Bleach Plant Materials Selection

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Alloys Under Consideration

Alloy Family	Example Alloys
Austenitic stainless steel	316L, 317L, Alloy 20
Super austenitic, 6% Mo stainless steel	254SMO, AL6XN
Lean duplex	2304, 2101
Lo molybdenum duplex	2003
Duplex	2205
Cast duplex	CD4MCU
Super duplex stainless steel	2507, Zeron 100
Nickel alloys	C276, 625, G30
Titanium	Titanium Grade 2

Bleach Plant Materials Selection

- O2 delignification
  - Historically 316L
  - Switched to 2205 for external stress corrosion cracking resistance
  - New reactors are now built out of lean duplex SS
- E stage
  - Alkaline conditions, less aggressive
  - 316L/317L
  - Lean duplex SS may be suitable
  - Avoid titanium with peroxide

Chlorine Dioxide, D Stage Materials Selection

- Resistance to oxidizing chlorides is necessary to prevent pitting and crevice corrosion
- Titanium is required up to the point of injection
- Stainless steel resistance depends on the ClO_2 residual and temperature
  - 317L and 6% Mo stainless steels traditional choices
  - Super duper austenitic 7% moly stainless steel is more resistant
  - 2205 or 2507 and cast equivalents now have wide applicability
- Nickel alloys corrode in neutral (pH>4) ClO_2

Chlorine dioxide pitting of 317L Eo Repulper

Closer view of the corrosion

Avoid using Nickel Alloys in Chlorine Dioxide

- Transpassive corrosion of a C276 D1 mixer
- May have no choice
  - Instrumentation
- Weld filler for 6% Mo SS
  - pH greater than 4, G30
  - pH less than 4, C276

Non-Metals for ClO_2 Service

- FRP is suitable for chlorine dioxide
  - Select resins based on temperature resistance
- Fluoropolymer lined piping, pumps, valves
  - PVDF, ECTFE, PTFE
- Dual laminates, FRP lined with a solid fluoropolymer lining
- PVC/CPVC less resistant, requires structural support
- Monolithic trowelled linings
- Tile and brick linings
  - 2507 duplex stainless steel lining is an alternative for towers

Sulfuric Acid Corrosion

- Sulfuric acid is corrosive to carbon steel, stainless steel and titanium
- Corrosion resistance depends on
  - Concentration
  - Temperature
  - Velocity
- Switch from carbon steel to PVDF lined pipe before acid is diluted
- Used for pH control in the bleach plant
  - Injected into chlorine dioxide lines

Sulfuric Acid Corrosion

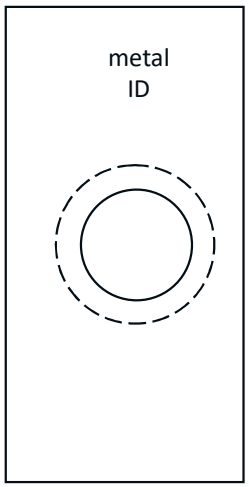
Alloy 20 casting
<10% acid
160° F
High velocity

Urea Hydrochloride

Pitting 316L

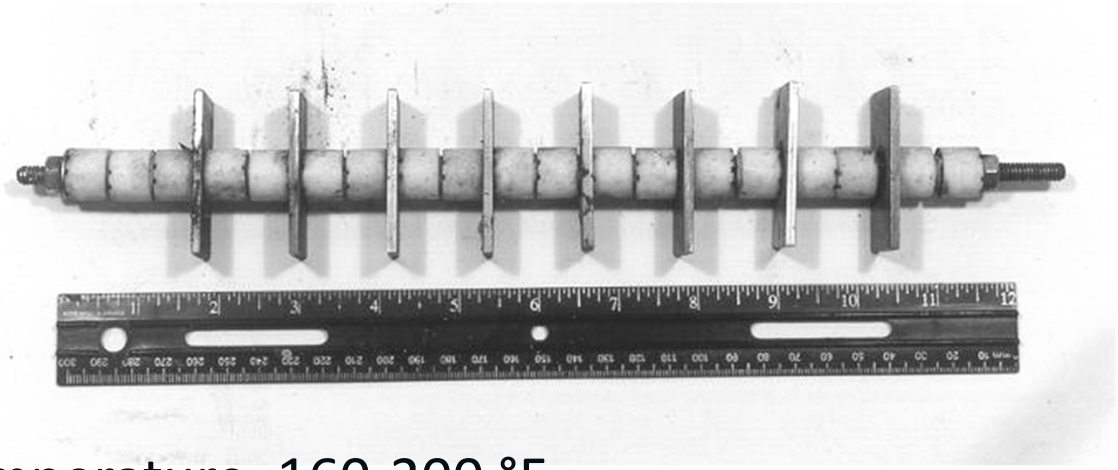
- Used for scale removal or pH control
- Can act like inhibited hydrochloric acid
- Breaks down if the concentration is too low or temperature too high

