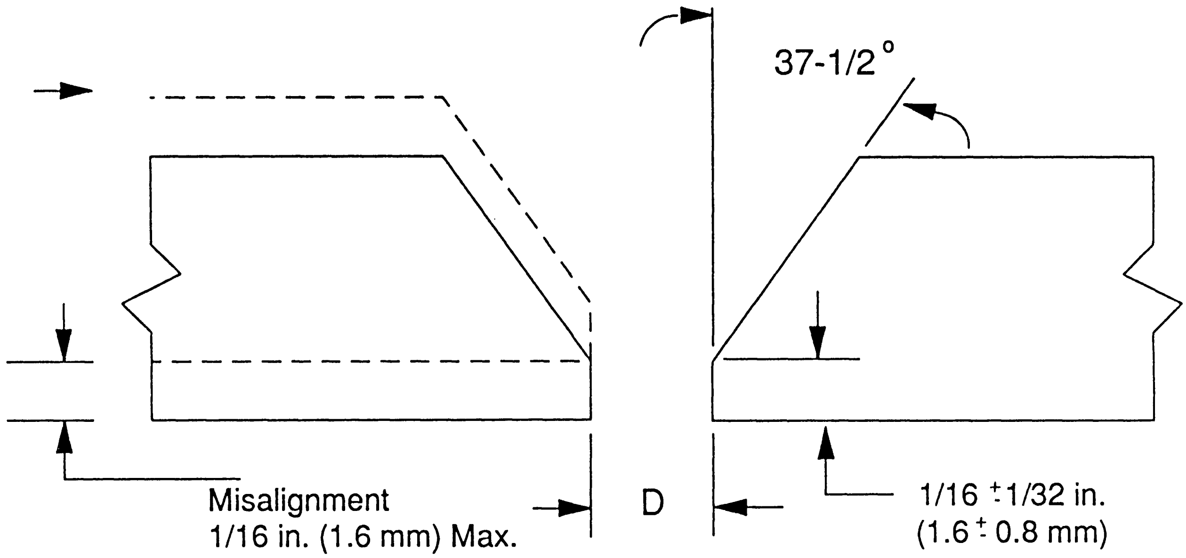

Figure 8. Typical joint design for pipe welded without consumable insert and GTAW root. D < diameter of filler wire for keyhole method. D > diameter of filler wire for continuous feeding method.

Table 1. Number of Coupons Where Weld Metal Corroded but Base Metal Did Not			
Welded with Higher Mo Filler Metal (625)		Welded with Matching Composition Filler Metal	
Stainless Steels			
		316L	3
Nitronic 50	0	Nitronic 50	5
		317L	5
		Sanicro 28	6
		Alloy 825	4
317LM	0	904L	1
JS/700	0	254 SLX	3
		317X	14
254 SMO	0	AL-6X	2
20 Mo-6	0		
Nickel Base			
		Alloy G	1
		Alloy G-3	1

Table 2. ASTM Specifications for 6% Mo Pipe

UNS	Specification	Filler Metal	Solution Anneal, Min.	Scale	Other
S31254 (254 SMO)	A312	None	2100°F (1149°C)	Free of Scale	Weld Repair Permitted
N08026 (20 Mo-6)	B464	None	2050°F (1121°C)	-	-
N08925 (25-6MO)	B673	None	2010°F (1099°C)	Remove Oxide	Cold Work Req. Class 1 & 2 NR. Class 3
N08367 (AL-6XN)	B675	None	2150°F (1177°C)	Remove Oxide	Cold Work Req. Class 1 & 2 NR Class 3
N08367 (AL-6XN)	B804	Required	2025°F (1107°C)	Remove Oxide & Passivate	-

Table 3. ASTM Specifications of 6% Mo, Ni Base Alloy and Ti Fittings		
UNS	**Alloy**	**Specification for Fittings**
S312254	254 SMO	A403
N08026	20 Mo-6	B366
N08925	25 6MO	B366
N08367	AL-6XN	B366
N10276	C-276	B366
N06022	C-22	B366
N06007	G	B366
N06030	G-30	B366
	Titanium Gr 2 and Gr 12	B363

Table 4. ASTM Specifications for Nickel Base Alloy & Titanium Welded Pipe					
UNS	**Specification**	**Filler Metal**	**Solution Anneal**	**Scale**	**Cold Work**
N10276 (C-276)	B619	None	Consult Producer	Free of Scale	Class II
N06022 (C-22)	B619	None	Consult Producer	Free of Scale	Class II
N06007 (G)	B619	None	Consult Producer	Free of Scale	Class II
N06030 (G-30)	B619	None	Consult Producer	Free of Scale	Class II
Titanium Gr2	B337	Optional	Annealed	-	NR
Titanium Gr12	B337	Optional	Annealed	-	NR

