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Abstract

Mills are currently increasing chlorine dioxide substitution to 50% and more in the chlorination stage in order to reduce dioxins. Re-examination of the Technical Association of the Pulp and Paper Industry (TAPPI) Phase II data base indicates that up to, at least 48% chlorine dioxide substitution there is no significant difference in alloy performance as determined in the Phase II evaluation program in bleach plant washer environments. Phase II data on localized corrosion replotted provides new and better guidelines on boundary conditions. Based on the wide range in pH, residual chlorine, temperature and chloride covered in these exposures it appears that the 6% Mo alloys can be expected to perform well except under the most extreme combinations of conditions. General corrosion rates for nickel base alloys in C stage do not exceed 0.2 mpy in the Phase II exposures, as compared to the 0.1-0.9 mpy in acidic D stage and 0.1-2.9 mpy in neutralized D stage environments. New data from the C stage of a short sequence bleach plant indicates that the nickel base alloy, C22, is as resistant in the vapor phase as in the liquor. Actual field experience indicates that the nickel base alloys are useful as washers and piping. In C stage environments too aggressive for 6% Mo alloys, nickel base alloys perform well. The cast C4C and wrought C22 alloys are useful in high intensity mixers handling chlorine. Titanium is the preferred material for high intensity mixers handling the chlorine dioxide used in C stage. In some mills titanium is also used for the chlorine high intensity mixer with an elaborate interlock and alarm system to prevent dry chlorine from reaching the titanium.

Alloys And The Environment

Table I presents the composition and Unified Numbering System (UNS) numbers of the alloys mentioned in this paper.

Mills are currently pursuing a variety of programs aimed at reducing dioxins. Substitution of chlorine dioxide for 50% or more of the chlorine in C stage is a major trend most mills are adopting. *Table II* adds the % of chlorine dioxide substitution to the previously published Phase II data on C stage environments[1]. Four of the eight mills were using substantial levels of chlorine dioxide substitution of 16,25,41 and 48 per cent. These data indicate that the conclusions on alloy performance in C stage already drawn and published from the Phase II C stage data are valid up to, at least, 48% chlorine dioxide substitution.

Behaviour of highly alloyed materials in C and C/D stage chlorination washer environments

Figure 1 plots the depth of pitting on the boldly exposed surface and the depth of crevice corrosion for three common stainless steels versus maximum residual chlorine, minimum pH, maximum temperature and chloride ion concentration as determined from the daily log sheets during the period of exposure. These Phase II data were previously published[1]. Percent of chlorine dioxide substitution is also given. Crevice corrosion is shown to be the primary mode of corrosion which is in accordance with field experience. The increase in corrosion resistance with increasing Mo content is clear, which also corresponds with experience.

In 7 of the 8 mills the 6% Mo alloy meets the criteria for superior performance (<5 mills base plate pitting and <5 mills

Table I
Composition of Alloys

Common Name	UNS	Cr	Ni	Mo	Other	
317L	S31703	18	14	3	-	
904L	N08904	21	26	4.5	2Cu	
AL-6XN®	N08367	21	25	6	-	0.2N
254SMO®	S31254	20	18	6	0.7Cu	0.2N
1925hMO®	N08925	20	25	6	1.5Cu	0.12N
20Mo-6®	N08026	24	33	6	3Cu	
25-6Mo®	N08926	20	25	6	0.8Cu	0.2N
Alloy 625	N06625	22	60	9	-	
Alloy G	N06007	23	48	6.5	2Cu	
Alloy G3	N06985	25	50	6.5	1Cu	
Alloy C276	N10276	16	58	16	4W	
C-22 Alloy	N06022	22	59	13	3W	
Cast C4C	N06455	16	65	16	2Fe	1W
Ti Code 12	R53400	-	.08	0.3	0.08C	.03N Bal Ti2
Ti Gr 2	R50400	-	-	-	0.01C	.03N Bal Ti