Mill Corrosion Testing



- 1” x 2” metal coupon
- All surfaces ground to 120 grit, except for 2101 and 2003 samples
- The labeled side is stamped with the metal ID. It is the mounted as the top side.
- A serrated PTFE crevice washer covers the central hole
- The rack assembly rods, plates and fasteners are made from 316L
- Coupons are weighed before and after testing

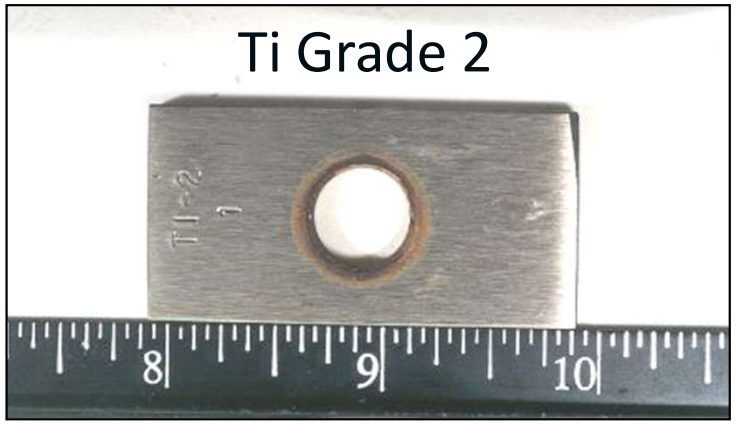
Mill #1 D2 Piping



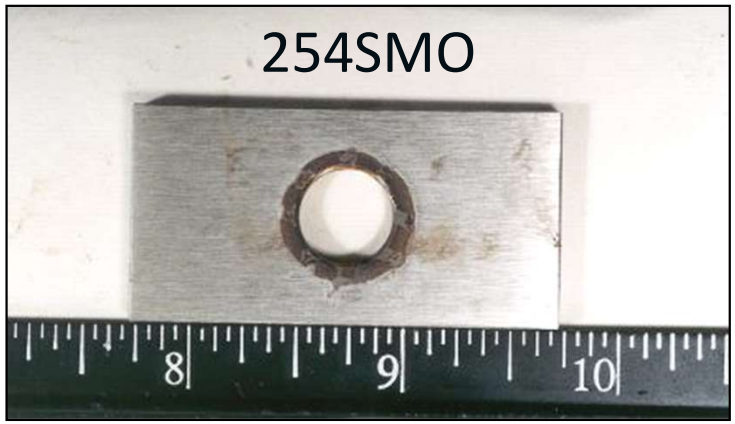
Temperature: 160-200 °F
pH: 3.3-4.0
ClO_2 concentration: 0.08 g/l
Test duration: ~345 days in the D2 filtrate tank
Materials: 317L, 2205, 254SMO, titanium