Table 5. Bleach Plant Piping Evaluation Summary		
	Chlorination	**Chlorine Dioxide**
Mixers-to-Tower (Vibration, High Residuals)	Clad Ni Base* Ni Base*	Titanium
Tower-to-Vat	6% Mo SS Ni Base Clad Ni Base	6% Mo SS Ni Base** Clad Ni Base**
Filtrate	6% Mo SS Ni Base Clad Ni Base	6% Mo SS Ni Base** Clad Ni Base**

* At ClO_2 substitution levels at 50% or higher, general corrosion is experienced proportional to nickel content. Optimal material selection for this application is not yet resolved (19).

** 6 months min. coupon corrosion rate tests suggested for Ni Base alloys for those mills adding caustic between the tower and vat. Corrosion rates appear to be site specific for mills adding caustic and maybe higher for higher Mo-content alloys (14). Corrosion rates for mills not adding caustic are reported to be <1 MPY.

Ni Base alloys include C-22, C-276, 625 the most resistant group; G-3 and G-30 in a somewhat less resistant group but similar resistance to 6% Mo SS.

Table A1. Base Metal Chemical Compositions (wt %)

Alloy	C	Cr	Ni	Mo	Cu	Co	Mn	Si	S	P	Fe	Ti	Cb	W	N	Other
316L	0.016	16.89	11.15	2.09	-	-	1.51	0.36	0.003	0.031	Bal	-	-	-	-	-
317L	0.012	18.60	14.80	3.59	-	-	1.46	0.45	0.005	0.022	"	-	-	-	-	-
317LM	0.019	18.01	14.91	4.15	0.13	0.30	1.00	0.52	0.021	0.018	"	-	-	-	0.046	-
Crucible T-317X	0.020	19.00	15.00	5.50	3.50	-	1.75	0.50	0.005	-	"	-	0.35	-	0.180	-
NITRONIC 50™	0.035	20.69	12.40	2.14	0.18	-	4.78	0.40	0.0120	0.023	"	-	0.13	-	0.230	Y-0.15
Jessop 700™	0.018	20.602	25.302	4.42	1.43	0.10	1.72	0.47	.0150.	0.021	"	-	0.22	-	0.037	Sn-0
Uddeholm 904L™	0.024	20.20	24.80	4.40	1.44	0.22	1.59	0.40	010	0.025	"	-	-	-	0.057	-
Avesta 254 SLX™	0.010	19.80	24.60	4.39	0.70	-	1.60	0.63	0.001	0.019	"	-	-	-	0.043	-
Avesta 254 SMO™	0.011	20.00	18.20	6.13	-	-	0.42	0.42	0.003	0.024	"	-	-	-	0.190	-
AL-6X™	0.028	20.42	24.82	6.08	1.07	-	1.50	0.29	0.001	-	"	-	-	-	0.055	-
Sanicro 28™	0.013	26.90	31.10	3.43	3.28	-	1.75	0.11	0.003	0.013	"	-	-	-	-	-
Carpenter 20Mo-6™	0.025	24.22	33.06	5.65		-	0.40	0.26	0.004	0.026	"	-	0.21	-	-	-
INCOLOY 825™	0.030	21.98	41.05	3.24	1.77	-	0.30	0.17	0.003	-	30.27	1.11	-	-	-	A1-0.08
HASTELLOY G™	0.009	22.19	40.38	6.43	1.88	2.40	1.47	0.25	-	-	19.37	-	2.18	0.81	-	Ta <0.05
HASTELLOY G-3™	0.008	22.76	43.59	7.01	1.85	3.49	0.82	0.37	-	-	18.15	-	0.19	0.94	-	Ta <0.06
INCONEL 625™	0.040	22.38	60.885	8.81	0.09	-	0.39	0.45	0.001-	0.009	3.15	0.28	-	-	-	Cb+Ta 3.51
HASTELLOY C-276™	0.004	15.18	55.15	15.82	-	2.07	0.49	0.03	0.009	-	5.79	-	-	3.76	-	-
E-Brite 26-1™	0.002	26.20	0.12	1.00	-	-	0.02	0.29	-	-	Bal	-	0.10	-	0.015	-
Crucible SC-1™	0.025	26.00	2.50	3.00	0.33	-	0.30	0.30	0.006	-	"	0.50	-	-	0.025	-
NYBY MONIT™	0.019	24.50	3.95	3.94	-	-	0.26	0.22	-	0.025	"	0.57	-	-	0.009	-
Uddeholm 44LN™	0.023	24.10	6.30	1.65	-	-	1.67	0.65	0.015	-	"	-	-	-	0.180	-
Schomac 30-2™	0.002	30.602	0.216	1.99	-	-	0.033	0.15	0.011	0.014	"	-	-	-	0.006	O_2-0.002
AL 29-4™	0.003	9.01	0.09	3.95	-	-	0.03	0.04	0.010	-	"	-	-	-	0.011	-
AL 29-4-2™	0.002	29.50	2.20	3.95		-	0.03	0.04		-	"	-	-	-	0.013	O_2-0.25
Titanium Code 12	0.080	-	0.08	0.30	-	-	-	-	-	-	0.03	Bal	-	-	0.030	O_2-0.15
Titanium Grade 2	0.020	-	-	-	-	-	-	-	-	-	0.03	"	-	-	0.016	H_2-0.0056