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Alloy	Product of:
AL-6XN	Allegheny Ludlum Steel Corporation
20Mo-6	Carpenter Technology Corporation
254SMO	Avesta Jernverks AB

Alloy	Product of:
1925hMo	VDM Technologies
25-6Mo	Inco Alloys International

Table II
Chlorination stage environments (TAPPI - Phase II)

Mill Stage	EE D/C	AA D/C	FF C	CC C	BB C	DD D/C	GG D/C	JJ D/C
% Cl O_2 Substitution	16	48	0	0	0	0.33	25	41
pH								
Av. Daily Min	2.0	1.9	1.6	2.0*	1.4	2.0	1.4	2.1*
Av. Daily Max	2.2	2.4	2.2		1.6	2.7	2.2	
Residual Cl_2 ppm								
Av. Daily Min	15	16	27	30*	50	50	148	320
Av. Daily Max	1	8	2		10	8	13	61
Temperature -°F	103	137	103	105*	114	98	138	109*
Temperature -°C								
(Av. Daily Max)								
Chloride - ppm	1500	5500	1900	1100	3500	1000	1500	1400

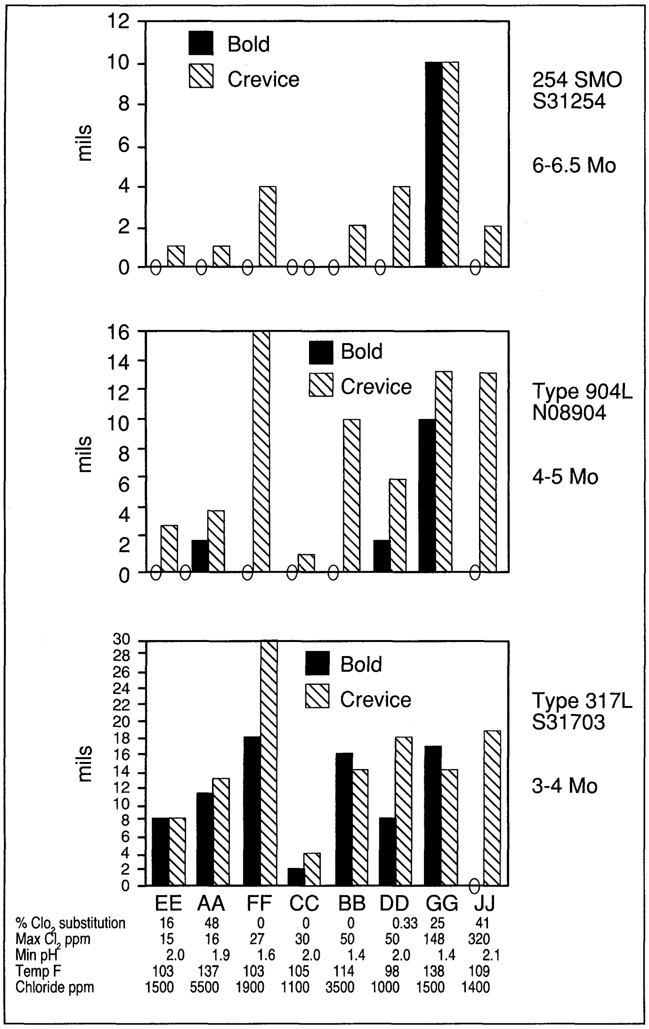


Figure 1 Depth of pitting in base plate and depth crevice corrosion - stainless steels - D/C & C stages.

crevice corrosion) established in ranking alloy resistance in earlier programs[2]. In the one mill where the 6% Mo alloy failed to meet these criteria, the low pH (1.4) combined with the high residual (148ppm), high temperature (138F) and 1400 ppm chlorides results in a C stage environment that appears to be too aggressive for 6% Mo. In mill BB where the pH was also 1.4, but residual chlorine was moderate (50ppm) and in mill JJ where residual chlorine was higher (320ppm) but pH was higher (2.1), 6% Mo met the criteria for superior performance. The 6% Mo alloy appears to be useful in a wide range of C and C/D stage environments as long as very high residuals are not combined with very low pHs and high temperatures. Good experience with the 75 plus 6% Mo washers placed in service since 1982 tends to support the broad applicability of the 6% Mo alloys for bleach plant service that the Phase II data suggested.