Visual Results

Ti Grade 2



254SMO



2205

317L

Test Results

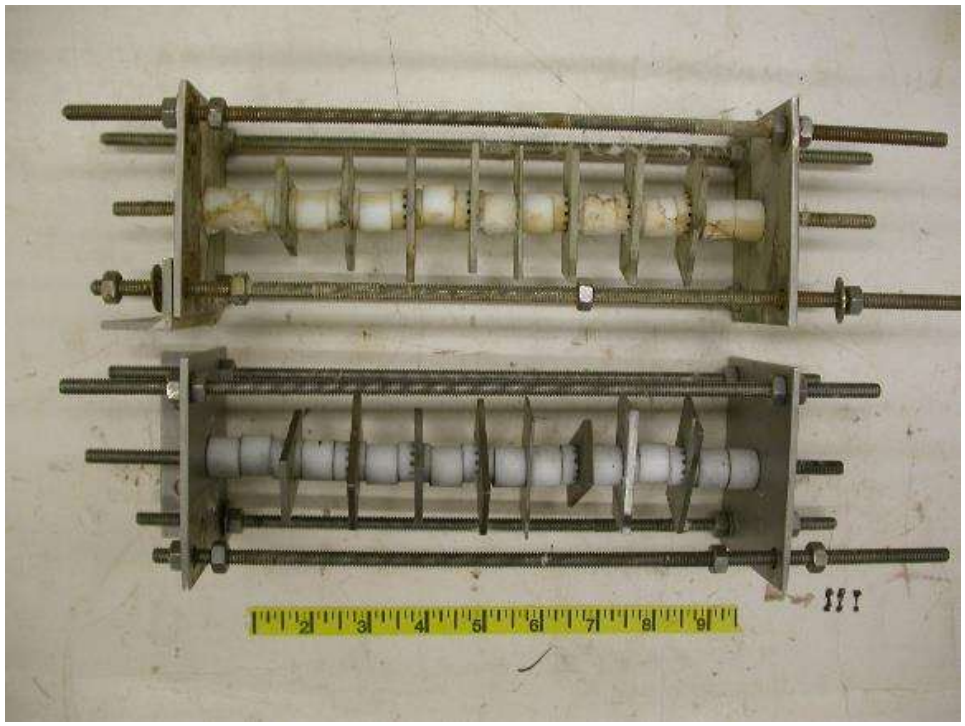
Alloy	Corrosion Rate (mil/yr)	Crevice Pitting	Open Pitting
Titanium Gr. 2	0		
254SMO (6% Mo)	0.26	X	
2205	0.20	X	X
317L	1.95	X	X

2205 was selected as the replacement material for 317L

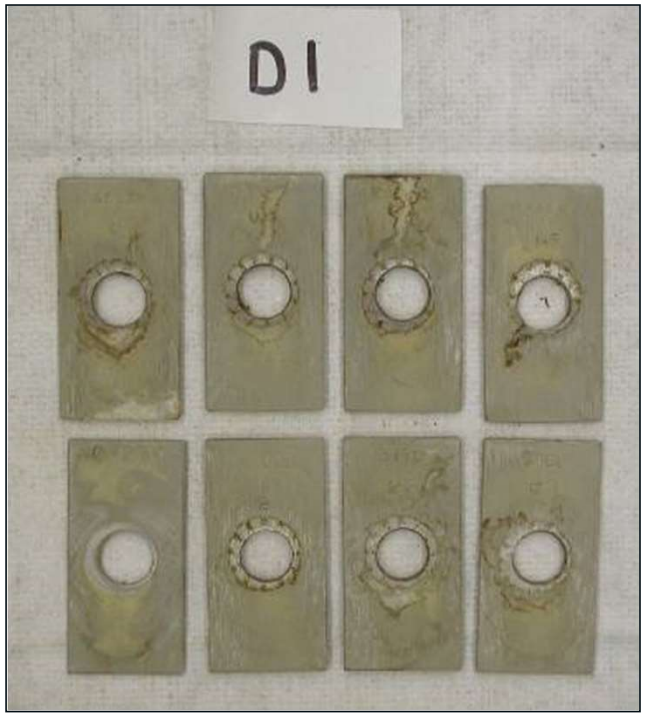
Mill #2 D1 and D2 Filtrate Tank and Piping