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Table A3. Alloys used in the Coupon Exposure Program were Produced by the Following Companies	
Name of Alloy	**Product of**
Crucible SC-1	Colt Industries
E-Brite	Allegheny Ludlum Steel Corp.
Hastelloy G	Haynes International
Hastelloy G-3	Haynes Internatinal
Hastelloy C-276	Haynes International
Hatelloy C-22	Haynes International
INCOLOY 825	Inco Family of Companies
INCOLOY 65	Inco Family of Companies
INCONEL 112	Inco Family of Companies
INCONEL 625	Inco Family of Companies
Jessop 700	Jessop Steel Company
NITRONIC 50	Armco, Inc.
NYBY Monit	Uddeholm Corporation
Sanicro 28	Sanvik, Inc.
Schomac 30-2	Showa Denko KK
Uddeholm 904L	Uddeholm Corporation
Uddeholm 44LN	Uddelhom Corporation
Chromenar 625	Arcos
Jungo 4500	Smitweld bv
Arosta 4462	Smitweld bv
AL-6X	Allegheny Ludlum Steel Corp.
AL-29-4	Allegheny Ludlum Steel Corp.
AL-29-4-2	Allegheny Ludlum Steel Corp.
Avesta 254 SLX	Avesta AB
Avesta 254 SMO	Avesta AB
Carpenter 20 Mo-6	Carpenter Technology Co.
Crucible T-317X	Colt Industries

Table A4. Differing Severity of Exposure Environments			
Environment	**1**	**2**	**3**
Base Metal	Resistant	Resistant	Pitted
WM	Resistant	Pitted	Pitted
HAZ	Resistant	Pitted	Pitted

Table A2. Filler Metal Compositions as Reported by Producers

Material	Filler Metal	C	Cr	Ni	Mo	Mn	Si	S	P	Fe	Ti	Cb	N	Cu
316L	E-316L-16													
317L	E-317L-16													
317LM	CHROMENAR 625													
317X	T-317X													
N 50_1	NITRONIC-50W	0.046	21.14	10.49	1.82	6.16	0.33	0.008	0.015			0.02	0.21	
N 50_2	IN 112													
700	IN112™													
904L	JUNGO 4500™	0.016	20.90	25.10	4.60	1.26	0.84	0.007	0.012	BAL				1.61
254SLX	254SLX	0.030	20	25	4.50	2.50	0.30	0.020	0.025					1.50
254 SMO	ENiCrMo-3	0.100	21	BAL	9.00	0.30	0.50			-		3.50		
AL-6X™	-	AUTOGENOUS												
S-28	SANICRO 28™	0.016	26.86	31.08	3.54	1.74	0.08	0.003	0.017					0.96
20Mo-6	ENiCrMo-3													
825	INCOLOY 65™													
G	-	SAME AS BASE PLATE												
G-3	-	SAME AS BASE PLATE												
625	INCONEL 625™													
C-276	-	SAME AS BASE PLATE												
E-Brite™	-	AUTOGENOUS												
SC-1	SC-1													
NYBY MONIT™	NYBY MONIT™	0.022	25.40	4.20	3.90		0.44	0.009			0.30	0.11	0.02	
44LN	AROSTA 4462™	0.015	22.60	8.90	3.00	0.95	0.96	0.011	0.022					0.06
30-2	SCHOMAC 30-2™	0.001	29.40	0.22	1.91	0.049	0.19		0.011					0.006
AL 29-4™	-	AUTOGENOUS												
AL 29-4-2™	-	AUTOGENOUS												
Ti 12	ASTM B348 GR 12													
Ti 2	ASTM B348 GR 2													