Figure 2 plots the depth of pitting and crevice corrosion for three nickel base alloys versus residual chlorine, pH, temperature and chloride ion concentration. Data for alloy C276, UNS N10276, and the two titanium alloys was not plotted as there was no pitting or crevice corrosion on these alloys in any mill exposure. All four nickel base alloys and the two titanium alloys meet the criteria for superior service in all 8 mills. These 6 alloys appear to be good candidates for those few low

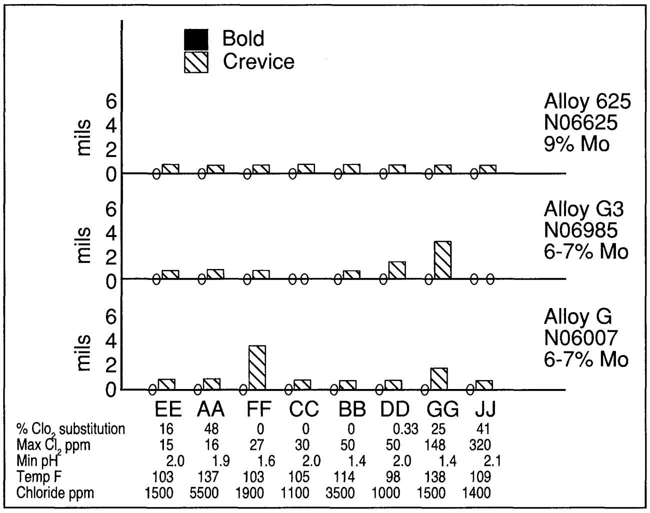


Figure 2 Depth of pitting in base palte and depth of crevice corrosion - nickel base alloys - D/C & C stages.

pH, high residual chlorine, high temperature conditions where the 6% Mo alloys may be marginal.

The general corrosion rates of alloys that were resistant to localized corrosion were not originally reported with the Phase II data as the most of the alloys suffered localized corrosion. To answer questions that have arisen about the general corrosion rates of the alloys that suffered little or no localized corrosion, the general corrosion rates of the four nickel base alloys and the two titanium alloys have been calculated and are shown in *Table III.*

Table III
General Corrosion rates -- Alloys resistant to localized corrosion
Phase II Data

Alloy	UNS No.	Corrosion rate -- mpy
G	N06007	<0.1 in 8 mills
G3	N06985	<0.1 in 7 mills
		0.1 in 1 mill
625	N06625	<0.1 in 7 mills
		0.2 in 1 mill
C276	N10276	<0.1 in 8 mills
TiCode 12	R53400	<0.1 in 8 mills
TiGr2	R50400	<0.1 in 8 mills

The periods of exposure varied from 6-7 months. Nickel base alloys exhibit negligible general corrosion rates of 0.1-0.2 mpy, and titanium alloys also exhibit negligible general corrosion rates in C and D/C stage environments up to, at least, 48% chlorine dioxide substitution. This compares with general corrosion rates of 0.1 - 0.9 mpy for nickel base alloy C276, in acidic D stage environments and with 0.1 - 2.9 mpy in long term exposures in neutralized D stage environments, Wensley and Reid report higher general corrosion rates ranging from 2.2 to 10.6 mpy for alloy C276, in short term tests[3]. The higher rates and the wide variation in general corrosion rates in Wensley and Reid's short term data are typical of general corrosion rates for alloys in the early period of protective film formation before the film is fully formed and fully protective.