<u>D1 Conditions</u>
Temperature: 140 °F
pH: 2 - 3
ClO2 residual: low

<u>D2 Conditions</u>
Temperature: 160 °F
pH: 5 - 6
ClO2 residual: low



Round 1 Immersion, One Year



Round 1 Test Results – No Pitting

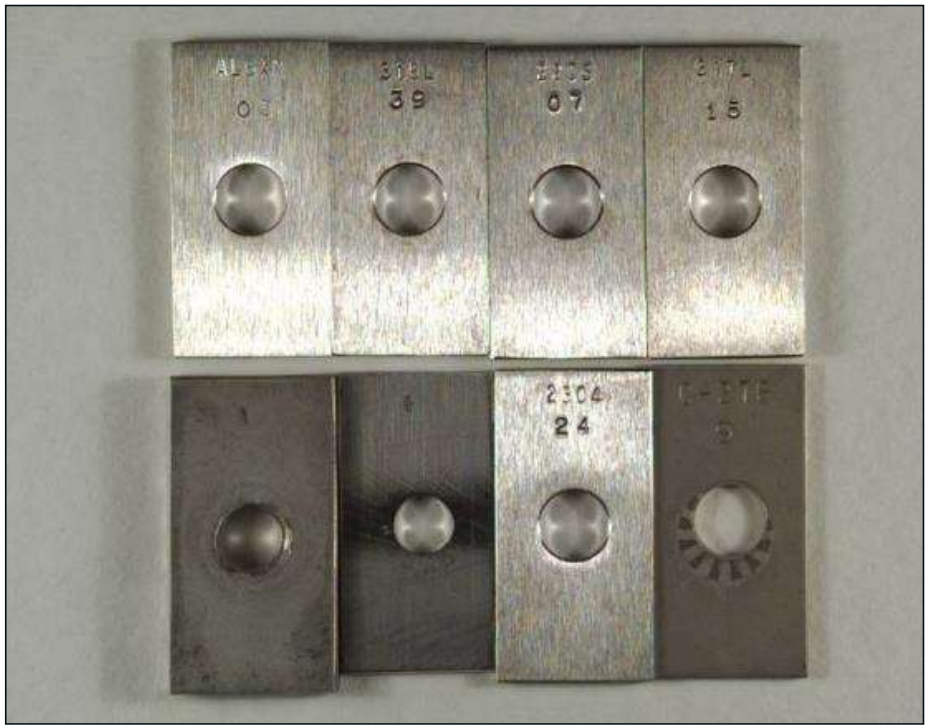
D1

Alloy	Corrosion Rate (mil/yr)
316L	0.000
317L	0.001
2205	0.001
CD4MCU	0.001
254SMO	0.000
AL6XN	0.001
625	0.001
C276	0.010

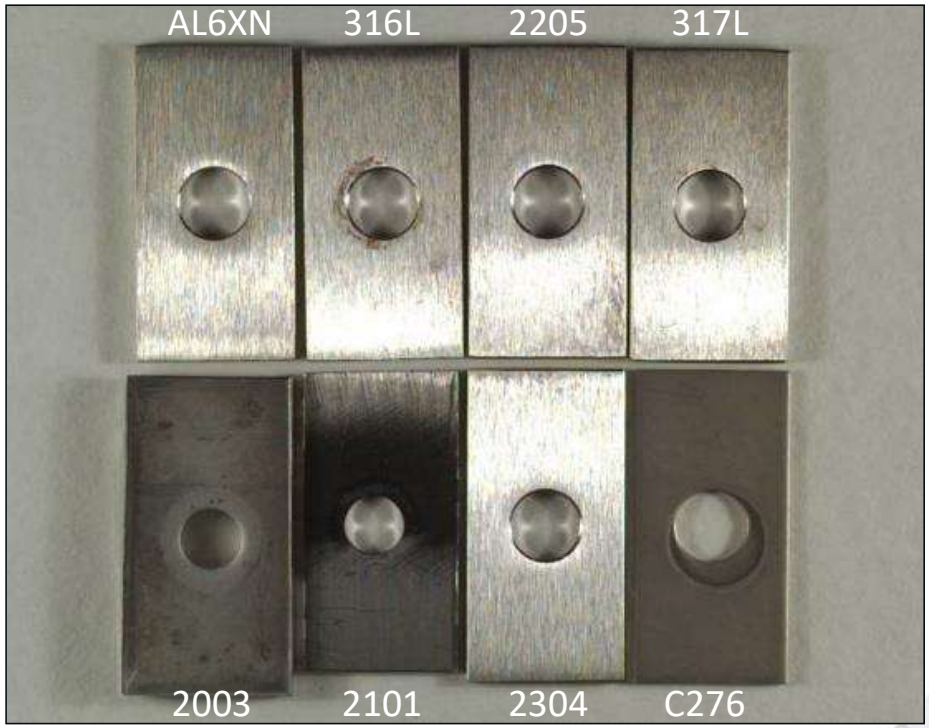
D2

Alloy	Corrosion Rate (mil/yr)
316L	0.001
317L	0.002
2205	0.000
CD4MCU	0.001
254SMO	0.000
AL6XN	0.003
625	0.056
C276	0.044