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Table A5. Range of Temperature, pH, chloride and oxiders (as chlorine)			
Bleach Plant Stage	C & D/C	D	H
Number in Test	8	8	3
ClO_2 Substitution	16-48%		
Temperature °F (°C)	103-138 (41-49)	128-176 (53-79)	88-132 (31-55)
pH	1.4-2.1	3.5 & 6*	7.5-9.5
Chloride ppm	1100-5500	Low - 5600	Low - 2453
Residual Oxidant (ppm, max)	15-320	8-181	58-1023

* In four of the D stage environments the normal pH of 3.5 was carried through to the vat where the specimens were exposed. In the other four D stage environments, NaOH was added to partially neutralize the acidic D stage liquor before it reached the vats.

Table A6. Nominal Composition of Alloys (wt%) used in the 11-month Pipe Tests in Chlorination Filtrate

Alloy	UNS	ASTM	C	Cr	Ni	Mo	Cu	N	
AL-6XN™	NO8367	B688	.03(*)	20	25	6	-	0.2	
20Mo-6™	NO8026	B463/B464	.03(*)	24	37	6	3	0.13	
254 SMO™[1]	S31254	-	.03(*)	20	18	6	0.7	0.2	
Polarit 778™[1]	[2]	-	.03(*)	20	22	6	0.8	0.2	
Alloy G-30	NO6030	B582	.03(*)	30	40	5	1.7	-	5Co 2.5W 15Fe
Alloy C-22	NO6022	B574/B575	.01	21	55	13.5	-	-	2.5Co 3W 5Fe
Alloy C-276 (Clad)	N10276	B574/B575	.01	16	55	16	-	0.01	2Co 4W
Alloy 625	NO6625	B443/B444	.04(*)	22	61	9	-	-	4Cb+Ta 3Fe

Alloy	Product of:
AL-6XN	Allegheny Ludlum Steel Corp.
20Mo-6	Carpenter Technology Corp.
254 SMO	Avesta AB
Polarit 778	Outokumpu OY

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(*) Maximum.

1 Polarit 778 and 254 SMO wre solution annealed initially at a temperature below 2150°F (1175°C) showing evidence of heavy precipitation at grain boundaries and in the direction of rolling. Reheat treatment at 2150°F (1175°C) dissolved precipitates and left grain boundaries clean and free of precipitates. AL-6XN, 20Mo-6 and 1925hMo were solution annealed once at 2150°F (1175°C). Their grain boundaries were also clean and free of precipitates.

2 Polarit 778 is awaiting its UNS number. Its composition falls between S31254 and NO8925.

Table A7. Production of Large Diameter Welded Stainless Steel Pipe	
Sequence of Operations to Make Longitudinal Welded Pipe (All Alloys)	
1.	Sheet or plate received and marked for identification
2.	Sheared to size (Steel hold down bars on shearing press)
3.	Roll formed to diameter desired (Steel rolls)
4.	Edges cleaned by power wire brushing with austenitic stainless steel wire brush
5.	Edges tack welded (autogenous GTAW) run on and run off tabs welded on. (If there is delay in going to the boom welder, cleaned edges are taped for protection)
6.	Longitudinal weld made on boom welder
7.	Run on and run off tabs sawn off
8.	Pipe sized for concentricity (Steel forming roll)
9.	Solution anneal for stainless alloys (but not nickel base alloys)
10.	Resized if necessary
11.	Pickled in Nitric-HF
For 6% Mo Stainless Steels which have been annealed at too low a temperature:	
12.	Re-solution-annealed at 2150°F (1175°C)
13.	Repickled in Nitric-HF to remove heat treating scale

Table A8. Daily Exposure Conditions During the Alternating Hardwood and Softwood Runs (14-months in ClO_2 Filtrate)

		Period 1	Period 2
Hardwood	pH	3.8 - 4.2	3.0 - 3.5
	Residual ClO_2, ppm	30 - 50	20 - 40
	Time, months	6.5	7
Softwood	pH	4.0 - 4.7	3.8 - 4.1
	Residual ClO_2, ppm	40 - 60	30 - 50
	Time, months	8.5	5

Table A9. Critical Pitting Temperature in 10% $FeCl_3$	
Base Metal	**Temperature, °C**
AL-6XN	72.5
G-30	60
625	90
C-22	>100
C-276	>100