Short sequence bleaching

In 1985, IMPCO started the first short sequence C/D - E/O - D low level bleach plant in North America at Mead Paper in Chillocothe, Ohio. This state-of-the-art technology utilized Compaction Baffle Filters and short sequence bleaching. The process operates with 20% chlorine dioxide substitution and a 145F temperature which is at the high end of the temperature range for current chlorination stage practice. The Compaction Baffle Filter, *Figure 3*, is completely sealed, containing the process liquid and vapor within the vat and hood. Coupon test racks were installed in the inlet box in the liquid and in the hood in the vapor zone. Results of a similar exposure in the chlorine dioxide stage at this mill were reported previously[4].

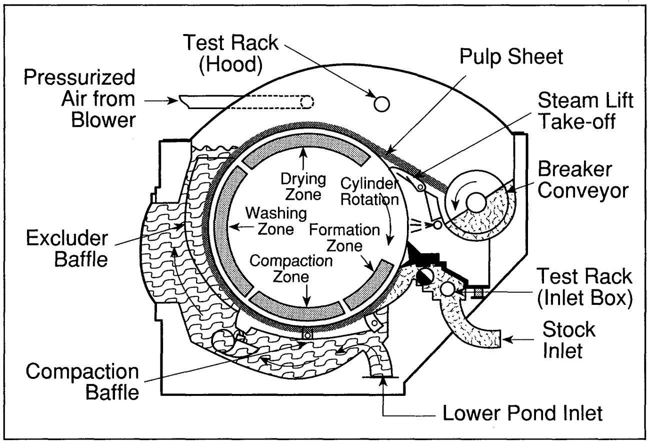


Figure 3 Compaction baffle filter.

Preparation For field testing

Welded specimens of 317L (S31703), AL-6XN® (N08367), 254SMO® (S31254), 1925hMO® (N08925) and C22 (N06022) were prepared, pickled and assembled on a conventional test rack for exposure. *Table IV* shows the results and the environmental conditions during exposure.

Discussion – After 13 months in the inlet box where the pH averaged 1.7, temperature 145F, and residual chlorine a trace, base plate pit depth was 9 mils and crevice corrosion depth was 10 mils for 317L. The base plate of one the three 6% Mo alloys had a 3 mil deep pit and a 2 mil depth of crevice corrosion. There was no pitting of the base metal of the other two 6% Mo alloys, but there was 9 mils depth of crevice corrosion on each. The nickel base alloy C22 was free of localized corrosion on the base plate and in the creviced area. The general corrosion rate was <0.1 mpy. The 254SMO® washer in the chlorination stage at this mill was carefully inspected after 5 years service during a design update and found free of localized corrosion. This is consistent with earlier findings indicating that alloys perform somewhat better in the washer itself than specimens submerged in the liquor in the vat[5].

In the vapor zone the base plate of the four stainless steels suffered substantial pitting and some crevice corrosion, whereas the nickel base alloy was completely resistant to localized corrosion. The general corrosion rate of the nickel base alloy in the vapor zone was <0.1 mpy as in the liquid phase.

Figures 4 and *5* show the comparative volume loss for the five alloys in the liquid and vapor phase.

Table IV Exposure in acidic chlorination stage of short sequence bleach plant.
Volume loss - mm³ and maximum depth of attack - mils.

	Inlet Box	Hood
pH	1.5-2.0	1.5-2.0
Cl_2 ppm	7 average	–
Temperature °F	145	145
Cl ppm	1170-2750	–
Exposure time	13 months	4 months
S31703 3-4 mo	20.2	260
BP	9	35
CC	10	12
N08367 6 Mo	4.3	23.8
BP	0	10
CC	10	12
S31254 6 Mo	4.2	60.1
BP	0	23
CC	9	7
N08925 6 Mo	4.2	118.6
BP	3	15
CC	2	9
N06022 13 Mo	1.2	1.0
BP	0	0
CC	0	0
CR - mpy	<0.1	<0.1