Round 2 Immersion, One Year, D2 Coupons



Top



Bottom

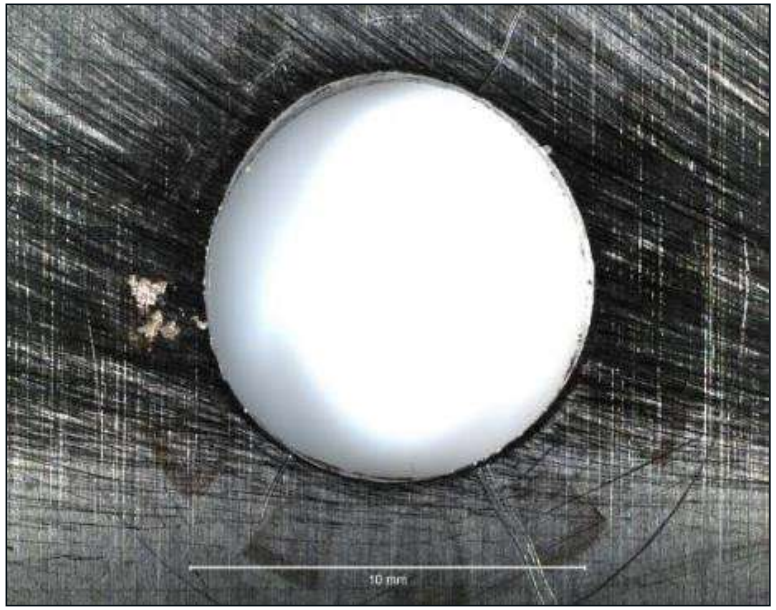
Round 2 D2 Pitting Detail

Bottom side 316L

Bottom side 317L

Round 2 D2 Pitting Detail

Top side 2101



Bottom side 2101

* Fine pitting was noted on bare metal surface

Round 2 Test Results

D1

Alloy	Corrosion Rate (mil/yr)
316L	0.001
317L	0.000
2101	0.000
2003	0.000
2304	0.000
2205	0.000
AL6XN	0.000
C276	0.007

D2

Alloy	Corrosion Rate (mil/yr)	Pitting, % Crevice Area
316L	0.022	55
317L	0.002	10
2101	0.008	6*
2003	0.000	
2304	0.000	
2205	0.000	
AL6XN	0.004	
C276	0.075	

Vapor Space, Two Years, D1 Test Results – No Pitting

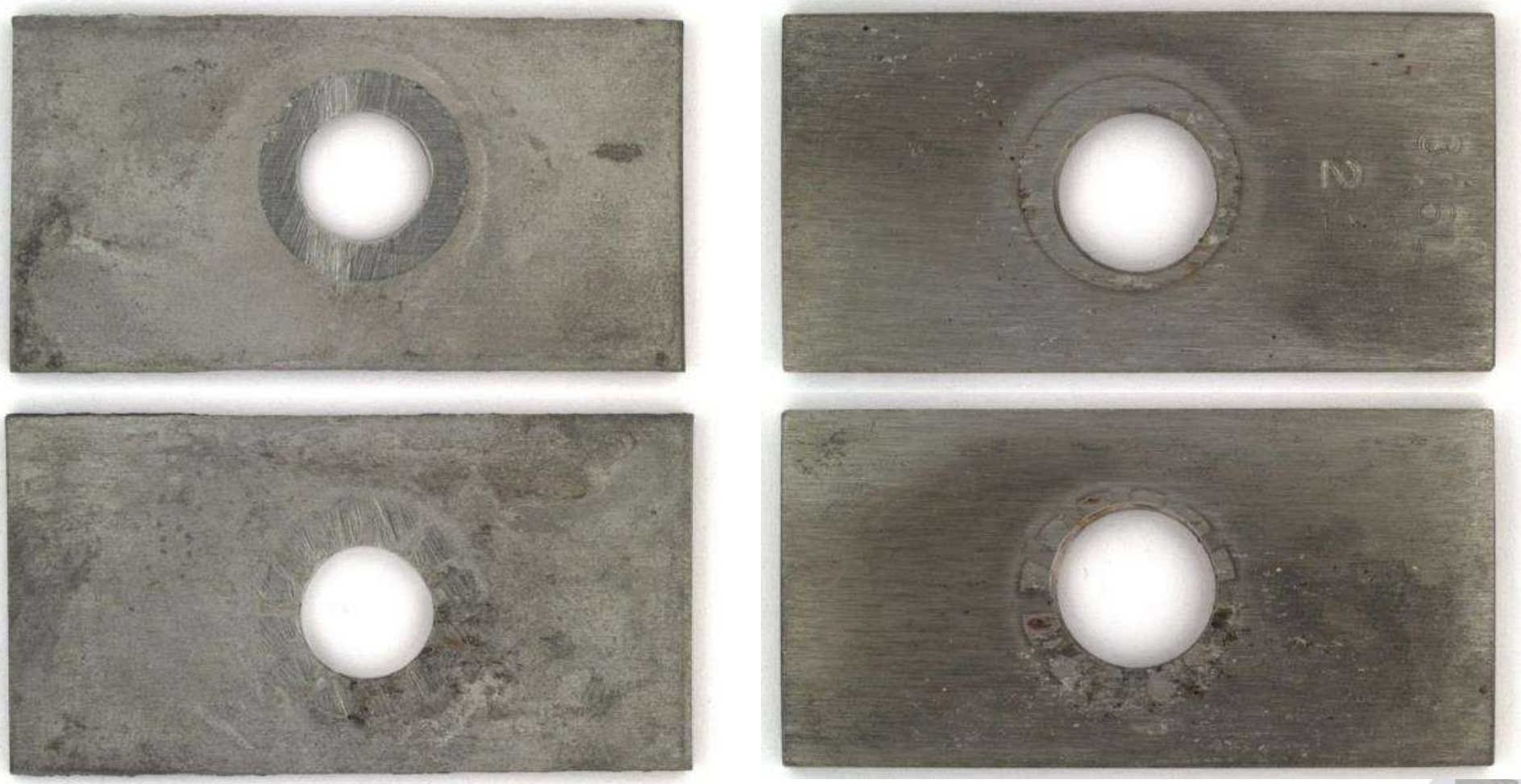
Alloy	Corrosion Rate (mil/yr)
316L	0.001
317L	0.001
2101	0.001
2003	0.001
2304	0.000
2205	0.001
AL6XN	0.001

Vapor Space, Five Years, D2 Test Results

Alloy	Corrosion Rate (mil/yr)	Damage Description
2101	0.054	Rough crevice and open area pitting
316L	0.035	Rough crevice and open area pitting
2304	0.033	Rough crevice and open area pitting
317L	0.012	Not as rough crevice and open area pitting
2003	0.000	Clean, few small crevice pits
2205	0.000	Clean, small crevice and open area pits
AL6XN	0.000	Clean, no pitting