Legend:
Alloy - Volume loss mm³
BP - Base plate pitting depth in mils
CC - Crevice corrosion depth in mils
CR - Mils per year corrosion rate

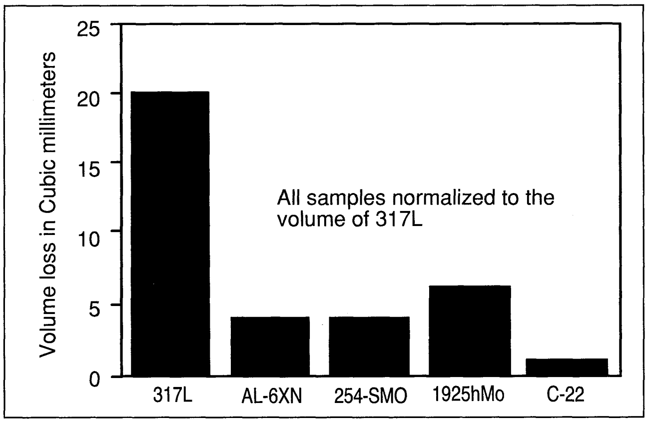


Figure 4 Chlorination inlet box (liquid phase) volume loss after 13 months exposure.

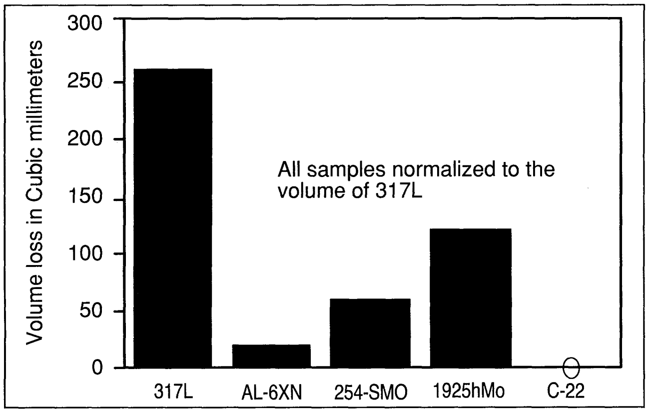


Figure 5 Chlorination hood (vapor phase) volume loss after 4 months exposure.

In other mills there has been some crevice corrosion on 6% Mo Compaction Baffle Washers in the area beneath the steam lift take-off under pulp pads which tend to accumulate in this area. Alloy C22 (N06022) has been used in this area successfully.

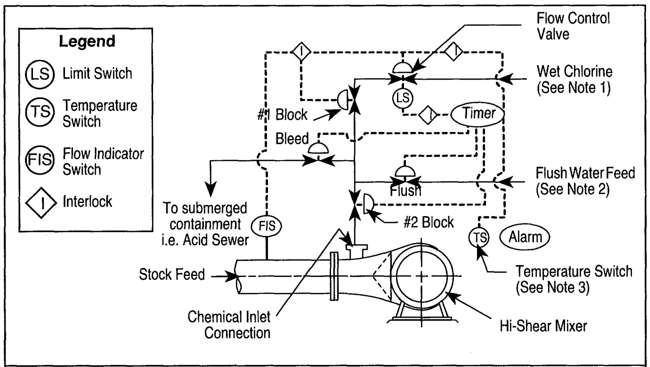
C Stage washer experience

A C22 washer was placed in service in an aggressive C stage in 1986. While no detailed inspection has been performed, operating forces have not encountered any problems. The washer is performing as would be anticipated from these data.

High intensity mixers

Alloys C4C (cast), C276 and C22, and commercially pure titanium are used in C stage high intensity mixers. For years nickel base alloys were preferred for the chlorine mixer because titanium is subject to pyrophoric reaction should dry chlorine come in contact with titanium. Titanium has been used for the chlorine mixer with the type of interlock and alarm system shown in Figure 6 to guard against dry chlorine reaching titanium during mill shutdown. Titanium is used for the chlorine dioxide mixer in those mills adding chlorine dioxide in the C stage. In a few mills chlorine and chlorine dioxide are mixed ahead of, or in the same mixer.

Historically, nickel base alloys have not performed well in chlorine dioxide mixers. In the late 1950s, commercially pure titanium was accepted as the preferred material of construction for mixers in this environment. Today, most mills are



Typical Interlock and Alarm System
for Titanium Mixer used in Chlorination Service

1. Flow control valve and #1 block valve to be interlocked with flow indicator switch in the mixer stock line to prevent flow control and #1 block valve from opening until mixer is full and stock is flowing.
2. Flush water timer activates when flow control valve is shut off as indicated by limit switch. SEQUENCE: Flush valves open for 10 seconds, then timer closes flush valve and #2 block valve and opens bleed valve. When system is ready to restart, operator will reset flush timer. This will close bleed valve and open #2 block valve. Flush valve remains closed.
3. Surface temperature switch (set for 200°F/93°C) to monitor any titanium burning inside the mixer. Switch to shut off the flow control and #1 block valve which will then initiate the flush water timer. Switch to also trigger an alarm.

Figure 6 Interlocks to prevent dry chlorine reaching titanium mixer.

utilizing various levels of chlorine dioxide substitution in the chlorination environment, which has raised the question: "At what level of chlorine dioxide should titanium be used instead of a nickel base alloy?" IMPCO, the Pulp Machinery Division of Ingersoll-Rand Company, has undertaken an extensive study of various stainless steels, nickel base alloys and titanium in 100% chlorine, 100% chlorine dioxide and ten mixtures of chlorine and chlorine dioxide in order to develop data that will answer this question. The results from this research are scheduled for publication later this year.

Conclusions

- Previously published TAPPI Phase II corrosion data on the performance of alloys in C and D/C stage washers are valid for chlorine dioxide substitutions of, at least, 48%.
- Phase II data indicated 6% Mo alloys should perform well in C stage environments with high residuals unless the pH is unusually low and the temperature unusually high. However 6% Mo alloys are susceptible to significant base plate pitting in the vapor zone. Good experience with over 75 6% Mo washers in bleach plant service tends to support and confirm the data from specimen exposure programs on the wide applicability of 6% Mo alloys for bleach plant service.
- Titanium and nickel base alloys are resistant to localized corrosion and have very low general corrosion rates in C stage liquid and vapor zone environments. These materials are suitable for washers and piping in those mills where 6% Mo alloys may be marginal. Nickel base alloys are useful in high intensity mixers handling chlorine.
- Titanium is preferred for chlorine dioxide stage high intensity mixers and for chlorine dioxide mixers in C stage in those mills substituting chlorine dioxide for chlorine in C stage. Titanium has been used in chlorine stage mixers with interlocks to prevent dry chlorine reaching titanium during mill shutdowns.

References

1. A. H. Tuthill, "Corrosion in aggressive bleach plant environments – results of Phase II exposure of 27 welded specimens in 19 United Sates and Canadian mills" TAPPI Engineering Conference, Dallas, TX, U.S.A., 1983.
2. A. H. Tuthill, "TAPPI Phase II corrosion test program", Proceedings of The 4th International Symposium on Corrosion in the Pulp and Paper Industry, Stockholm, Sweden.
3. D. A. Wensley and D. C. Reid, "Corrosion of nickel base alloys in chlorine Dioxide washer service", Corrosion/90 Las Vegas, NV, U.S.A., 1990.
4. A. H. Tuthill and D. E. Bardsley, "Performance of highly-alloyed materials in chlorine dioxide bleaching" TAPPI Engineering Conference, Seattle, WA, U.S.A., Sept. 1990.
5. A. H. Tuthill, "Comparison of test data and actual performance of 316L bleach plant washers" Materials Performance, 22 (7), pp. 45-51, July 1983.

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