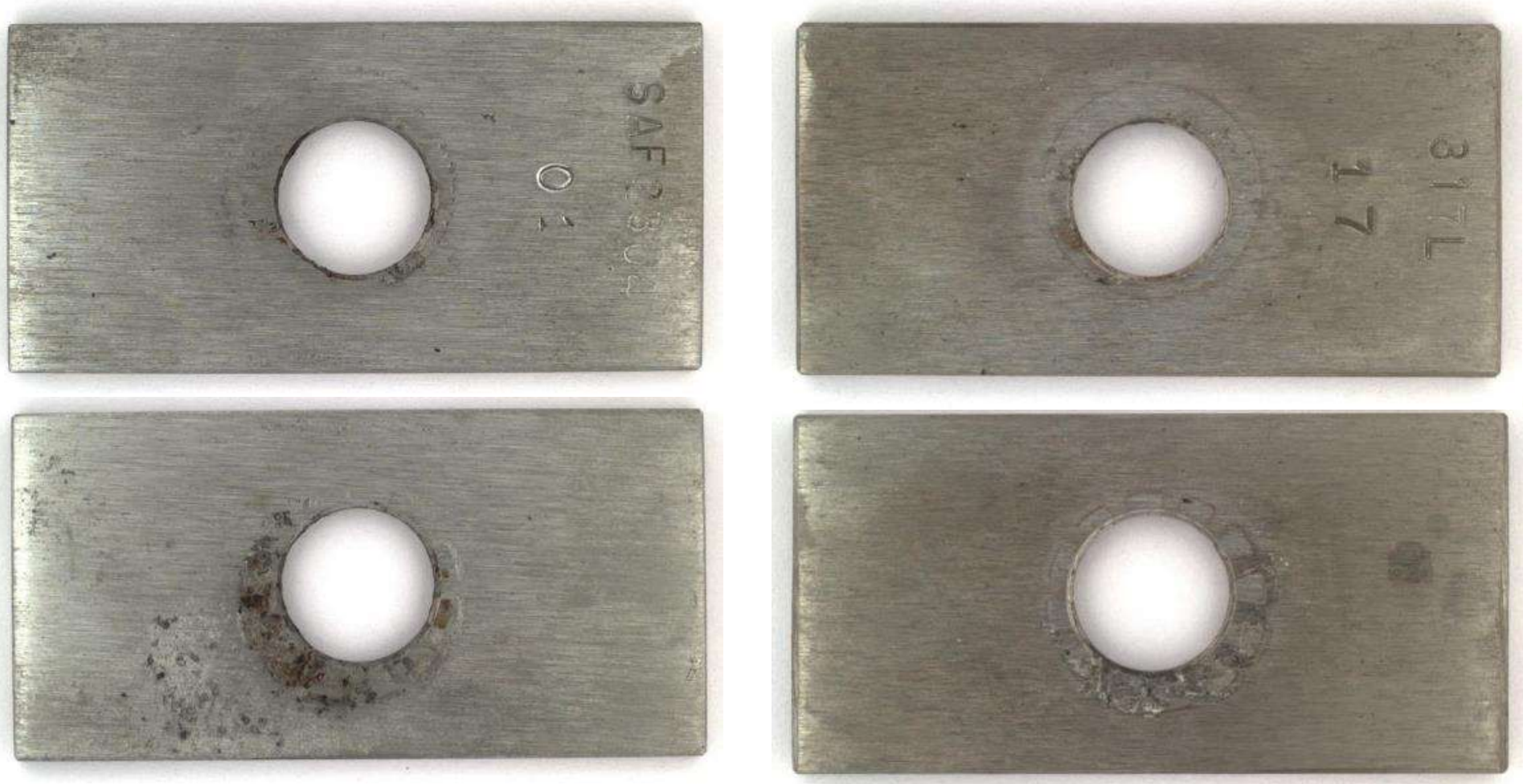
LDX2101

316L



2304

317L



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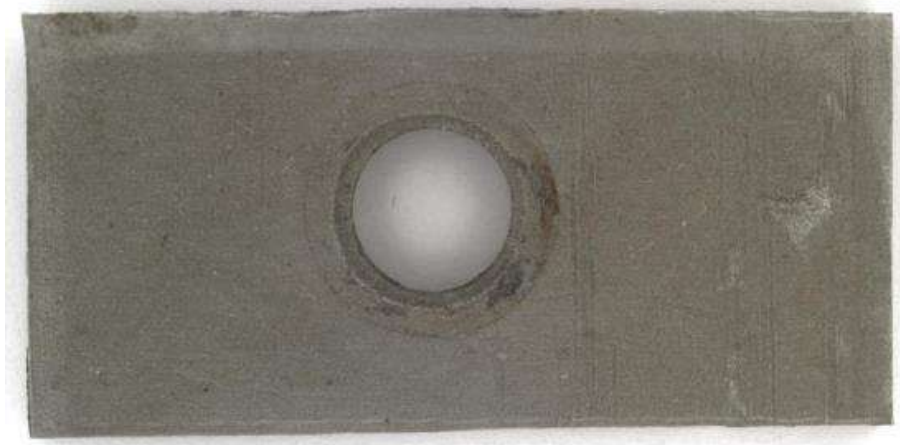
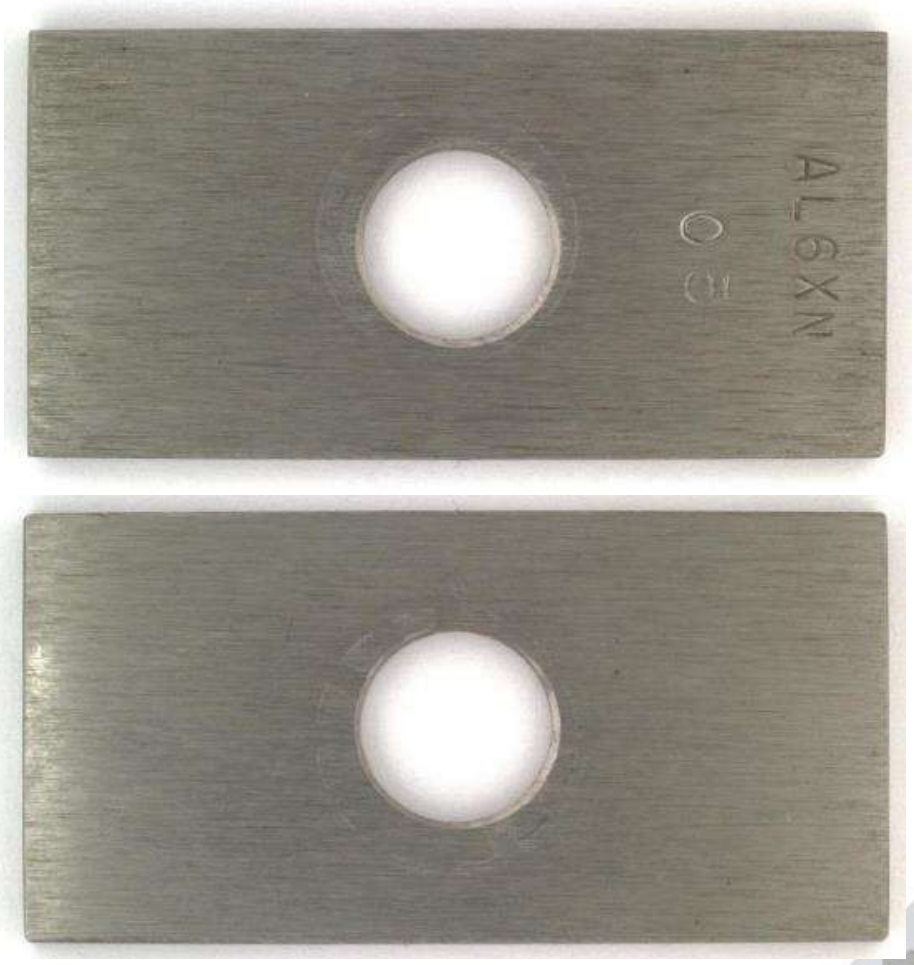
2003



2205

AL6XN



This was the only alloy that did not pit in the D2 vapor space

Mill #2 Recommendations

Based on variability in corrosivity and D2 vapor space results

- D1 piping 316L, consider 2205 (lean duplex is not available as piping)
- D1 filtrate tank consider 2205
- D2 piping 2205
- D2 filtrate tank 6% Mo stainless steel, consider 2507

Summary Bleach Plant Damage Mechanisms

- Under insulation stress corrosion cracking
- Peroxide corrosion of titanium
- Pitting and crevice corrosion of stainless steel in acidic, chloride containing bleaching oxidizers
- Transpassive corrosion of high nickel alloys in ClO2
- Oxidative attack of organic resins
- Tile lining degradation
- Acid corrosion of metals and non-metals

Summary Bleach Plant Materials Selection

- The bleach plant is not as corrosive as it once was
  - Improved operations has led to lower chlorine dioxide residuals
  - Lower alloys than those used in the past may be suitable
  - 2205 should be substituted for 317L
  - Super duplex SS can be substituted for 6% moly stainless steel
  - Know residual, pH and temperature
- Test materials

Resources

- TAPPI
  - Technical Information Papers / Conference Papers
  - Corrosion of Plastics and Rubber in Process Equipment – Experiences from the Pulp and Paper Industry
- WRC Bulletin 488 Damage Mechanisms for Fixed Equipment in the Pulp and Paper Industry
- Nickel Institute Stainless Steels and Specialty Alloys for Modern Pulp and Paper Mills
- AMPP
  - Sulfuric Acid
  - Clad Linings

Questions?